# Investigation of Lactam- Based Kinetic Hydrate Inhibitors and the Synergetic Effect of Solvents

By

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# Abbreviations

| | |
|---|---|
| $\Delta G$ | Gibbs free energy |
| $\Delta G_{crit}$ | Energy barrier for gas hydrate nucleation |
| $\Delta G_{s}$ | Surface excess free energy |
| $\Delta G_{tot}$ | Total free energy in the system |
| $\Delta G_{v}$ | Volume excess free energy |
| $\Delta H$ | Enthalpy |
| $\Delta S$ | Entropy |
| 2-ACap | 2-Acrylamido-caprolactam |
| 2-MACap | 2-Methacrylamido-caprolactam |
| 5-MH | 5-Methyl-1-hexyn-3-ol |
| AA | Anti-agglomerant |
| AIBN | 2,2’-Azobis-*iso*-butyronitrile |
| APYD | 1-Acryloylpyrrolidine |
| BDGE/ DBGE | Butyl diglycol ether |
| BuA | *n*-Butyl acrylate |
| CNT | Classical nucleation Theory |
| DEGEE | Diethylene glycol monoethyl ether |

| | |
|---|---|
| DIW | Deionized water |
| DMF | *N*,*N*-Dimethylformamide |
| DMMAm | *N*,*N*-Dimethylmethacrylamide |
| DMSO | Dimethyl sulfoxide |
| DPGBE | Di(propylene glycol)butyl ether |
| EO-PO-EO | Ethoxylate-propoxylate-ethoxylate |
| GPC | Gel permeation chromatography |
| HBuGCl | Hexabutylguanidinium chloride |
| HEN | Heterogenous nucleation |
| HET | Hydrate equilibrium temperature |
| HON | Homogeneous nucleation |
| iBGE | *iso*-Butyl glycol ether |
| iHex(EO)OH | 2-((4-Methylpentyl)oxy)ethane-1-ol |
| iHexOl/4-MePeOl | 4-Methyl-1-pentanol |
| iPeCOOH | 4-Methylvaleric acid |
| iPeCOONa | Sodium 4-methyl pentanoate |
| KHI | Kinetic hydrate inhibitor |
| LCH | Labile Cluster Hypothesis |
| LDHI | Low dosage hydrate inhibitor |

| | |
|---|---|
| MAm | Methacrylamide |
| MAPYD | *N*-Methacryloylpyrrolidine |
| MC | Monte Carlo |
| MD | Molecular dynamics |
| MEG | Mono-ethylene glycol |
| MeOH | Methanol |
| MMA | *N*-Methylmethacrylamide |
| $M_n$ | Number-average molecular weight |
| MOlMA | *N*-Methylol methacrylamide |
| $M_w$ | Weight-average molecular weight |
| n/r | Not reached |
| nBGE (BGE) | *n*-Butyl glycol ether (2-butoxyethanol) |
| NDMHMAm | *N*,*N*-Dimethylhydrazidomethacrylamide |
| Net$_3$HCl | Triethylamine hydrochloric acid |
| NIPMAM | *N*-*iso*-Propyl methacrylamide |
| NMR | Nuclear magnetic resonance spectroscopy |
| NPyMA | *N*-(Pyrrolidine-1-yl)methacrylamide |
| OctylMAm/MMAm | *N*-Octylmethacrylamide/*N*-methylolmethacrylamide |

| | |
|---|---|
| PAP | Poly(acryloylpyrrolidine) |
| PDI | Polydispercity index |
| PEGMA-9 | Poly(ethylene glycol) monoethyl methacrylate |
| PiPOx-AAc/Apr | Poly(2-*iso*-propyl-2-oxazoline) |
| $pM_5$ | Poly(*N*-hydroxypentylacrylate) |
| PNIPMAM | Poly(*N*-*iso*-propylmethacrylamide) |
| ppm | Parts per million |
| PVCap | Poly(*N*-vinyl caprolactam) |
| PVCapBGE | PVCap 50 wt.% in BGE |
| PVCapEND | PVCap polymer with mercaptosuccinic acid as a chain transfer agent |
| PVIMA | Poly(*N*-vinyl-*N*-methylacetamide) |
| PVME | Poly(vinyl methyl ether) |
| PVP | Poly(*N*-vinylpyrrolidone) |
| r | Cluster radius |
| RC5 | Rocking cell 5 |
| $r_{crit}$ | Critical size radius |
| SCC | Slow constant cooling |

| | |
|---|---|
| SEC | Size exclusion chromatography |
| sH | Structure H |
| sI | Structure I |
| sII | Structure II |
| SNG | Synthetic natural gas |
| $T_a$ | Rapid hydrate formation temperature (°C) |
| $t_a$ | Rapid hydrate formation time (min) |
| TBAB | Tetra (*n*-butyl) ammonium bromide |
| tBGE | *tert*-Butyl glycol ether |
| TBGE | Triethylene glycol monobutyl ether |
| TBPB | Tetrabutylphosphonium bromide |
| $T_{cl}$ | Cloud point temperature (°C) |
| $T_{dp}$ | Temperature of deposition (°C) |
| $T_{eq}$ | Hydrate equilibrium temperature (°C) |
| THF | Tetrahydrofuran |
| THI | Thermodynamic hydrate inhibitor |
| TMDD | 2,4,7,9-Tetramethyl-5-decyne-4,7-diol |
| TMDD-EO10 | 2,4,7,9-Tetramethyl-5-decyne-4,7-diol decaethoxylate |

|  |  |
|---|---|
| $T_o$ | Onset temperature for hydrate formation (°C) |
| $t_o$ | Onset time for hydrate formation (min) |
| TPAB | Tetrapentylammonium bromide |
| VCap | *N*-Vinyl caprolactam |
| VIMA | *N*-Vinyl-*N*-methylacetamide |
| VP | *N*-Vinylpyrrolidone |
| wt.% | Weight percent |

# Summary

Gas hydrate formation in flow lines is of notorious concern for the oil and gas industry, and it only gets bigger because of the never-ending pursuit of oil and gas compels the industry into deeper and colder waters. Gas hydrate can form and agglomerate into plugs, jeopardizing hydrocarbon production. Therefore, a variety of methods have been developed to inhibit gas hydrate formation. One of these is to utilize chemicals in the form of low dosage hydrate inhibitors (LDHI), which consists of two categories, kinetic hydrate inhibitors (KHI) and anti-agglomerants (AA). KHIs, the focus of this thesis, are mixtures of one or more water-soluble polymers in solvents and synergists.

In order to find KHI chemicals with better inhibiting capabilities and/or environmental properties, the mechanism as to how KHIs operate must be better understood. The understanding of gas hydrate formation and the effect of different KHIs has been enriched by a large number of experimental studies using a plethora of research techniques, gaining insight into the gas hydrate nucleation and growth processes, coupled with the possible modes of action of KHIs. Investigations were carried out on both the macroscopic and microscopic scale. Despite all these endeavours, no clear consensus on the inhibition mechanism exists in the hydrate community, which limits the ability to design improved KHIs. Therefore, investigating new KHI polymers and synergists can help understand the structure-activity relationship and factors involved in the KHI mechanism.

This PhD study consists of two main agendas, 1) investigating different compounds for their potential capabilities as synergist with probably the most well-known industrial KHI polymer, poly(*N*-vinyl caprolactam) (PVCap) and 2) investigating novel alternatives for PVCap as KHIs which also contain pendant caprolactam rings. Several excellent new synergists were discovered and a new class of acrylamido-based caprolactam polymers were synthesized and developed to give good KHI performance. In addition, the stability of PVCap and related KHI polymers was studied at a wide range of conditions including temperature and pH. This is relevant for field applications at extreme conditions.

In another study, literature and experimental studies were used to determine if there is a correlation between polymer cloud point and KHI inhibition performance. The results showed that a low cloud point, near the hydrate formation temperature, was useful for high KHI performance of a polymer but only if certain criteria are met. These include low molecular weight, pendant hydrophobic groups of an optimal size close to the polymer backbone and the correct neighbouring hydrophilic functional groups. Finally, a new class of non-amide-based polymers, polyvinylaminals, were investigated as KHIs. For testing the inhibition capabilities, for both the synergist mixtures and the novel polymers, high-pressure rocking cells with synthetic natural gas mixture with either slow constant cooling or isothermal test regime were mainly used. These studies have resulted in nine journal publications.

# Table of Contents

# List of Journal Publications

I. Dirdal, E. G.; Kelland, M. A., Does the Cloud Point Temperature of a Polymer Correlate with Its Kinetic Hydrate Inhibitor Performance? *Energy & Fuels* **2019**, 33, (8), 7127-7137.

II. Kelland, M. A.; Zhang, Q.; Dirdal, E. G.; Mady, M. F., Reliability and Performance of Vinyl Lactam-Based Kinetic Hydrate Inhibitor Polymers after Treatment under a Range of Conditions. *Energy & Fuels* **2021**, 35, (2), 1273-1280.

III. Kelland, M. A.; Dirdal, E. G.; Ree, L. H., Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly(*N*-vinylcaprolactam). *Energy & Fuels* **2020**, 34, (2), 1653-1663.

IV. Dirdal, E. G.; Kelland, M. A., Further Investigation of Solvent Synergists for Improved Performance of Poly(*N*-vinylcaprolactam)-Based Kinetic Hydrate Inhibitors. *Energy & Fuels* **2021**, 35, (24), 20103-20116.

V. Kelland, M. A.; Dirdal, E. G., Powerful Synergy of Acetylenic Diol Surfactants with Kinetic Hydrate Inhibitor Polymers—Choosing the Correct Synergist Aqueous Solubility. *Energy & Fuels* **2021**, 35, (19), 15721-15727.

VI. Kelland, M. A.; Dirdal, E. G., Boronic and Organic Acids as Synergists for a Poly(*N*-vinylcaprolactam) Kinetic Hydrate Inhibitor. *Energy & Fuels* **2021**, 36, (1), 333-340.

VII. Dirdal, E. G.; Kelland, M. A., Synthesis and Investigation of Polymers of 2-Methacrylamido-caprolactam as Kinetic Hydrate Inhibitors. *Energy & Fuels* **2020**, 34, (6), 6981-6990.

VIII. Dirdal, E. G.; Kelland, M. A., Alternative Lactam-Based Kinetic Hydrate Inhibitors─ Investigation of Polymers of 2-Methacrylamido-caprolactam. *Energy & Fuels* **2022**, 36, (6), 3107-3118

IX. Kelland, M. A.; Dirdal, E. G.; Zhang, Q., High Cloud Point Polyvinylaminals as Non-Amide-Based Kinetic Gas Hydrate Inhibitors. *Energy & Fuels* **2020**, 34, (7), 8301-8307.

# 1 Theory

## 1.1 The Physical Properties of Water

Since gas hydrates, or clathrate hydrates, consist mainly of water, it is essential to understand the physical properties of water both in its liquid and solid phase.[1]

Most of the physical properties of water are dominated by the formation of hydrogen bonds between water molecules. Hydrogen bonds is therefore the principal interaction in liquid water and the same holds for ice and clathrate hydrates.[2] The hydrogen atoms carry a positive charge, while the oxygen atom carries a negative charge. Furthermore, the number of hydrogen atoms in a water molecule that can form the positive ends of hydrogen bonds, equal the number of lone pairs on the oxygen atom that can form the negative ends. This charge distribution is the reason for water being a strongly dipolar molecule, and the water dipole molecules attract each other and form aggregates through hydrogen bonds. Extensive three-dimensional network in which each oxygen atom is tetrahedrally bonded to four hydrogen atoms by means of two covalent bonds and two hydrogen bonds as the result. Due to mutual acceptance and donation of hydrogen bonds the hydrogen bonding allows the attachment between water molecules. This is done in such a way that the central water molecule is surrounded in a tetrahedral manner by the other four. Bonds that form in this way are relatively strong and give the structure rigidity. Hydrogen bonds are much stronger interactions than dipole-dipole interactions are, which goes under the common name van der Waals forces. These dipole-dipole interactions make it possible for most materials to form condensed phases. However, hydrogen bonds are many times weaker than chemical bonds.

The existence of hydrogen bonds makes it possible for water to be in a liquid phase at room temperature, although its molecular weight alone should dictate a gas phase. Without these bonds, water would be even more difficult to condense than oxygen, nitrogen and carbon dioxide. Also, water would melt about −100 °C and boil at about −90 °C.[1,3–7]

One particular peculiarity of water is its capability to expand upon freezing, thus the liquid phase is denser than the solid phase. This clearly shows that water in its solid phase have a more “open” structure than in its liquid phase, thus there is more space between molecules than there would be in the liquid phase. When water freezes, ice is formed, and this substance have a more open lattice, hence substantial lower density, than the liquid water it came from. The formation of water in its solid phase (ice) is energetically (enthalpy, $\Delta H$) favored process, because of the extraordinary amount of energy that is releases as heat as additional hydrogen bonds form (exothermic process). The formation of ice is however not favored by the entropy ($\Delta S$) because the water possesses a more ordered structure in the solid phase.[1,7]

When energy is introduced to ice, it melts. In the melting process monomeric water molecules occupy holes in the remaining “icelike” lattice, hence causing the density of water to be greater than that of ice. The open structure partially collapses as more hydrogen bonds are broken, but at the same time the kinetic energy of molecules increases as the temperature is increased. Therefore, the elevated kinetic energy decreases the density of water because the molecules occupy a greater volume. But at the same time this will cause more water molecules to be trapped. Initially the trapping of monomeric water molecules outweighs the expansion in volume due to the increase in kinetic energy. Thus, the density increases from 0 °C to 4 °C. So at 4 °C the water will have its greatest density.

Beyond 4 °C the increase in density due to the collapsing of the hydrogen-bonded clusters of water molecules is overtaken by the decrease in density due to the increasing molecular motion resulting from the rise in temperature. Beyond this temperature the density decreases with increasing temperature, because of predomination of expansion.[3,7]

There are similarities as well as distinct differences in the thermophysical and mechanical properties of ice and gas hydrates, although the physical appearance and refractive index between them are very similar. Therefore gas hydrates and ice have a different phase behavior, and the thermal conductivity of gas hydrates is over four times lower than ice. Provided adequate pressure, gas hydrates will be stable at temperatures above and below the normal freezing point of ice (0 °C). Thus pressure have a tremendous impact on gas hydrate. Ice on the other hand is normally stable at low temperatures, therefore virtually independent of pressure (except at very high pressures).[8] There are nine known types of ice crystals, hence it is no surprise that there are three known gas hydrate structures.[7] Gas hydrates allow a solid water phase to form at an elevated temperature above the normal freezing point of water (0 °C).[6]

## 1.1 Gas Hydrate in General

The discovery of the existence of gas hydrates was done in 1810 by Sir Humphrey Davy when he was studying chlorine.[9] It is possible, however, that it the discovery took place in 1778 by Priestley. In the beginning gas hydrates was looked upon as mere scientific curiosity, until it was realized in 1934 by Hammerschmidt that it was not ice but gas hydrates formation that plugged natural gas pipelines on cold days.[10] This event captivated the scientific and engineering interest, and caused a large series of investigations on gas hydrate stability conditions, gas hydrate structures and on gas hydrate prevention. This resulted in methods for not only calculating gas hydrate equilibrium conditions for any gas composition, but also prevent gas hydrate from forming by addition of inhibitors or gas dehydration.[8,11,12]

The definition of clathrate is a substance in which atoms or molecules are trapped within the crystalline framework of other molecules. Gas hydrates is a type of clathrate, where the crystalline framework is made up of water molecules and the trapped atoms or molecules consists of different gasses (Figure 1.1).[3,4,13] The water molecules orient themselves in the most energy effective manner so that the number of hydrogen bonds are maximized.[14] Typical gas hydrate forming gases are light, nonpolar and generally have a low solubility in water. These gases are commonly methane, ethane, propane, *iso*-butane, $N_2$, $CO_2$, $SO_2$, $H_2S$ and other low molecular gasses which commonly constitute natural gas.[15,16]

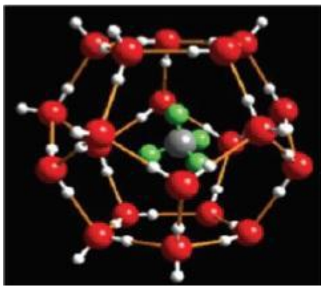


Figure 1.1. Schematic of methane hydrate surrounded by water molecule cage.[5]

Given the right conditions of pressure and temperature, typically high pressure (> 30 bar) and low temperatures (< 20 °C), these gases can stabilize the hydrogen-bonded water molecule cages.[17] In addition, the pressure and temperature conditions must be thermodynamically appropriate to the specific gas in order for gas hydrates to form. This highly organized cage structure would be in dynamic equilibrium with free flowing water molecules, perpetually forming and collapsing without the central gas atoms or molecules. For this reason, in the absence of the gas atoms or molecules, gas hydrates would be unstable. The stability of the gas hydrate is caused by van der Walls-type interactions between the water molecule lattice and the entrapped gas atoms or molecules. A delicate balance of forces, both hydrophilic and hydrophobic, among water molecules and the gas atoms or molecules gives the gas hydrate stability (Figure 1.2).[4,16]

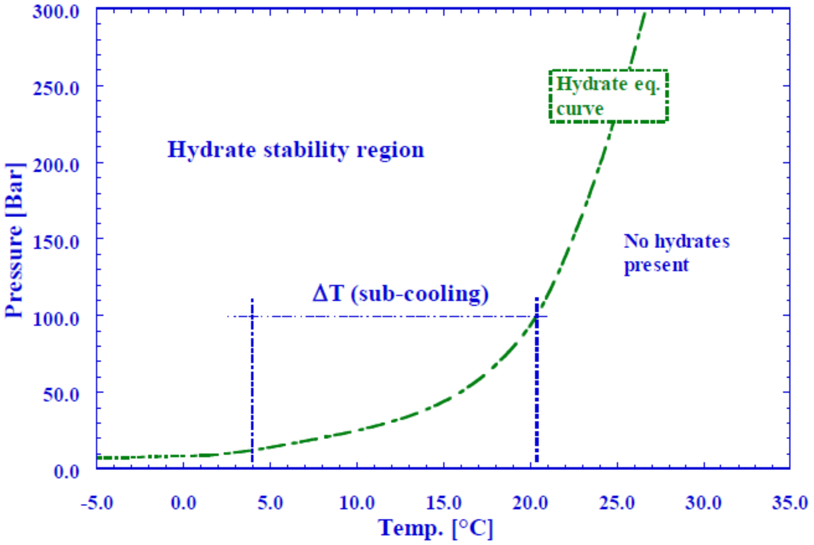


Figure 1.2. A general pressure against temperature graph for natural gas hydrate.[13,18]

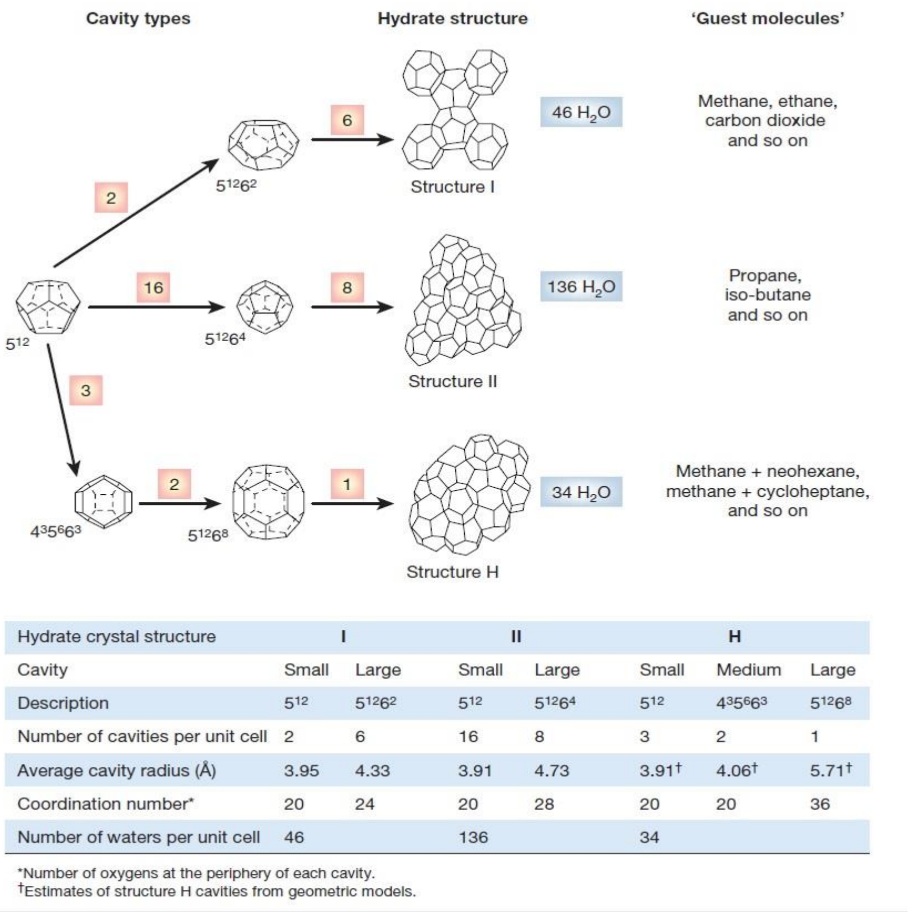
Because of the extraordinary amount of energy that is released as heat as additional hydrogen bonds form, the formation of gas hydrate is energetically (enthalpy, ΔH) favored process. Gas hydrate formation is thus an exothermal process. The formation of these additional hydrogen bonds causes a more ordered structure to take form. Therefore the formation of gas hydrate is not favored by entropy (ΔS).[1,7] Thus, gas hydrates are nonstoichiometric, snow-like, crystalline solids where gases of certain molecular weight stabilize the hydrogen bonded water molecule cages.[4,13,16,17,19] Further, gas hydrate mainly consist of water, and therefore does it have many similarities with ice. The water molecules from a repetitive geometric lattice, commonly referred to as a cage, around a central atom or molecule of gas.[4,16] The structure of the water lattice is determined by the size of the guest atom or molecule in addition to the composition of the gas.[20] This structure usually have 12, 14 or 16 sides.[4,16]

## 1.2 Gas Hydrate Structure

In association with other water molecules, water molecules have the unique property that they can form four tetrahedrally-disposed hydrogen bonds. Of these bonds, half will be acceptors and half will be donors. Water can for this reason form polymeric three-dimensional, four-connected network structures.[21] In these structures there will be hydrogen atoms pointing away from the faces, and all these will not be hydrogen bonded in a formed cavity.[4] These will thus act as potential points of attachment to other cavities or molecules. Gas hydrate can crystalize in different structures, three of which are more common, namely Structure I (sI), Structure 2 (sII) and Structure H (sH).[22,23] These structures differ by the type of water cages present in the crystal lattice and how these water cages are joined to each other and held together by van der Waals forces. It is the gas molecules, their relative size compared to the cavity and the relative stabilities of the structures that mainly determines which gas hydrate structure that forms. It is also possible that the shape and chemical nature of the gas molecule may influence the type of gas hydrate structure formed.[24] The gas composition does not only determine which of the gas hydrate structures that forms, but also at which pressure and temperature it will crystallize. Hence, every gas hydrate structure has its very own pressure and temperature equilibrium curve.[4] Therefore is the formation of gas hydrate structures related to the gas molecule size to the cavity size, the gas composition, the thermodynamic conditions of pressure and temperature. The resulting regular geometric arrangement, or crystal lattice, that is most thermodynamically stable will form. This gas hydrate structure will have the lowest free energy.[15,16]

The $H_{40}O_{20}$ pentagonal dodecahedron is the characteristic feature of the water structure of gas hydrates. This structure has 12 pentagonal faces, $5^{12}$, 20 vertices and 30 edges. Because each water molecule is four-coordinated when these polyhedra are linked together, they have a geometry that is close to tetrahedral and have the same donor/acceptor ratio as in ice.[25] The pentagonal dodecahedron is incapable of filling space in any face-sharing periodic arrangement without bond breakage. Therefore, different polyhedra are necessary to provide the three-dimensional repeating patterns necessary for making the crystal structure, and the interstices between the $5^{12}$ cages are filled with other cavities that relieve the strain.[19,25] Different polyhedra are generated when the pentagonal dodecahedra are either joined by sharing faces or separate links.[25]

If the other polyhedra are the 14-hedra, with 12 pentagons and two hexagons, $5^{12}6^{2}$, Structure I is formed. And if the other polyhedra are the 16-hedra, with 12 pentagons and four hexagons, $5^{12}6^{4}$, Structure II is formed. Finally, if the other polyhedra are the 12-hedra with three butagons, six pentagons and three hexagons, and another polyhedra consisting of 20-hedra with 12 pentagons and eight hexagons, Structure H is formed (Figure 1.3).[19,25]



| Hydrate crystal structure | I | | II | | H | | |
|---|---|---|---|---|---|---|---|
| Cavity | Small | Large | Small | Large | Small | Medium | Large |
| Description | $5^{12}$ | $5^{12}6^2$ | $5^{12}$ | $5^{12}6^4$ | $5^{12}$ | $4^35^66^3$ | $5^{12}6^8$ |
| Number of cavities per unit cell | 2 | 6 | 16 | 8 | 3 | 2 | 1 |
| Average cavity radius (Å) | 3.95 | 4.33 | 3.91 | 4.73 | 3.91† | 4.06† | 5.71† |
| Coordination number* | 20 | 24 | 20 | 28 | 20 | 20 | 36 |
| Number of waters per unit cell | 46 | | 136 | | 34 | | |

*Number of oxygens at the periphery of each cavity.
†Estimates of structure H cavities from geometric models.

Figure 1.3. A schematic of the polyhedra that makes up the three gas hydrate structures, Structure I, Structure II and Structure H.[19]

The distances within the different polyhedra are small enough for the van der Waals forces across the diameters of the voids to be sufficiently attractive to cause collapse of the relatively weak hydrogen-bonded framework structure. Therefore all the different gas hydrate structures must fill the space within their cavities to prevent hydrogen-bond strain and breakage, and thus stabilize the structures.[19,25] It is necessary to fill the voids with molecules which do not interfere or compete with the hydrogen bonding of the clathrate water structure. This can be done by any molecule, provided that the molecule does not have strong hydrophilic properties and that the dimensions fit within the cavity.[25] The gas hydrate formers can be immiscible or miscible with water and in a liquid or vapor state.[2] In addition, these molecules can not exceed a diameter of 10 Å or they will be too big to fit within the gas hydrate cavities.[4]

It is not necessary for all the cages to be occupied by a molecule for the crystal to be stable. At maximum occupation however, all the cages are occupied by only one molecule, 1 mole of gas hydrate of either structure yields about 0.15 mole hydrocarbon gas and 0.85 mole water (15 mole% hydrocarbon gas and 85 mole% water).[8,15,26–28]

### 1.2.1 Structure I

Structure I consist of two types of cavities, a small pentagonal dodecahedral cavity and a large tetrakaidecahedral cavity. The small pentagonal dodecahedral cavity is denoted $5^{12}$ (12 pentagonal faces in the cavity), while the large tetrakaidecahedral cavity is denoted $5^{12}6^{2}$ (12 pentagonal faces and 2 hexagonal faces in the cavity).[8,26] The unit cell formula of Structure I gas hydrate is $(S)_2(L)_6 \cdot 46H_2O$, with the water framework consisting of two small (S) 12-sided ($5^{12}$) cages and six large (L) 14-sided ($5^{12}6^{2}$) cages. This means that the unit cell contains a total of eight cavities (six small and two large) made up of 46 hydrogen-bonded water molecules. The unit cell have a dimension of 12.03 Å.[2,15,23,29]

Typically gas hydrate formers for Structure I are light hydrocarbons including methane and ethane (molecules with diameters of 4.2-6 Å), which make up most of the molecules in the structure. In addition to the light hydrocarbons, nonpolar molecules like argon, carbon dioxide and nitrogen also take part in the structure (molecules with diameters of < 4.2 Å).[4,11,15,19,25]

Structure I hydrate predominates in the natural environment on earth.[19] In conjunction with oil and gas production, Structure I hydrate will only form if the natural gas is enriched with methane and that the heavier hydrocarbon constituents are kept at a bare minimum.[13] If as little as 0.5 % propane should be in the natural gas blend, then Structure II will be formed.[26,30]

### 1.2.2 Structure II

Structure II also consists of two types of cavities, a small pentagonal dodecahedral ($5^{12}$) cavity and a large hexakaidecahedral cavity. The large hexakaidecahedral cavity is denoted $5^{12}6^4$ (12 pentagonal faces and 4 hexagonal faces in the cavity).[8,26] The unit cell formula of Structure II gas hydrate is $(S)_{16}(L)_8 \bullet 136H_2O$, with the water framework consisting of 16 small (S) 12-sided ($5^{12}$) cages and 8 large (L) 16-sided ($5^{12}6^4$) polyhedral cages. This means that the unit cell contains a total of 24 cavities (16 small and eight large) made up of 136 hydrogen-bonded water molecules. The unit cell have a dimension of 17.31 Å.[2,15,23,29]

For Structure II the typical formers are also light hydrocarbons including propane, *iso*-butane and cyclopentane (molecules with diameters of 6-7 Å). The light hydrocarbons contribute most to the structure, but some nonpolar molecules like krypton and xenon also assist.[4,11,15,19,25]
Structure II hydrate is the most encountered structure with regards to the oil and gas industry. This is due to that most raw natural gas will be a blend of various components. This means that in addition to methane, the mixture typically contains some propane and butane.[13]

### 1.2.3 Structure H

Structure H consists of three types of cavities, the small $5^{12}$ cavity, a midsized $4^35^66^3$ cavity and a large $5^{12}6^8$ icosahedral cavity.[8,26] The unit cell formula of Structure H gas hydrate is $(S)_3(M)_2(L)_1\bullet 34H_2O$, with the water framework consisting of three small (S) 12-sided ($5^{12}$) polyhedral cages, two medium (M) 12-sided ($4^35^66^3$) polyhedral cages and one large (L) 18-sided ($5^{12}6^8$) polyhedron cage. This means that the unit cell contains a total of 6 cavities (three small, two medium and one large) made up of 34 hydrogen-bonded water molecules.[2,15,23,29]

Typical gas hydrate formers for Structure H are combinations of small and large molecules. The small molecules like methane and xenon stabilize the small and medium cavity, while larger molecules like 2,2-dimethylbutane and cycloheptane stabilize the larger cavities (molecules with diameter of 7-9.8 Å).[4,11,19,25] This hydrate structure is rarely found in the field although it have been found naturally.[13,31,32]

### 1.2.4 Abnormal Transition of Hydrate Structures

Transformation between different types of hydrate cages which are facilitated by rotations or insertion/removal of pairs of water molecules, have been observed in molecular dynamics simulations.[33] During the initial nucleation phase different cages including $5^{12}$, $5^{12}6^2$, $5^{12}6^3$, $5^{12}6^4$ and $4^35^66^3$ have been identified. This indicates the existence of a disordered solid which is not one of the typical hydrate structures.[34,35] Results from molecular dynamics studies have shown that the abnormal $5^{12}6^3$ cage can serve as a link between sI and sII hydrate. This will facilitate the growth of the thermodynamically preferred sI phase from the initially formed sII phase which is kinetically favored.[34,36] Although, sII hydrate is kinetically favored for methane systems even though sI hydrate is the thermodynamically stable phase, due to the relatively large fraction of small $5^{12}$ cages compared to large cages in sII hydrate.[34,37] Hence, the $5^{12}6^{3}$ cage represent a possible explanation for observations regarding cross-nucleation and transformation between sI to sII gas hydrate.[38,39] The intermediate $4^{1}5^{10}6^{2}$ cage can act as a transformation between sI and sH hydrate.[36]

## 1.3 Gas Hydrate Formation

Mass transfer and heath transfer effects are related to the challenges in gas hydrate nucleation and growth.[11] Consequently, in the absence of mass transfer and heath transfer resistances, it should be expected that when nucleation of gas hydrates initiates somewhere in the liquid water, it will rapidly spread out to the entire body of water. Computer simulations on liquid water have shown that any macroscopic sample of liquid water has uninterrupted hydrogen bond paths spanning the entire volume of the sample, at or below room temperature. In turn, these dendritic pathways provide the routes for a rapid movement of $H^+$ and $OH^-$ by a direction sequence of exchange hops. It has been observed that the phase transition is almost instantaneous and accompanied by a burst of energy as heat at the onset of gas hydrate formation.[2]

The detailed mechanism behind the formation of gas hydrate has yet to be determined. The process of gas hydrate formation has many similarities with that of crystallization and can thus be divided into a nucleation phase and a growth phase. Therefore, gas hydrate formation is empirically considered to be a two stage process, consisting of consecutive stages of nucleation and growth, eventually leading to massive accumulation of gas hydrate (Figure 1.4).[28,40,41]

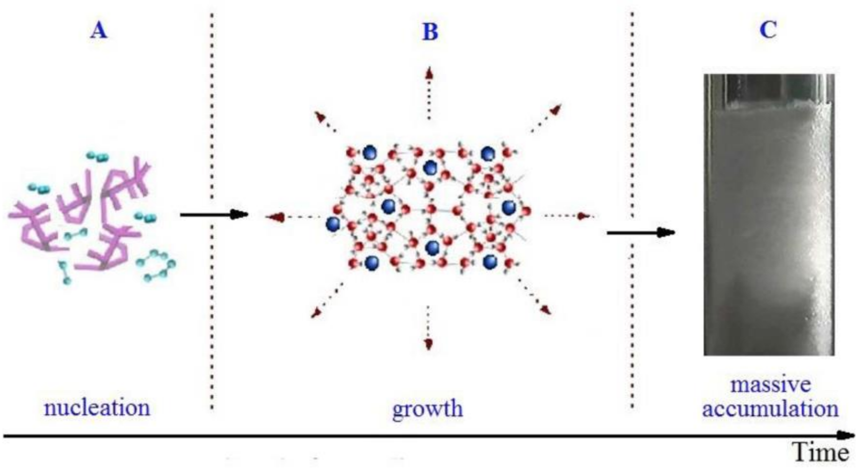


Figure 1.4. Illustrative schematics of nucleation (A), growth (B) and massive accumulation (C) process of gas hydrate.[40]

## 1.4 Gas Hydrate Nucleation and Nucleation Theories

There exist two types of nucleation, namely homogeneous nucleation (HON) and heterogenous nucleation (HEN). Homogeneous nucleation is a process that only takes place in the absence of impurities with only two phases involved.[42,43] Due to thermodynamic fluctuations clusters of molecules formed may either grow or shrink.[41] A bimolecular collision by an autocatalytic nature is most likely to proceed, since the nucleation process involves too many molecules that everyone can collide at once. In addition to this, homogeneous nucleation requires a relatively high subcooling, much higher than heterogeneous nucleation. Unlike homogeneous nucleation, heterogeneous nucleation takes place in the presence of foreign matter or on a surface. Because of this, homogeneous nucleation is rarely observed in the real world and is an unusual form of nucleation.[40,41,43] From a free energy of the system point of view, it is more favorable to form hydrates on a two-dimensional surface than a three-dimensional nucleus in the bulk water phase. The interfacial energy required to overcome the nucleation phenomenon is lowered by the presence of a third phase.[41] Gas hydrate nucleation in real systems is expected to be heterogenous nucleation given that impurities most likely are involved, in addition to foreign surfaces like a pipe wall or container of some sort.[40,43]

Gas hydrate nucleation is by nature a free energy-driven, intrinsically stochastic, dynamic and statistically random process. When water molecules cluster around gas molecules complete or incomplete crystal embryos are formed. Nucleation of gas hydrates involves small aggregates that are formed which in turn becomes seeds for gas hydrate growth.[28] Sustainable gas hydrate growth is only achieved if the nuclei is able to reach a critical size that in turn can overcome the free energy barrier.[40]

Because gas hydrate nucleation occurs at the molecular level, thus with nanoseconds time scale and nanometer length scale, it possesses a challenge to be detect experimentally. Just adding to the challenge is the aforementioned stochastic nature of gas hydrate nucleation.[40,41] Because of these difficulties, obtaining direct evidence of nucleation is strenuous, and molecular simulations have been preferred over experiments to study nucleation pathways.[41] There exists five major conceptual theories that have been proposed for gas hydrate nucleation, namely classical nucleation theory (CNT), labile cluster hypothesis (LCH), nucleation at interface hypothesis, local structuring mechanism and the blob mechanism.

### 1.4.1 Classical Nucleation Theory (CNT)

This theory has been well studied for crystallization, but due to the analytical simplicity of the theory it also found its use in clathrates.[41] Originally CNT was developed in the 1920s for condensation of vapor into a liquid. Later it has been applied by analogy to crystallization of supersaturated solutions.[44,45] It has commonly been applied to predict both the height of the free energy barrier and the rate of nucleation.[44,46] The activation barrier towards nucleation is described in the CNT theory as the sum of the increase in free energy due to creation of new interface and the decrease in the energy from creating a more stable phase. Gibbs developed a thermodynamic description of CNT, by defining the free energy change required for cluster formation as the sum of the free energy for the phase transition and the free energy change for the surface formation.[41] Due to local temperature (energy), mass and pressure (concentration) fluctuations, gas hydrate embryos will continuously form and shrink.[40] When embryos nucleate volume excess free energy (negative and favorable) and surface excess free energy (positive and unfavorable) is set up against each other (Figure 1.5). The volume excess free energy is caused by solute molecules integrating into either the bulk, interior of the embryonic nuclei or both. The surface free energy is caused by solute molecules becoming part of the surface of the clustering sub-critical sized embryos.[40,41]

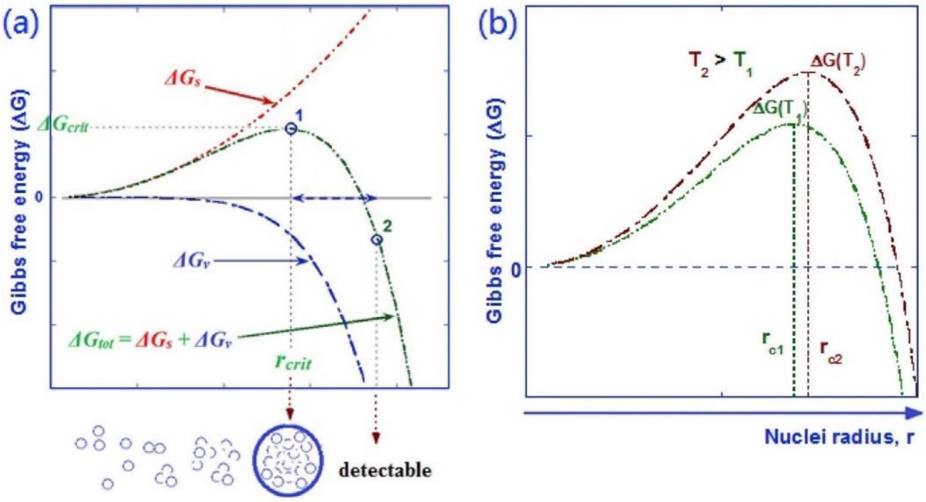


Figure 1.5. Schematic representation of free energy barrier of gas hydrate nucleation and critical nuclei size, (a) as a function of cluster radius and (b) as a function of temperature.[40]

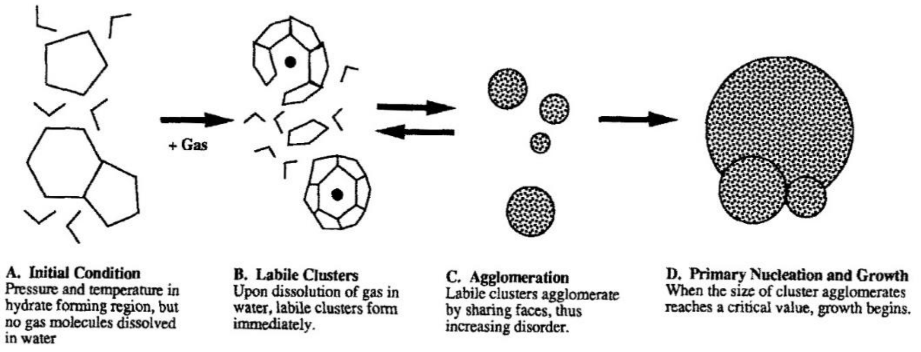
From Figure 1.5 it is shown that the sum ($\Delta G_{tot}$) of surface excess free energy ($\Delta G_{s}$) and volume excess free energy ($\Delta G_{v}$) is a function of cluster radius (r). At point 1, the cluster radius will reach a peak, and at this point the energy level is termed the energy barrier for gas hydrate nucleation ($\Delta G_{crit}$). It corresponds to a specific size of nuclei, which is at this point termed the critical size ($r_{crit}$).[40] The free energy barrier correlates to the increase in the free energy at the critical size. The positive surface free energy term dominates at the critical size beyond which the total free energy continuously decreases and the growth becomes energetically favorable.[41] Thus, gas hydrate nuclei with $r \geq r_{crit}$ are energetically favorable to sustain growth and become macroscopically detectable at point 2.[40] By means of random fluctuations the critical size of gas hydrate is attained, and subsequently, the gas hydrate growth becomes spontaneous.[41] The critical nuclei size is not a constant, but increases as a function of increasing temperature and decreasing degree of subcooling.[43] Therefore will the unfavorable excess surface energy ($\Delta G_S$) dominate the available system energy for nucleation. The system energy is not sufficient to overcome the critical work of nucleation at this state. This changes as the system is cooled further into the hydrate region. Here the latent energy for nucleation increases, while the critical nuclei size and the critical work for nucleation decreases.[40] Hence, the energy barrier that must be overcome to form the critical sized clusters, would be lowered by a smaller critical nuclei size. When the free energy barrier is reduced sufficiently by continuously increasing the supersaturation, the nucleation will eventually become spontaneous.[4]

Various studies in the literature have adopted a unified approach for nucleation and growth by treating nucleation using classical theory and the modeling growth phase as a chemical reaction.[19,46] However the classical nucleation theory has two major shortcomings. First, macroscopic treatment of the hydrate nucleus leads to substantial errors in excess free energy and critical size estimations.[47] Second, it lacks the insight into both the nucleation pathways and the exact structure of hydrate structures.[41]

### 1.4.2 Labile Cluster Hypothesis (LCH)

This theory was aimed at overcoming one of the shortcomings from CNT, by providing insight into the nucleation pathways. It was first proposed as a hypothesis for hydrate nucleation from ice.[48] The concept was extended with the essence that hydrate nucleation process initiates from pure water molecules, and the foundation for LCH was formed.[49,50] Also proposed was a new induction nucleation parameter of gas molecules to cavity size ratio. In addition, a kinetic mechanism with multiple intermediary steps and the system modeled as a set of chemical reactions for the hydrate formation was also proposed.[48] As a consequence of this, two different nucleation pathways for construction of sI and sII gas hydrate were suggested.[41] The LCH contains these key elements (Figure 1.6):[48–52]

1. Transient, labile ring structures exist in pure liquid water without guest molecules present. These ring structures could be pentamers or hexamers.
2. The labile water structures will immediately form labile clusters (unstable entities that readily undergo change) once dissolved gas molecules are present in the liquid water phase.
3. The labile clusters diffuse in water as single entities and agglomerate due to "hydrophobic bonding". This type of bonding is caused by attraction between the non-polar molecules within the water clusters. In a stochastic process these metastable agglomerates will either dissolve or grow as long as they are smaller than the critical size. Until this critical size is reached, a quasi-equilibrium exists between the metastable nuclei and the liquid-like cages. After this the labile clusters will gradually grow, combine and agglomerate into critical size nuclei to initiate subsequent growth. The LCH assumes that there exists an energy barrier for cluster agglomeration.[40]



**A. Initial Condition**
Pressure and temperature in hydrate forming region, but no gas molecules dissolved in water

**B. Labile Clusters**
Upon dissolution of gas in water, labile clusters form immediately.

**C. Agglomeration**
Labile clusters agglomerate by sharing faces, thus increasing disorder.

**D. Primary Nucleation and Growth**
When the size of cluster agglomerates reaches a critical value, growth begins.

Figure 1.6. Schematic of the labile cluster hypothesis (LCH).[49]

### 1.4.3 Nucleation at Interface Hypothesis

This hypothesis is a variation of the LCH, where the assembly of the labile clusters take place on the vapor side of the vapor-liquid interface, opposed to the liquid side as in LCH.[53,54] The hypothesis consists of these key elements to describe cluster formation:[4,54,55]
1. Gas molecules are transported to the vapor-liquid interface.
2. The gas molecules are then adsorbed onto the vapor-liquid interface.
3. The adsorbed gas molecules migrate due to surface diffusion to suitable locations where water molecules would take in the gas and form either partial or complete cages.
4. The process continues with more gas and water molecules joining on the vapor side of the interface, forming cavities until critical nuclei form and grow. When the critical size is reached, the energetically favored growth process continues.

### 1.4.4 Local Structuring Mechanism

A major criticism on the concept of LCH comes from calculations where it was shown that the energy barrier for cluster agglomeration is much higher than that for cluster disintegration. This results in that it is much more thermodynamically favorable for a labile cluster to decompose rather than to agglomerate. Thus, upon providing evidence against LCH, a new mechanism was suggested, the local structuring mechanism, by the use of molecular simulations on $CO_2$ hydrate within the classical statistical mechanics framework.[56]

The mechanism is based on the assumptions that free energy barrier to nucleation remains unaltered by the limited simulation size, within the chosen parameter space a minimum energy path exist and that nucleation is governed by equilibrium thermodynamics.[41,56] Further, this mechanism assumes that dissolved gas molecules triggers nucleation.[40] Local structuring mechanism is based on these key elements:[40,41,56]

1. The dissolved gas molecules will be rearranged into spatial configurations that are similar to the geometric in the hydrate phase (local ordering), due to thermal fluctuations.
2. The water structures around the re-ordered gas molecules will be perturbed, which is in opposed to the water molecules in other places in the bulk.
3. The local ordering of the guest molecules induces ordering of the host molecules, and the number of these locally rearranged structures may surpass a critical value comparable to that of a critical nucleus. The eventual outcome will be the formation of a critical nucleus as a result of the interaction of rearranged gas molecules and the perturbed water molecules around them. Upon attaining the critical nucleus, the perturbed water molecules rearrange to form a proper hydrate framework which lead to hydrate crystallization.

What governs the ordering of the molecules, be it water ordering driven by gas molecules, or gas ordering driven by water molecules, is a more fundamental difference between the local structuring mechanism and labile cluster hypothesis.[41]

Although $CO_2$ chemically reacts with water, and is thus not a typical hydrocarbon guest, a similar model to the labile cluster hypothesis was proposed based on molecular dynamics studies on methane hydrate.[34,57–60] The results were similar to those proposed by LCH in that water molecules surrounded clusters of methane molecules. However, there was a difference in that the structure was amorphous rather than crystalline as proposed by LCH.[34,41,57–59]

It has also been shown that enclathered methane in solution is exceedingly rare[61] and that when liquid water molecules form clusters around dissolved methane, the clusters are not similar to those in the crystalline hydrate structure.[62] Further, movement of water molecules into position around the central methane molecule appears to be strongly correlated with the motion of the methane molecule. It also appears that a high degree of methane coordination is necessary for cage formation. In addition, the absence of the hydrate like solvation shell without the presence of neighboring methane strongly favors the local structuring mechanism over the labile cluster hypothesis.[58]

### 1.4.5 Blob Mechanism

The blob mechanism is one of the most recent hypotheses on hydrate nucleation. A blob is in this context a cluster of multiple gas molecules separated by water molecules that could survive temporarily in a solution. In the presence of thermal and mass fluctuations, interaction with the surrounding water molecules causes repeatedly nucleation into cages and dissolvement. The blobs are precursors in the nucleation pathway of clathrate hydrate. By using molecular dynamics simulations on gas molecules similar to methane and $CO_2$, it describes a multistep hydrate crystallization process with the following steps (Figure 1.7):[63]

1. From the supersaturated solution, reversible formation of blobs occurs. This is caused by fluctuations in temperature and in mass.
2. Once the blob exceeds the critical size, the blob will continue to grow for a period of time and become an amorphous clathrate via face-sharing of newly joined cages. Amorphous clathrate is different from a blob because that water molecules in the blob are not yet locked into cages, whereas in an amorphous clathrate the water molecules are hydrogen bonded affixing the polyhedral cages within. Amorphous clathrate is a metastable intermediate considered as a hydrate precursor. The metastability is also caused by the mixture of structures synthesizing several transient cage configurations ($5^{12}$, $5^{12}6^2$, $5^{12}6^3$, $5^{12}6^4$) that differ from the type and proportion of fixed cages in the final crystalline structure of hydrates.

3. From this continuing growing and ripening amorphous clathrate nanocrystals of stable sI and metastable sII hydrate form.

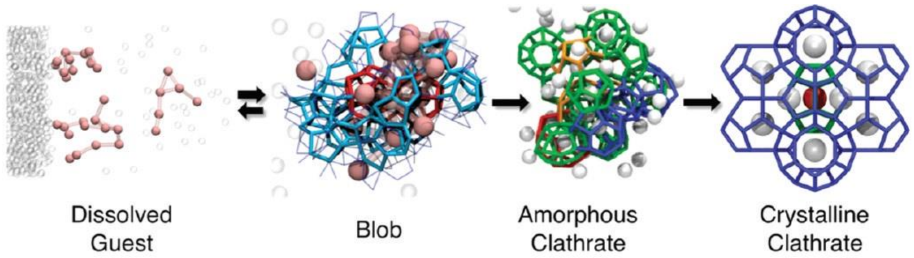


Figure 1.7. Schematic of the steps in the blob mechanism.[64]

These molecular dynamics simulations indicates that there is no observable preference for where the nucleation occurs, it could be either in the bulk solution or in the gas-liquid interface.[63] Results from both simulations and experiments indicate that gas hydrate nucleate through metastable polymorphs or non-equilibrium states of partial order, rather than directly into the thermodynamically favorable sI or sII hydrate.[33,35] During the initial nucleation phase different cages including $5^{12}$, $5^{12}6^2$, $5^{12}6^3$, $5^{12}6^4$ and $4^35^66^3$ have been identified. This indicates the existence of a disordered solid which is not sI nor sII.[34,35] Results from molecular dynamics studies have shown that the $5^{12}6^3$ cage can serve as a link between sI and sII hydrate. This will facilitate the growth of the thermodynamically preferred sI phase from the initially formed sII phase which is kinetically favored.[34,36] Although, sII hydrate is kinetically favored for methane systems even though sI hydrate is the thermodynamically stable phase, due to the relatively large fraction of small $5^{12}$ cages compared to large cages in sII hydrate.[34,37] Hence, the $5^{12}6^3$ cage represent a possible explanation for observations regarding cross-nucleation and transformation between sI to sII gas hydrate.[38,39]

To some extent, the blob mechanism combines and further develop the labile cluster hypothesis, nucleation at interface hypothesis and local structuring mechanism, by representing a balanced emphasis on not only the roles that both water and guest molecules have, but also their interactions in the stabilization and formation of cluster structures. The main differences between the blob mechanism and the aforementioned hypothesis and mechanism, by the different perspectives and emphasis they possesses are:[40]

- The importance of the role gas molecules has in the hydrate nucleation are underestimated by the labile cluster hypothesis.
- In order for a cluster to reach the critical size for sustainable growth, it must first overcome the free energy barrier.
- The importance of the amount of gas molecules required for effective local rearrangement are overestimated in the local structuring hypothesis.
- It would be beneficial for gas and water to nucleate into cages by a spatial configuration of the dissolved gas molecules near the vapor-liquid interface.
- The assumption made in the interfacial nucleation hypothesis that nucleation starts from the vapor side of the interface may work against it.

Despite all the benefits of the blob mechanism, several things remain unclear:[40]

- It is not certain if the blob mechanism has a role in the "memory effect" phenomenon.[65,66]
- As a function of size and driving force it is not certain for how long a blob could survive in the solution.
- It is not certain how the metastable amorphous clathrate transform into stable and organized crystalline structures.

Within the research community there seems to be an agreement that water clusters coordinated by gas molecules has an important role in the nucleation mechanism. Furthermore, gas hydrate nucleation seems to happen through amorphous solids resembling hydrates.[34,35,67–71] There is also indications that stochasticity is present even int the nucleation mechanism pathways,[72] because of more direct alternative pathways to the crystalline clathrate have been defined.[33,73] These proposed nucleation theories herein serve as good conceptual aids for the study of hydrate nucleation, although none of them has been fully verified.[40]

## 1.5 Crystal Growth

After the critical size of the hydrate is reached in the nucleation process, the crystal growth process commences. Crystal growth practically takes place right after the nucleation process, where these self-sustainable hydrate nuclei continue to grow in both quantity and size.[40] The growth of gas hydrates is considered as a complicated interfacial phenomena, which involves multicomponent (gas, water and hydrate) distribution in multiphase (gas, liquid and hydrate) at multiscale (macroscopic-scale and microscopic-scale) level.[71,74] The analysis of this phenomena involves intrinsic kinetics of phase change, fluids flow, heat transfer and mass transfer.[75] At macroscopic level the rate of gas hydrate growth can typically be quantified based on the gas consumption rate. This rate is calculated from the measurement of pressure and temperature[76–79] as well as other direct visualization techniques on the morphology and thickness of the hydrate film.[79–82] At microscopic level hydrate growth can be considered as a combination of three different factors:[4]

1. Mass transfer of both water and gas molecules to the growing hydrate surface.
2. The intrinsic kinetics of hydrate growth at the surface of the hydrate.
3. Transport of heat released from the exothermic hydrate formation reaction away from the frontier of the growing crystal surface.

A kinetic model for hydrate growth can thus be structured based on the particular controlling mechanisms postulated: Mass transfer, intrinsic growth kinetics, heat transfer or a combination of them. These mechanisms are often coupled and either one of them could be dominating, depending on the condition for hydrate growth, during the process of hydrate growth. In total there are 27 classical and state-of-the-art models for hydrate growth, which can be categorized according to their controlling mechanism postulated:[40,75]

- Intrinsic growth kinetics (reaction kinetics) model
  - Arrhenius-type rate equation[46,83]
  - Five pseudo-elementary reactions with rate constants[84]
  - Arrhenius-type rate equation with sub-cooling as driving force[85,86]
  - First order rate law in terms of mole fraction of hydrate forming gas[87]
- Mass transfer limited models
  - Fugacity difference of gas phase with population balance model[88,89]
  - Concentration difference between gas and liquid phase[89]
  - Concentration difference with advanced nucleation model[90]
  - Concentration difference with particle size analysis[91]
  - Concentration difference of $CH_4$ between oil phase and equilibrium[91,92]
- Heat transfer limited models
  - 1D conductive heat transfer model[93]
  - 1D convective and conductive heat transfer model[94]
  - 1D convective heat transfer model[79]
  - 2D transient heat conduction model[95]
- Mass transfer and intrinsic growth kinetics (reaction kinetics) limited model
  - Concentration difference with mass transfer and reaction kinetics[96,97]

    - Mass transfer at liquid-vapour interface and reaction kinetics[98]
    - Shrinking core model with diffusion or reaction coupled[99–102]
    - Molecular diffusion with 1st order formation kinetics of $H_2O$[103–105]
    - Molecular diffusion with 1st order formation and dissociation kinetics of $H_2O$[106]
    - Molecular diffusion with 1st order formation kinetics of $CO_2$[107]
    - Reaction-limited and diffusion-limited schemes with induction time[108]
- Heat transfer and intrinsic growth kinetics (reaction kinetics) limited model
    - Kinetic rate coupled with heat transfer model[109]
    - Kinetic rate coupled with heat convection model[110]
    - Surface kinetic rate coupled with heat transfer model[111]
    - Equilibrium model in sandy porous medium[112–115]
- Fluid flow, heat flow and intrinsic growth kinetics (reaction kinetics) limited model
    - Kinetic rate equation for both hydrate formation and dissociation[116]
    - Kinetic rate equation based on model of Kim et al.[117,118]
    - Simple slug flow model coupled with kinetic rate and heat flow[119]

Further, it seems that the majority of the model formulations depend largely on the configurations of the hydrate reactor, the formation technique for making hydrate and the contact patterns of the multiphase fluids (gas-liquid-hydrate, liquid, liquid, hydrate). A unified model describing hydrate growth connecting all the physical behaviour observed from different domains is yet to be developed, despite the various models proposed. In order to achieve this, a combination of multiscale physics in the model formulation would be required.[75]

## 1.6 Gas Hydrate Management

Four essential elements are necessary for gas hydrate formation, with the absence of only one of these elements would make gas hydrate formation impossible. This is what inhibition methods aim to control or eliminate. These four essential elements are:[120]

- The presence of water.
- The presence of hydrate forming compound in natural gas (for example methane).
- The condition of high pressure.
- The condition of low temperature.

There is a wide selection of methods available for diminish the risk or preventing gas hydrate formation and deposition, which are:[28,30,121]

- Dehydrating the mixture by separating out the water phase or by removing the hydrocarbon phase. Either way, one of the components must be removed.
- To keep the pressure low and outside the hydrate equilibrium zone.
- To add another gas in order to modify the gas phase.
- To convert the water into transportable hydrate particles without the use of chemicals.
- To use active heating or passive heat retention at the system pressure in order to keep the temperature above the hydrate stable zone.
- To treat with chemicals.

In deep sea operations, the ambient operation conditions of high pressure and low temperature are very conductive to the process of gas hydrate formation. Therefore, in such cases the above traditional approaches, except chemical treatment, may be ineffective due to either extreme conditions or high cost. Consequently it appears that the use of inhibitors will be the most effective solution.[122]

There are two different chemical classes, all of them are now used in the field, which can accomplish the task to prevent gas hydrate plugging:[13]

- Thermodynamic hydrate inhibitors (THIs)
- Low dosage hydrate inhibitors (LDHIs)

Both kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs) goes collectively under the name LDHIs. The reason for this is because compared to THIs the effective concentration of 10−60 wt.% of the produced water,[33,36,41,42,68] the sufficient quantity used for inhibition are normally numerous times lower.[13] The adequate concentration of these LDHIs is currently expected in the range 0.5−4 wt.% versus the water rate.[123] In the following, only the chemical treatment will be mentioned, with emphasis on the KHIs.

### 1.6.1 Thermodynamic Hydrate Inhibitors (THIs)

Chemical inhibition with THIs is by far the most commonly used method used for hydrate control, it has been used for a long time and continues to be the industry standard. This type of inhibitor works as an antifreeze by involving the water in a thermodynamically favorable relationship, so that it is not available for interaction with the gas.[16,124] The activity of the water molecules is lowered because the THI outcompetes the water molecules for hydrogen bonds. Thus, the hydrate equilibrium curve is shifted toward lower temperatures and higher pressures (shifted towards the left in Figure 1.2). Consequently, the operating conditions is forced out of the gas hydrate stable region, and the system operates in the vapor-liquid region.[5,124] These inhibitors have the ability to shift the equilibrium requirements for hydrate formation to higher pressures and lower temperatures.[125–127] This works because as ice, gas hydrates consist of stable hydrogen bonded structures. Therefore, hydrates can be prevented by the same means. In this way the operating conditions falls outside of the hydrate forming region.[6,120] THIs ability to shift the equilibrium conditions enabling them to melt formed gas hydrate as well.[13]

By the addition of THI the temperature for which hydrates may be formed is decreased. This decrease in thermodynamic temperature for hydrate formation is synonymous to freezing point depression, which is basically what these inhibitors causes. The most powerful THIs are the compounds that is causing the largest freezing point depression for water.[5,128,129]

Typical THIs include alcohols, glycols and salts. Among these are methanol (MeOH, $CH_3OH$), mono-ethylene glycol (MEG, $HOCH_2CH_2OH$), diethylene glycol, sodium chloride, calcium chloride and potassium formate.[6,16,123,127,129,130] Because of their low cost and widespread availability, methanol and ethylene glycol are most common among these.[120,124] Because methanol easily vaporizes and concentrates in free water, it is preferred over other inhibitors such as glycols or salts. Methanol is injected into the gas phase, which carries it to the site where methanol dissolves in free liquid water and provides hydrate inhibition.[30] Methanol is also a relatively small molecule. This small size allows it to react at a fast rate with the surface of hydrate solids. Further, hydrate disassociation occurs more rapidly with methanol than with glycol, thus methanol melts hydrates more effectively.[131] However, methanol is highly flammable and toxic.[31] In addition, methanol can poison catalyst in downstream processing facilities.[31,121]

The biggest drawback with THIs is the shear volume that must be used. This puts stress on the logistics, transport and storage facilities. Required effective dosages are in the range of 10−60 wt.% of the produced water.[24,26,123,128,130,132] In severe conditions the needed dosage can be from 20 wt.% to over 70 wt.% of the total volume of water production. This translates to a daily usage of between 10 and 40 $m^3$/day of inhibitor, for a typical deep water offshore system.[127] Therefore research on LDHIs as potential replacements are in focus.

### 1.6.2 Anti-Agglomerants (AAs)

Anti-agglomerants (AAs) are a class of LDHIs that not completely prevents gas hydrate from forming but prevent gas hydrate from agglomerating thus making them transportable as a non-sticky slurry. Hydrophobic moieties then function to keep individual hydrate particles separated and dispersed in the liquid phase. Hence, AAs permit hydrates to form but by dispersion remediate their agglomeration, deposition and plugging.[6,133] AAs enables a higher degree of sub-cooling since they allow the formation of gas hydrate, although manages the formed hydrate to not agglomerate.[13] AAs are added in relatively low concentrations of < 1 wt.%.[24] There is a limit to the amount of water, water cut, there can be in the system in order for the AAs to operate properly. The water cut should not exceed 50 %,[18,134] Although some laboratory experiments indicate water cut up to 90 % is tolerable. If the water cut is to high then the resulting hydrate slurry will be too viscous for transport.[18]

There exist two subclasses of AAs, both of which are in commercial use:[13]

- Production or pipeline AAs
- Gas well AAs

Both subclasses allow hydrates to form but they prevent them from agglomerating and subsequently accumulating into larger masses. Pipeline AAs enables the hydrates to form as a transportable non-sticky hydrate particle slurry dispersed in the liquid hydrocarbon phase. Gas well AAs disperse hydrate particles in an excess of water.[13]

Production or Pipeline AAs

There exist two essential structural features that these types of AAs must possess in order to function properly. They need a "hydrate-philic" (hydrophilic) head (seeks hydrate crystal surfaces) that can incorporate itself within the hydrate crystals. Further, they need a "hydrate-phobic", or "oleophilic" (hydrophobic), tail that serve to disperse the hydrate crystals into the liquid hydrocarbon phase. The most powerful among these are certain surfactant of quaternary ammonium and phosphonium salts with at least two *n*-butyl, *n*-pentyl or *iso*-pentyl groups. In addition they contain one or two long hydrophobic ("hydrate-phobic") tails (Figure 1.8).[135] The quaternary center is usually the “hydrate-philic” headgroup and can bind to the hydrate particles. The open $5^{12}6^{4}$ cavities on the hydrate surface can be penetrated by the butyl/pentyl groups, which then can even be embedded in the hydrate surface once the hydrate grows around the alkyl groups. The long hydrophobic tail will prevent further growth at that surface, and it will make this surface more attractive towards the hydrocarbon phase. The hydrate particle can with ease disperse into the hydrocarbon phase when sufficient amount of AA molecules are attached to its surface. In addition, these hydrophobic tails on these quaternary AAs will prevent hydrate from growing or adhering to the pipe walls, making them effective corrosion inhibitors.[18]

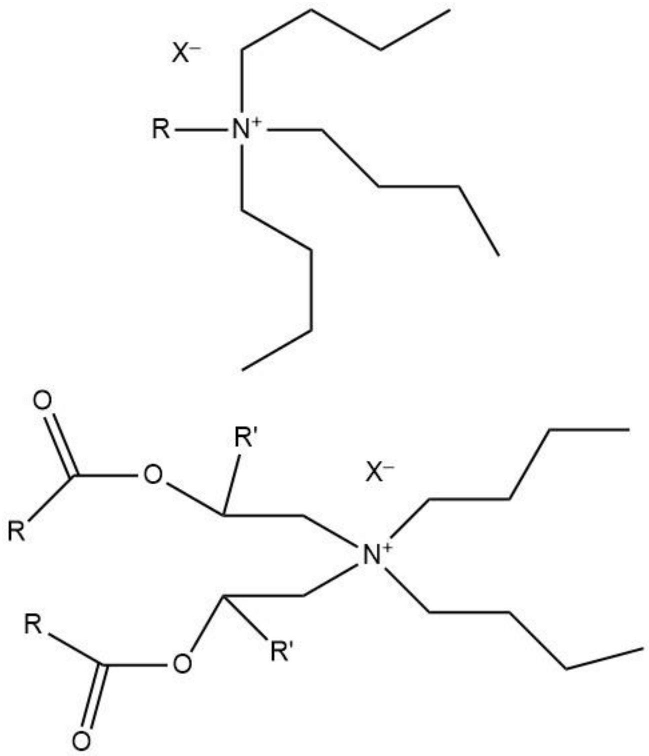


Figure 1.8. Schematic of examples of both single (top) and twin tail (bottom) butylated quaternary AAs, where R = long alkyl chain, R’ = H or $CH_3$ and X = counter ion.[13]

AA are surface active components that absorb to the hydrate surface, resulting in a lyophilic or oil-wet surface. This results in reduction of the possibility of strong attractive hydrogen bonding between hydrate particles, leading to flocculation and dispersions rather than agglomeration and hydrate plugs. Further, hydrate crystals can only agglomerate if they are "water-wetting", while "oil-wetting" hydrates do not accumulate into plugs. This suggests that the bulky hydrophobic tails prevent the hydrate crystals from becoming covered by a water-layer, in addition to keeping hydrate crystals dispersed in the oil phase and keeping them physically separated. It can be envisaged that the former plays a crucial role in the agglomeration process when the water surrounding individual hydrate crystals coalesces and thereafter builds up.[136,137]

Gas Well AAs

The hydrate particles are dispersed by these AAs in the excess water and transported in the aqueous phase.[13] Polyether amines are AAs that operates in this manner and they have been used in fields (Figure 1.9).[138,139]

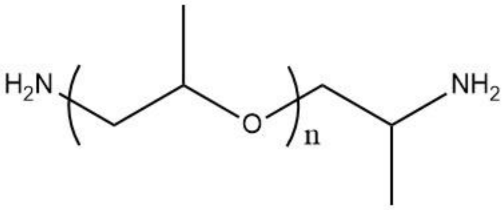


Figure 1.9. Schematic of an example gas well AA of the type polyether diamine.[138]

### 1.6.3 Kinetic Hydrate Inhibitor (KHI)

Kinetic hydrate inhibitor (KHI) is the other class of LDHIs, and they are usually water-soluble polymers or oligomers. In order for these polymers to function as a KHI some structural features must be present within the polymer. This is achieved by incorporating hydrophilic and hydrophobic moieties into the polymer. The hydrophilic functional groups of the polymer usually consist of amide, imide or amine oxide groups, moieties that are capable of making strong hydrogen bonds.[2,13,18] For best performance of the polymer hydrophobic functional groups must accompany the hydrophilic functional groups either directly or adjacent.[140] These features consist of enabling the polymer to have both hydrophilic and hydrophobic capabilities making the polymer amphiphilic. The hydrophilic portion will ensure that the polymer can make hydrogen bonds to water molecules, both in the liquid water and/or to the surface of hydrate particles.[2] The hydrophobic feature will ensure that the role of hydrophobicity and the phenomenon of hydrophobic hydration will control the activity of the polymer in water.[140]

The pendant groups should be close to or part of the polymer backbone. This will reduce the amount of freedom with the corresponding loss of entropy, making the local change in Gibbs free energy ($\Delta G$) less negative.[141] In addition, the polymer backbone should be methylated as several gas hydrate experiments indicates.[142–145] This ensures an open polymer structure which maximize the polymer surface area/hydrodynamic. Further, the efficiency of the KHI polymer will be determined by the pendant groups by their structure, spacing between them, number of them present and the way they are attached to the polymer backbone. For example, the KHI performance have been found to increase with increasing ring size for poly(*N*-vinyl lactam)s, probably because of the increased hydrophobicity of the lactam ring. Another factor which also is crucial for the efficiency of the KHI polymer is the length of the polymer backbone itself, in other words the molecular weight of the polymer.[5] A bimodal distribution of the molecular weight gives better nucleation inhibition.[146] However, it is beneficial that the majority of the polymer is of low molecular weight, with a smaller portion being of higher molecular weight.[18] The majority of the polymer should have a low molecular weight for optimal performance, this results in around 8-10 repeat units and a molecular weight in the range of 1200-2000 g/mol for most good KHI classes.[18,147] The bulk of commercially available KHI polymers and copolymers are based on the monomers *N*-vinylcaprolactam (VCap), *N*-vinylpyrrolidone (VP) and *N*-*iso*-propyl methacrylamide (NIPMAM), as well as hyperbranched poly(ester amide)s based on di-*iso*-propanol amine and various cyclic anhydrides (Figure 1.10).[13]

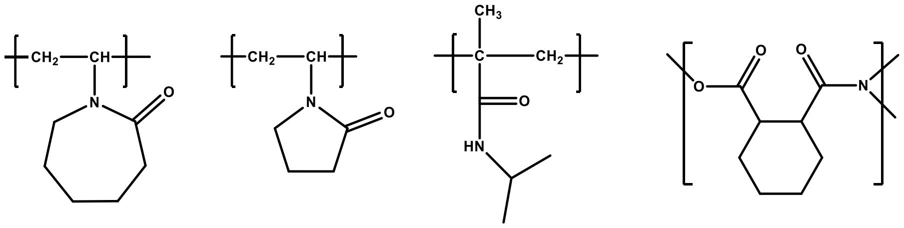


Figure 1.10. Structures of common KHIs, from left to right: Poly(*N*-vinylcaprolactam) (PVCap), poly(*N*-vinylpyrrolidone) (PVP), poly(*N*-*iso*-propylmethacrylamide) (PNIPMAM) (polyvinylic KHIs) and the esteramide unit in hyperbranched poly(ester amide)s.

Because of the amphiphilic nature of these polymers they will have a cloud point ($T_{cl}$) when heated as a aqueous solution.[148–152] In fact this thermoresponsive behavior is seen in many KHI aqueous solutions, with poly(*N*-vinyl caprolactam) (PVCap) $T_{cl}$ about 30-40 °C and poly(*N*-*iso*-propyl methacrylamide) (PNIPMAM) $T_{cl}$ about 35-45 °C as examples.[153] If the temperature is increased above the $T_{cl}$, hydrogen bonds between the amide group and water molecules will break causing an uprise in hydrophobic interactions. This in turn promotes the release of the bound and structured water and the swollen conformation collapses, causing aggregation of the polymer strands.[154] This often occurs 5-15 °C above the $T_{cl}$ point and is denoted as the temperature of deposition ($T_{dp}$).[155]

In a KHI solution the water-soluble polymer is often dissolved in a carrier solvent. One of the tasks this carrier solvent does is of the more obvious type, sufficiently dilute the KHI polymer solution to enable it to be injected and pumped over long distances in umbilical flow lines. The other task is not that obvious, but none the less if it occurs, the impact on the efficiency of the KHI polymer can be tremendous. The carrier solvent can enhance the hydrate inhibiting properties of the polymer, thus act as a synergist with the KHI polymer. The solvent synergism is therefore able to increase the application performance window of the pure KHI polymer or reduce the total polymer dosage.[156] This carrier solvent is often a low molecular weight alcohol, glycol or glycol ether, like methanol, ethanol, monoethylene glycol (MEG) and 2-*n*-butoxyethanol (BGE).[135]

The KHI formulation consists usually of two parts, the water-soluble polymer and the carrier solvent. The polymer makes up the minority of the solution, typically contributing 10-30 wt.%, while the carrier solvent counts for the majority of the solution with typically 70-90 wt.%.[135,156] The concentration range of added dosages of an KHI solution is usually 0.1-1.0 wt.%.[24,120,147,157–159] The KHI solution will delay the formation of gas hydrate in a system.

### 1.6.4 Cloud Point ($T_{cl}$)

For many KHI polymers there is a correlation between them having a low cloud point ($T_{cl}$) and good inhibition performance. It has been theorized that the benefit for a KHI to have a low cloud point are that the polymer surface area/hydrodynamic volume ratio is maximized whilst maintaining water-solubility, the hydrophobic interactions of the polymer at a temperature when hydrogen bonds are about to break down is maximized and the concentration at interfacial regions (gas-water or oil-water) where hydrate formation first occurs are greater.[153]

However, experimental evidence suggest that a low cloud point should not be the first factor to consider when designing a KHI polymer. Although the cloud point is low, the performance of the KHI polymer is poor if the sizing of the hydrophobic groups are not optimal. The optimal size seems to be in the range of three to six carbon atoms depending on their type of hydrophilic functional group they are attached to and their position on the polymer. Moreover, if criteria like pendant hydrophobic groups of an optimal size close to the polymer backbone, the correct hydrophilic functional groups and low molecular weight are fulfilled, a low cloud point near the hydrate formation temperature appears to be beneficial for high KHI efficiency.[153] In addition, the polymer may be more active near the gas-water or oil-water interface where hydrate formation is likely to occur first.

### 1.6.5 Solvent Synergist

The synergistic phenomenon arises when the combined effect of two or more compounds exceed the expected effect the mixture would have. This phenomenon can be utilized to get the same or better effect with a total dosage that is less than the dosages required by the individual components.[160,161] The totally opposite can also occur, where the combined effect of two or more components worsen the expected performance. This is an antagonistic phenomenon.[160] Synergetic effect on KHI polymers have been found for both polymeric and nonpolymeric compounds. Nonpolymeric compounds that have shown synergistic effect with KHI polymers are alkylated guanidinium salts, trialkyl amine oxides, ionic liquids and onium salts (quaternary ammonium or phosphonium salts) (Figure 1.11).[162–166]

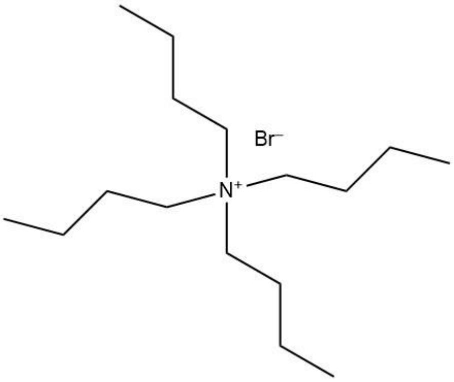


Figure 1.11. Example of an onium salt (quaternary ammonium salt) represented by tetra (*n*-butyl) ammonium bromide (TBAB).

It is especially beneficial if the solvent can be used as a synergist with the KHI polymer. These solvents can either be added upon making aqueous KHI solutions or used as a solvent during synthesizing KHI polymers.[167–170] Many solvents have been reported as beneficial regarding their synergetic effect on KHI polymers, including ketones, alkyl lactates, glycol ethers and alcohols, with the last two as the most effective compound classes. Regarding the glycol ethers, the best synergism was achieved when the alkyl chain contained at least three glycol units when used together with PVCap.[171] Laboratory research have shown that the most effective synergist together with PVCap within this class of compounds are monoglycol ethers containing three to four carbon atoms in the alkyl chain and phenylpropylene glycol.[171–173] Representative glycol ethers include 2-butoxyethanol (ethylene glycol monobutyl ether), 2-*iso*-propoxy-ethanol, *iso*-2-butoxyethanol, propylene glycol butyl ether and monobutyl ether (diethylene glycol). Of these, 2-butoxyethanol (BGE) is preferred because it is a good synergist, it is cheap, has a high flash point and it is approved offshore as mutual solvent (Figure 1.12).[173] It have been shown that glycol ethers with five to six carbon atoms also induce good KHI synergy with PVCap.[169]

Higher homologs were found to be insoluble in saltwater (3.5 %), and lower homologs were shown to exhibit low to no synergetic effect.[171]

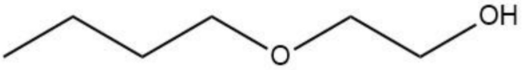


Figure 1.12. Schematic of 2-butoxyethanol (BGE).

Regarding the alcohols, rapports on them acting both synergistic and antagonistic when used together with PVCap have been put forward. Alcohols containing three to five carbon atoms have been reported to affect the performance of PVCap positively, although a smaller positive effect than monoglycol ethers.[171,174] Solvents with one or two glycol functional groups generally gave better synergetic effect than the corresponding alcohol.[169]

Together with PVCap, 4-methyl-1-pentanol have shown outstanding synergistic effect in gas hydrate experiments (Figure 1.13).[169,170] An antagonistic effect on the performance of PVCap have been reported for smaller alcohols with one to three carbon atoms. Further, branching and not just the molecular weight of the alcohol affects the synergetic performance.[175]

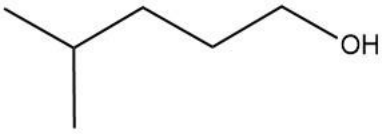


Figure 1.13. Schematic of 4-methyl-1-pentanol.

The synergistic effect by the solvents with PVCap was observed to apparently relate to the size and shape of the hydrocarbyl tail (alkyl or aryl) in addition to the hydrophobicity/water solubility limit. Thus it was shown that synergy was not confined to alkyl groups of three to five carbon atoms but tail sizes of up to even seven carbon atoms also gave good synergy with PVCap.[169]

## 1.7 Kinetic Hydrate Inhibitor Mechanism

Since there exists multiple theories describing gas hydrate nucleation and growth, it should come as no surprise that only hypotheses describe the different reported KHI mechanisms. Therefore, no consensus on the inhibition mechanism exists in the hydrate community. The understanding of the gas hydrate system as well as the effects of different KHIs on gas hydrate formation have been enriched by a large number of experimental studies on KHIs. In addition, computational modelling like molecular dynamics (MD) and Monte Carlo (MC) simulations have also been applied to study KHI mechanisms. Four hypotheses aimed to describe the KHI mechanism have thus far arisen from this research, which are described in the following.

### 1.7.1 Adsorption Inhibition Mechanism Hypothesis

The hypothesis assumes that the polymeric KHI molecules would adsorb onto some part of the growing surface of clustering hydrate particles, altering the morphology and/or lowering the rate of crystal growth.[176] By blocking both the transport of guest molecules and water molecules from reaching the hydrate surface the hydrate nuclei are hindered from further growth, thus not reaching critical size. This is assumed to be achieved by the pendant groups of the KHI polymer. Thus the pendant functionalities of the KHIs enable the adsorption of the polymer onto the growing hydrate surfaces (Figure 1.14).[52,177] This occurs generally via hydrogen bonding and hydrophobic interactions. Further growth of the hydrate is thereby effectively restricted and the likelihood of macroscopic hydrate formation is reduced, because of the hydrate surface coverage by the polymer.[159,177]

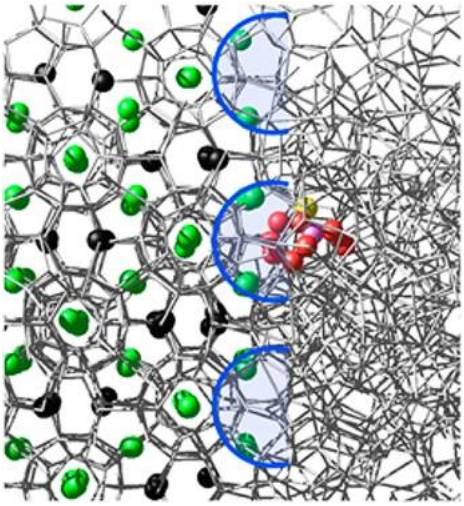


Figure 1.14. In this model the green and black spheres represent the gas molecules in small and large cages of the gas hydrate. The large open cavities on the hydrate surface are presented as blue arcs where the mostly red coloured PVCap monomer are located in the middle one.[178]

Several gas hydrate experimental studies give support to the adsorption inhibition mechanism. Amongst them the effect of PVP on sI methane hydrate formation was investigated as well as the effect of PVP and PVCap on sII methane-ethane-propane hydrate.[179,180] These experimental studies suggest that polymer binding onto the hydrate lattices caused the gas incorporation and nucleation to be retarded. A more stable clathrate hydrate forms in the presence of KHI when compared to a system free of KHI. This suggest that there is a compositional or structural difference between the systems, and that this could be attributed to the KHIs adsorption to the hydrate surface. An observed consequence of this is the reduced dissociation rate outside the hydrate phase boundary when KHI are in the system.[181]

MD simulations on the effect of PVP and PVCap in the presence of methane hydrate formation give their support to this mechanism,[182] as do various other computational models.[177,183–185] One of these studies identified that charge distribution on the edge of the inhibitor and congruence of the size of the inhibitor with respect to the available space at the surface of the hydrate binding site, as molecular characteristics that lead to strongly binding inhibitors.[182] The adsorption of KHIs has been proposed to be caused by hydrogen bonds between the amide groups and the water molecules on the hydrate surface.[18,159] MC simulations demonstrated that the adsorption was a result of hydrogen bonding in the hydrate-gas interface.[185] MD simulations was used to study the role of hydrogen bonding and the effect of a hydrate-water interface. Here it was shown that hydrogen bonding does not affect the affinity of KHIs adsorption on hydrate cages, contrary to prior suppositions. The simulation showed that the carbonyl oxygen of PVCap did not contribute to the adsorption.[178,186] Instead the affinity was attributed as a result of entropic stabilization arising from the presence of cavities at the surface of the hydrates. These large open cavities on the hydrate surface are accommodated by the hydrophobic methylene groups of the lactam rings of PVCap. The rest of the polymer, backbone and amide group, are located outside of the open cavities.[178] It was shown that the amide oxygen, like the carbonyl group, enhance the solubility of the KHIs but they do not enhance the adsorption affinity.[186] Further, when the size of the gas molecule is comparable to the size of the cage the attractive interaction between open cage and gas is maximized.[178] Another study complements these results when it showed that surfactants with long alkyl chains exclusively bind to the half-cages of the hydrate surface through their hydrophobic tails.[187] From these studies, methods towards maximizing the hydrophobic interaction while maintaining water solubility were considered important factors for ensuring strong bonding of the polymers into the hydrate surface.

Other simulations on PVP indicates that a different inhibition mechanism than surface-docking might be present was postulated.[188,189] In these simulations the PVP polymers was located at some distance from the surface of the hydrate. Further indications showed that the PVP polymers are effective at preventing nucleation and to destabilize sub-critical hydrate clusters, but hydrate clusters that have grown substantially beyond the critical size are not affected.[189,190] Molecular simulations was done on one KHI containing a methylated backbone, poly(dimethylaminoethyl methacrylate) (PDMAEMA) and PVP.[190,191] Here it was shown that unlike PDMAEMA, PVP goes through rapid conformation changes during the simulation. It was argued that the methyl groups in the backbone of PDMAEMA sterically hindered the polymer from making these conformation changes and increasing the polymers surface-to-volume ratio. Although, how close a specific type of KHI polymer chain strands is from or sits on the hydrate lattice and how strong the adsorption would be is difficult to quantify.

Another interesting molecular simulation involves the implementations of the Gibbs-Thomson effect to give support to the adsorption inhibition mechanism.[186,192,193] In these simulations the growth of hydrate crystals was either diminished or haltered by the strongly adsorbed surfactants through the development of stationary curved clathrate surfaces (Gibbs-Thomson effect). MC simulations also observed the creation of curved crystal surface in the presence of adsorbed polymers (Figure 1.15).[184] The hydrate surface in which PVCap had adsorbed onto, thus covering, hindered new water molecules and gas molecules from approaching. As only the surrounding area grows the surface becomes concave. The Gibbs-Thompson effect lowered the growth in the PVCap concaved regions.[186] This effect relies on a strong adsorption onto the growing hydrate surface. This is because the curved surface is thermodynamically unstable, and will thus flatten very quickly after desorption.[192] For PVCap, irreversible adsorption is achieved when at least two lactam rings are trapped in open hydrate cages and there is no preference in the spacing between the trapped lactam rings.[186] Polymers will in general be able to adsorb more strongly onto the hydrate surface since they have more available sites for adsorption than monomers. There will also be a time interval between the adsorption event and a noticeable reduction in crystal growth due to the curvature being small initially after adsorption.[192]

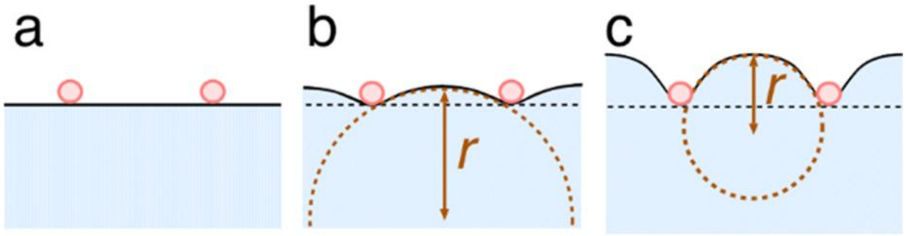


Figure 1.15. In this schematic which depicts the hydrate growth process in the presence of a KHI, the blue area represents gas hydrate and the red spheres are inhibitor molecules irreversibly bound to the water-hydrate interface.[192]

### 1.7.2 Perturbation Inhibition Mechanism Hypothesis

This mechanism has a different mode of action than the previous mention mechanisms. Here the KHI polymers does not act on the hydrate embryos or crystals, but rather on the water phase. It is assumed that the dissolved KHI molecules prevent the water molecules from gathering and forming complete cages by effectively perturbing the water phase. Hence only incomplete water cavities which is insufficient to form hydrate nuclei would emerge in the presence of the KHI polymer chains.[157] Multiple experimental studies support the perturbation inhibition mechanism hypothesis. They include the effect of PVP and PVCap on sII methane-propane hydrate formation,[140] the effect of PVP on both sI methane/carbon dioxide and sII propane/*iso*-butane hydrate formation[194] as vell as the effect of PVCap on sII synthetic natural gas (SNG) hydrate.[195] In addition to the experimental studies that gives support to this mechanism, several MD simulations also concur. In one of these, dissociation of both sI and sII hydrate occurred despite there were no direct contact between PVP and PVCap and the hydrate particles.[188] This indicates that the work mode of polymeric KHIs can be by perturbation.

Another study postulates a two-step mechanism for hydrate inhibition, which is indeed a combination of the perturbation and adsorption mechanisms. First the water and guest molecules structures are being disrupted thus increasing the barrier for nucleation. Then successive adsorption of inhibitor to the hydrate surface retards the hydrate growth.[182] Moreover, from their results charge separation at the end of the inhibitor, similar to the charge separation found in water, secures a strong adsorption to the hydrate surface. In addition the size must also be able to accommodate the available binding sites on the surface of the hydrate.

### 1.7.3 Nucleation Site Interface Inhibition Mechanism Hypothesis

The three aforementioned mechanisms are the major ones, but a less popular mechanism for polymeric KHI is proposed in the literature. The idea of this mechanism is that the polymer chains may cover or interfere with suitable nucleation sites to prevent *in-situ* formation of nuclei. Experimental support comes from studies on cationic starches on sI hydrates of methane, methane-ethane mixture and sII hydrate of methane-propane mixture.[196] In a real system the fluids are in contact with the pipe wall and impurities contained in the system. This will present numerous sits of nucleation that are impractical to be interfered by polymers achieving full coverage.

# 2 Experimental Methods

## 2.1 Syntheses

### 2.1.1 Synthesis of 2-Methacrylamido-caprolactam (2-MACap) Monomer

2-Methacrylamido-caprolactam (2-MACap) was synthesized based on the described method.[197] In a round bottom flask α-amino-ε-caprolactam (1 g, 7.8 mmol) was dissolved in dichloromethane (20 mL). Then triethylamine (0.789 g, 7.8 mmol) was added and the flask was cooled to 0 °C on an ice bath. Methacryloyl chloride (0.816 g, 7.8 mmol) diluted in dichloromethane (10 mL) was added dropwise to the solution in the round bottom flask while vigorously stirring on the ice bath. The mixture was stirred and slowly heated to room temperature overnight (Figure 2.1). Afterwards the reaction mixture was washed with NaCl brine. Then the organic phase was extracted, washed with DIW and dried with $Na_2SO_4$. The precipitated $NEt_3HCl$ (s) was filtered off and solvent was removed *in vacuo* on a rotary evaporator to yield 2-methacrylamido-caprolactam (2-MACap). $^1$H NMR confirmed that the resulting product was pure and it was thus used without further purification steps.

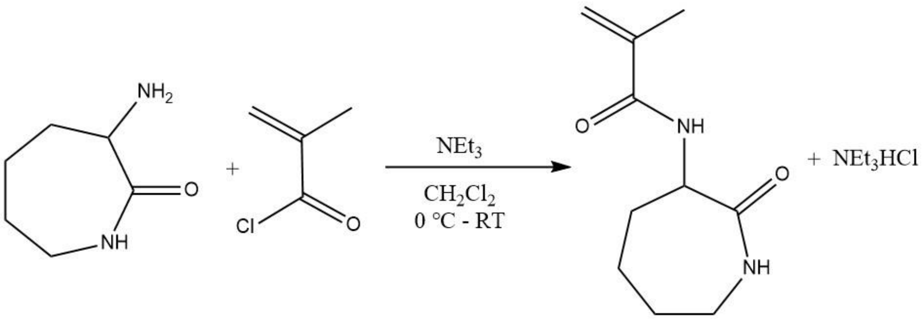


Figure 2.1. Synthesis of 2-MACap.

### 2.1.2 General Polymerization Procedure for Poly(2-methacrylamido-caprolactam) (Poly(2-MACap)) Homopolymer and Copolymer Synthesis

The polymerization synthesis was done in the same general manner for all homopolymers and copolymers. 2-MACap (0.50 g, 2.50 mmol) was dissolved in dimethyl sulfoxide (DMSO) (2 g) in a Schlenk flask with a magnet. AIBN (1 wt.%, 0.005 g) was added and the solution was flushed with dinitrogen using the standard pump-fill technique. While the solution was stirring, it was heated to 70 ℃ and left to react under the protection of dinitrogen overnight. Then the poly(2-MACap) solution was cooled to room temperature and the product was left in solution. The copolymerizations followed the same steps as for the 2-MACap homopolymer, except that in the first step the desired amount of comonomer was added depending on the monomer ratio in the copolymer required. $^1$H NMR showed that all monomer was consumed.

### 2.1.3 Synthesis of 2-Acrylamido-caprolactam (2-ACap) Monomer

The synthesis of 2-acrylamido-caprolactam (2-ACap) is similar to the 2-MACap synthesis and is based on the same described method.[197] α-Amino-ε-caprolactam (5 g, 39.01 mmol) was dissolved in dichloromethane (20 mL) in a round bottom flask. Then triethylamine (3.95 g, 39.01 mmol) was added and the solution was cooled to 0 ℃ on an ice bath. Acryloyl chloride (3.53 g, 39.01 mmol) diluted in dichloromethane (5 mL) was added dropwise to the solution in the round bottom flask with vigorous stirring on the ice bath. Afterwards the mixture was slowly heated to room temperature while stirred overnight (Figure 2.2). The resulting white precipitate was filtered off and washed with dichloromethane. The combined solvents were then removed *in vacuo* on a rotary evaporator to yield 2-acrylamido-caprolactam (2-

ACap). $^1$H NMR confirmed that the resulting product was pure and was used for polymerizations without further purification.

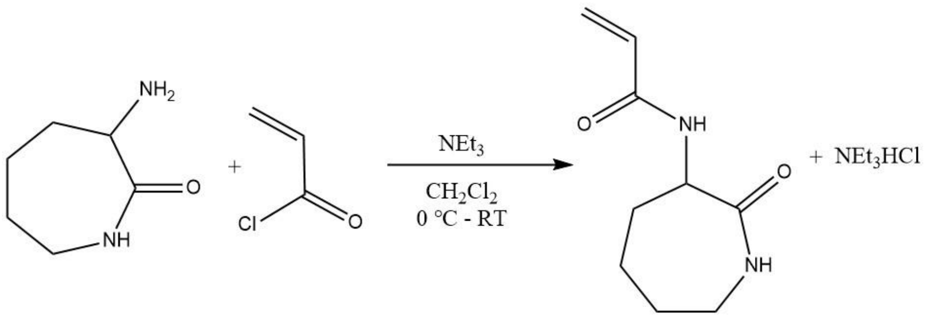


Figure 2.2. Synthesis of 2-ACap.

### 2.1.4 General Polymerization Procedure for Poly(2-acrylamido-caprolactam) (Poly(2-ACap)) Homopolymer and Copolymer Synthesis

The polymerization synthesis was done in the same general manner for all copolymers. 2-ACap (0.50 g, 2.50 mmol) was dissolved in DMSO (2 g) in a Schlenk flask with a magnet. The desired amount of comonomer was added depending on the monomer ratio in the copolymer required. AIBN (1 wt.%) was added and the solution was flushed with dinitrogen using the standard pump-fill technique. While the solution was stirring, it was heated to 70 °C and left to react under the protection of dinitrogen overnight. Then the copolymer solution was cooled to room temperature and the product was left in solution. $^1$H NMR showed that all monomer was consumed.

### 2.1.5 Synthesis of 2-((4-Methylpentyl)oxy)ethane-1-ol (iHex(EO)OH)

This monoglycol ether was not commercially available and was therefore attempted synthesized. The synthesis was based on the described method.[198] In two separate glass vessels, 4-methyl-1-pentanol (3 g, 29.40 mmol) was mixed with toluene (20 mL) and sodium hydroxide (NaOH) (1.29 g, 32.25 mmol) was dissolved in methanol (10 mL), respectively. The two solutions were then introduced into a two-necked round-bottom flask with a distilling column connected. Here the solution was vigorously stirred overnight at 110 °C. The solvent was then removed from the reaction mixture *in vacuo* on a rotary evaporator. Afterwards the solution was dissolved in tetrahydrofuran (THF) (30 mL) and 2-bromoethanol (2.83 mL, 38.14 mmol) was added dropwise. This mixture was then left at room temperature to react overnight. Afterwards the solids were filtered off and the solvent removed from the reaction mixture *in vacuo* on a rotary evaporator. The resulting brown liquid, with a yield of 86 %, was confirmed by $^1$H NMR that the product was pure and it was thus used without further purification steps.

### 2.1.6 Synthesis of Acryloylpyrrolidine (APYD)

Pyrrolidine (8 g, 112.48 mmol) was added to dichloromethane (20 mL) in a round bottom flask, on an ice bath which cooled the solution to 0 °C. Triethylamine (11.38 g, 112.46 mmol) was added to the solution. Dropwise acryloyl chloride (10.18g, 112.47 mmol) in dichloromethane (10 mL) was added to the solution with stirring. The solution was left to reach room temperature with stirring overnight. Afterwards the reaction mixture was washed with NaCl brine. Then the organic phase was extracted, washed with DIW and dried with $Na_2SO_4$. Solvent was removed *in vacuo* on a rotary evaporator to yield acryloylpyrrolidine

(APYD). $^1$H NMR confirmed that the resulting product was pure and it was thus used without further purification steps.

### 2.1.7 Polymerization of VCap in 4-Methyl-1-pentanol (iHexOl)

In a Schlenk flask with a magnet, *N*-vinyl caprolactam (VCap) (2 g, 14.36 mmol) was dissolved in 4-methyl-1-pentanol (4 g, 39.15 mmol). 2,2'-Azobis-*iso*-butyronitrile (AIBN) (1 wt.%, 0.06 g) was added and the solution was flushed with nitrogen using the standard pump-fill technique. While the solution was stirring, it was heated to 80 °C and left to react under the protection of nitrogen for 18 h. Then the formed poly(*N*-vinyl caprolactam) (PVCap) solution was cooled to room temperature and the product was left in solution.

## 2.2 Experimental Equipment and Procedures

### 2.2.1 Cloud Point Measurement

For measurement of the cloud point ($T_{cl}$), a concentration of 2500 ppm of the polymer in deionized water (DIW) was carefully heated. The heating was done in such a manner that the temperature of the solution increased by approximately 2 °C/min while maintaining a visual observation for any sign of haze. If the solution was hazy even at room temperature, it was cooled down in an ice bath before measurement was initiated. The $T_{cl}$ was determined as the temperature where there where a first observed haze in the solution. The measurement was repeated minimum one more time for verification and to show reproducibility.

### 2.2.2 Kinetic Hydrate Inhibitor Performance Testing

The KHI performance testing was conducted on a multi-rocking cell apparatus, The Rocking Cell 5 (RC5) apparatus supplied by PSL Systemtechnik, Germany. This apparatus contains a cooling bath where five high-pressure stainless steel rocking cells, supplied by Svafas, Norway, are rocked. The cells have an internal volume of 40 mL and a stainless-steel ball inside each cell is used for agitating the test solution. Both the cooling bath and the cells are equipped with temperature sensors in addition to each cell having pressure sensors (Figure 2.3).

Figure 2.3. Top: The RC5 apparatus in its operational status. Bottom: Closeup of the five cells positioned in the water bath of the RC5 apparatus.

Standard natural gas mixture (SNG) (Table 2.1), which preferentially forms Structure II gas hydrate as the most thermodynamically stable phase, was the gas mixture used in these tests.

Table 2.1. Composition of the synthetic natural gas mixture (SNG) used in the KHI performance testing.

| **Component** | **Mol %** |
|---|---|
| Methane | 80.67 |
| Ethane | 10.20 |
| Propane | 4.90 |
| *iso*-Butane | 1.53 |
| *n*-Butane | 0.76 |
| $N_2$ | 0.10 |
| $CO_2$ | 1.84 |

All experiments were conducted by pressurizing to 76 bar with this gas mixture at an initial temperature of 20.5 °C. The hydrate equilibrium temperature ($T_{eq}$) at 76 bar for this particular gas mixture have previously been determined to be 20.2 ± 0.05 °C by standard laboratory dissociation experiments warming at 0.025 °C/h for the last 3-4 °C. This correlated well with calculations done by the Calsep PVTSim software.[199,200] During experimental tests, each cell was a closed pressurized system. Both the slow constant cooling (SCC) and the isothermal test method was used as experimental procedures. These test methodologies enable the relative performance of various compounds to be compared. In order to investigate these compounds under field conditions, further testing is required.

Slow Constant Cooling Test Procedure

The slow constant cooling method (SCC) was utilized to validate the KHI potential for the different compounds in this research. It was used as the standard screening method for KHI potential. This experimental procedure investigates the degree of sub-cooling (temperature below $T_{eq}$) each compound cand withstand before macroscopic hydrate formation occurred. The procedure for high-pressure kinetic hydrate inhibition testing by the use of constant cooling is summarized in the following:[145,145,169,170]

1. At least one day in advance prior to initialization of the KHI test, the polymer, and if applicable the synergist, was dissolved to the desired concentration in deionized water prior to initializing the test.
2. To each of the five cells, 20 mL test solution was usually added. The test solution consisted of various additives dissolved in distilled water.
3. A sequence of vacuum and pressurizing with SNG was applied in order to replace the air with SNG in the cells. First vacuum then pressurizing with SNG to 3-5 bar, then depressurizing before a final round with vacuum.
4. After this procedure, the system was pressurized to the experimental pressure of 76 bar with SNG.
5. The cells cooled from 20.5 °C to 2.0 °C with a cooling rate of 1.0 °C/h while being rocked at a rate of 20 rocks per minute with an angel of 40°.

The initial pressure was 76 bar and the temperature were decreased from 20.5 °C to 2 °C during a slow constant cooling experiment. Because each cell is being a closed system there will be a linear pressure decrease from which both the onset temperature for hydrate formation ($T_o$) and the rapid hydrate formation temperature ($T_a$) can be observed (Figure 2.4). $T_o$ is defined as the temperature at the first observable deviation from this linear pressure decrease. It is quite possible that the hydrate nucleation initiated at a molecular level prior to this, since this is the first macroscopic observation of hydrate formation done by an observation on a linear pressure decrease. However, these experiments are not capable of detecting nucleation which possibly happens earlier. A rapid pressure decrease can be observed with varying interval after the $T_o$ have occurred. $T_a$ is defined as the temperature at which the pressure decrease is at its steepest, in other words where the hydrate formation is at its fastest.

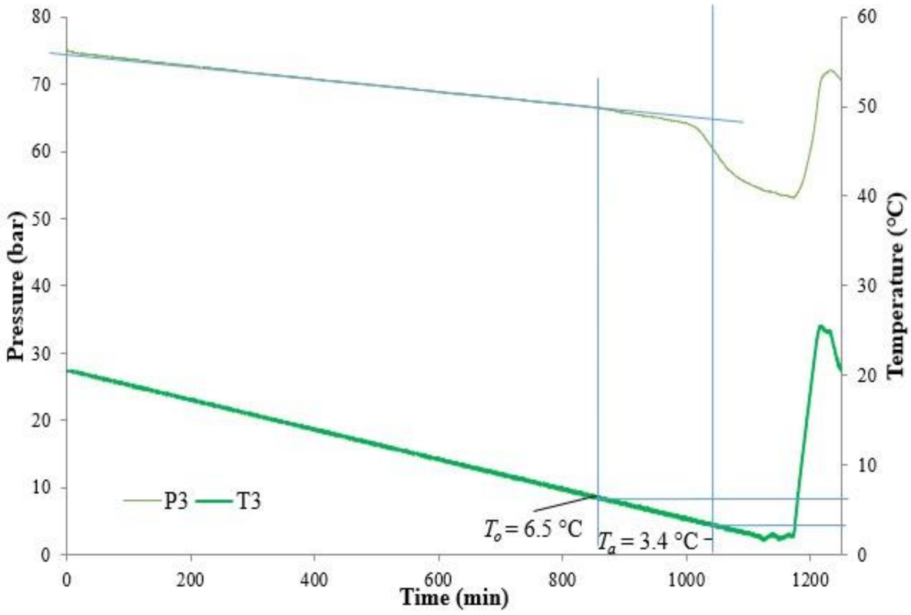


Figure 2.4. Standard constant cooling experiment for cell 3 containing 2500 ppm PVCap and 5000 ppm cyclohexanol as synergist, where both $T_o$ and $T_a$ is determined.

In order to ensure statistical validity of the results 8-10 individual experiments for each compound were conducted. Exceptions were made in the case where there where limited amount of compound or other challenges such as precipitation that caused loss of test solution. Hydrate nucleation is by nature a stochastic process. Hence some scattering of the data was to be expected, and ± 10-15 % scattering where typically observed in a set of 10 experiments. No systematic error, leading to consistently better or worse results, where observed from the five cells.

Isothermal Test Method

This test method was utilized to investigate for how long a compound could prevent hydrate formation at a predefined sub-cooling. This method was only used for the compounds that had the best KHI capabilities in order to further separate them. The test method are similar to the SCC method and are described in the following:[170]

1. At least one day in advance prior to initialization of the KHI test, the polymer, and if applicable the synergist, was dissolved to the desired concentration in deionized water prior to initializing the test.
2. To each of the five cells, 20 mL test solution was usually added. The test solution consisted of various additives dissolved in distilled water.
3. A sequence of vacuum and pressurizing with SNG was applied in order to replace the air with SNG in the cells. First vacuum then pressurizing with SNG to 3-5 bar, then depressurizing before a final round with vacuum.
4. After this procedure, the system was pressurized to the experimental pressure of 76 bar with SNG.
5. The cells cooled from 20.5 °C to 4.0 °C over one hour with a cooling rate of 10 °C/h without rocking.
6. Upon reaching the experimental test temperature of 4.0 °C, the rocking commenced with a rate of 20 rocks per minute with an angle of 40°. During this experimental run the temperature is kept at 4 °C for an extended period, making the pressure graph horizontal.

The time which the first sign of any pressure drop, first deviation from the horizontal pressure graph occurs, is defined as $t_o$. A rapid pressure decrease can be observed with varying interval after $t_o$ have occurred. This is where the pressure decrease is at its steepest, or in other words the hydrate formation is at its fastest. The time at which this occurs is defined as $t_a$ (Figure 2.5).

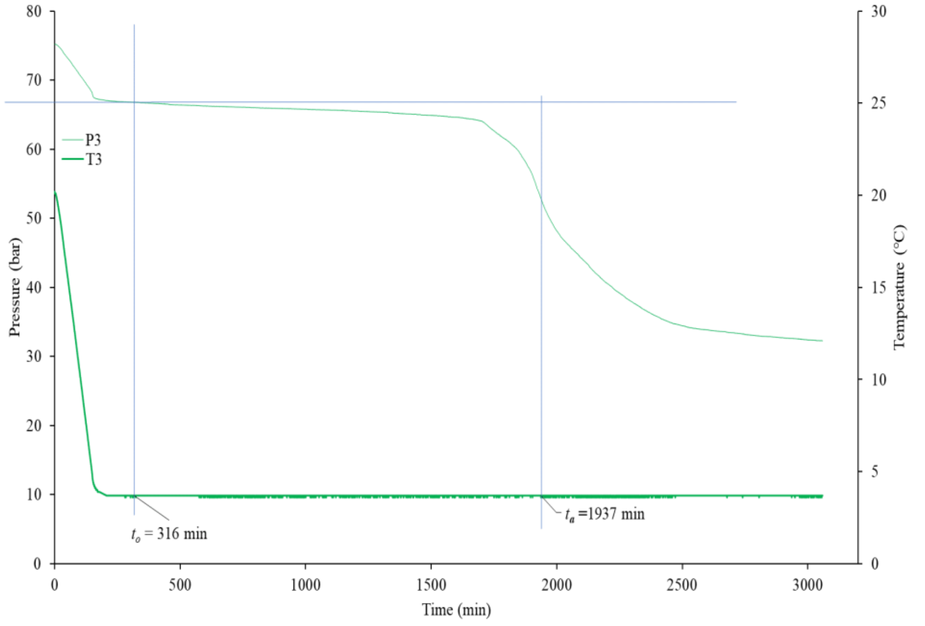


Figure 2.5. Graph from one cell with both $t_o$ and $t_a$ determined during an isothermal experiment. In this example the cell contained 2500 ppm PVCap and 2500 ppm iHexOl.

# 3 Objectives

One of the most common kinetic hydrate inhibitors (KHIs) polymer commercially available and used to combat gas hydrate formation in oil and gas field production flow lines is poly(*N*-vinylcaprolactam) (PVCap) and related copolymers. KHI polymers that have a good performance in inhibiting gas hydrate usually accommodates a low cloud point. It is known that the addition of certain solvents to the KHI polymer can enhance its ability to hinder gas hydrate formation, thus act synergistically together. Neither the KHI polymer nor the synergistic mechanism are fully understood.

In this PhD the objectives were:

- Investigate if the cloud point of a polymer correlates with its KHI performance (Paper I).
- Investigate the reliability and performance of some vinyl lactam-based KHIs under a range of treatments (Paper II).
- Investigate different types of solvents for their potential synergetic effect with PVCap (Paper III and IV).
- Investigate the potential synergetic effect of acetylenic diol surfactants with different KHIs (Paper V).
- Investigate the potential synergetic effect of alkylboronic acids and organic acids with PVCap (Paper VI).
- Investigate and synthesize polymers/copolymers of 2-methacrylamidocaprolactam (2-MACap) and 2-acrylamidocaprolactam (2-ACap) as KHIs (Paper VII and VIII).
- Investigate high cloud point polyvinylaminals as non-amide based KHIs (Paper IX).

The results from the completed studies are presented and discussed briefly in the following chapter, and the main conclusions are summarized in chapter 5. The details are given in the full papers, which are attached in the Appendices.

# 4 Summary of Results and Discussions

## 4.1 Paper I: Does the Cloud Point Temperature of a Polymer Correlate with Its Kinetic Hydrate Inhibitor Performance?[153]

In a kinetic hydrate inhibitor (KHI) formulation the main active compound is one or more water-soluble polymers. These polymers contain both hydrophilic and hydrophobic entities, which makes the polymers amphiphilic and causes them to often exhibit low cloud points ($T_{cl}$) when heated as aqueous solutions. A phase change occurs as the polymer loses water-solubility and the solution therefore turns cloudy at $T_{cl}$.[148–152] This is also known as lower critical solution temperature. Most KHI polymers contain an amide group, and the amide-water hydrogen bonds will disrupt resulting in increased hydrophobic interactions if the solution is heated above the $T_{cl}$. The swollen conformation collapses as the release of both bound and structured water is promoted. This causes aggregation of the polymer strands.[154] If there is added more heat to the solution, the polymer will deposit, known as the deposition point temperature ($T_{dp}$). Most polymers used in commercial formulations possesses this thermosresponsive behavior. Interestingly, many of the most active KHI polymers have a low $T_{cl}$ which is often not far above the equilibrium temperature for gas hydrate formation. Notably mentioned are poly(*N*-vinylcaprolactam) (PVCap) with a $T_{cl}$ of about 30-40 °C and poly(*N*-*iso*-propylmethacrylamide) (PNIPMAM) with a $T_{cl}$ of about 35-45 °C, depending on several factors such as molecular weight and method of manufacture (Figure 4.1).

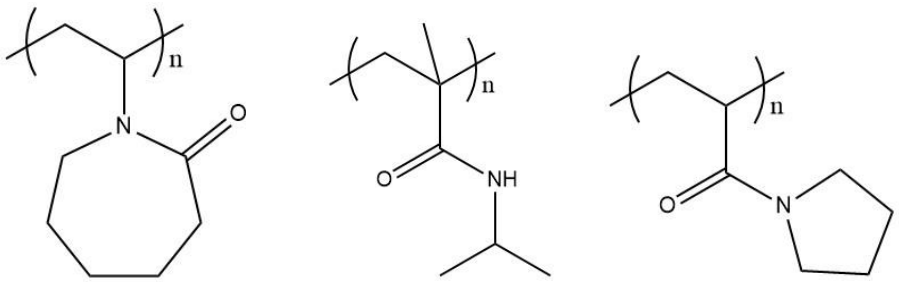


Figure 4.1. Schematics of homopolymers of low cloud points, from left poly(*N*-vinylcaprolactam) (PVCap), poly(*N*-*iso*-propylmethacrylamide) (PNIPMAm) and poly(acryloylpyrrolidine) (PAP).

Many reports from the literature supports the theory that lowering the cloud point of a KHI polymer increases its performance. PVCap which has a low cloud point, outperforms poly(*N*-vinylpyrrolidone) (PVP) which has a high cloud point.[52,201] As the pendant alkyl group was increased, which made the polymer more hydrophobic resulting in lower cloud point, the KHI performance of poly(*N*-alkylacrylamide)s increased.[142,154,202,203] This was also observed for a series of ring-opened poly(2-alkyl-2-oxazoline)s when the alkyl group length was increased.[204] When either expanding the pendant alkyl groups or expanding the ring size depending on the polymer class, the cloud point was decreased while the KHI performance increased for the polymers poly(*N*-vinyl lactam)s of ring size five to eight carbon atoms, ring-alkylated PVPs, polyvinylalkanamides, polyglycines, poly(2-vinyl-4,4-dimethylazlactone)s and alkylated polymethacrylamides (Figure 4.2).[205–209] Each of the employed methods, N-alkylation, ring expansion and copolymerization, resulted in lower cloud point and improved performance of 3-methylene-2-pyrrolidone.[210] By adding some hydrophobic groups to the KHI polymer it is possible to lower the cloud point and improve the performance. Large hydrophobic groups can be added in two general ways: Added as a polymer end-cap or copolymer block group as well as added as a side chain in a very hydrophobic monomer.

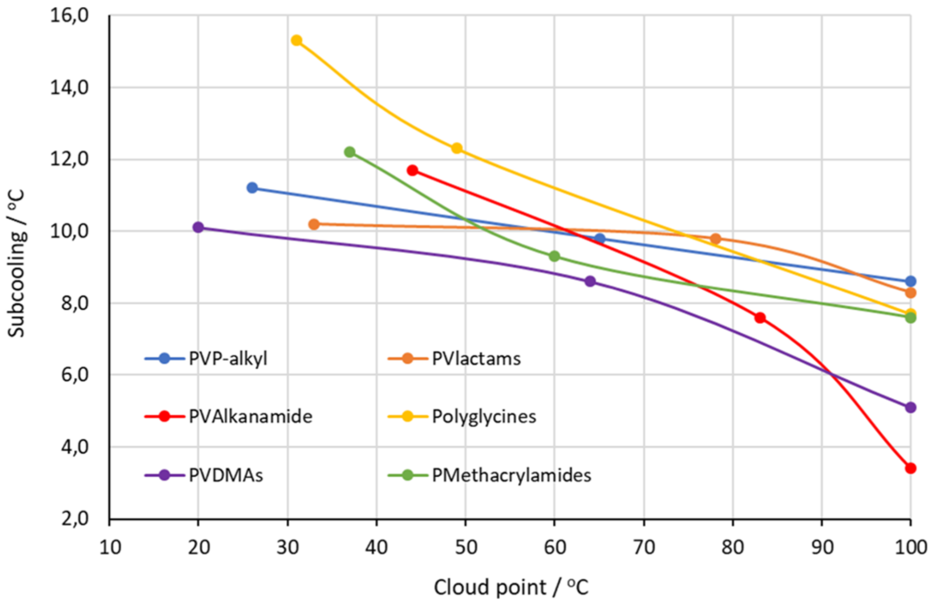


Figure 4.2. Average onset temperature for KHI test of polymers at a concentration of 2500 ppm with a sII hydrate forming gas.

There are some exceptions to the principle that lower cloud point equals better KHI performance:

- The polymerization method and subsequent polymer molecular weight.
- Adding a methyl group to the monomer units in a polyvinyl backbone to open up the polymer structure.
- Copolymerization with a more hydrophilic monomer which also helps on opening up the polymer structure.
- Adding terminal hydrophilic polyether chains to a hyperbranched polymer.

Slow constant cooling KHI experiments were conducted on specially designed KHI polymers in order to give answers to the questions in the following:

1. Is the size of the pendant hydrophobic groups important?

A low-molecular-weight polymer poly(vinyl methyl ether) (PVME) and a short polymer series of ethoxylate-propoxylate-ethoxylate (EO-PO-EO) block copolymers, with varying EO to PO ratio where the only hydrophobic groups of the main backbone are methyl groups from the PO monomer units. All these methylated polymers had a low cloud point, but a poor KHI performance. Further support to the theory that low cloud point is not the most crucial factor if the hydrophobic groups are too small was found for a polymer with pendant ethyl groups, the esteramide derivative of poly(2-*iso*-propyl-2-oxazoline) (PiPOx-AAc/Apr), which also has some methyl groups.

2. Can we see a trend in the KHI performance for a polymer class with varying cloud points but never with optimal size groups for interaction with hydrate cavities?

The same short series of EO-PO-EO block polymers also answers this question, in that there is no observable trend in KHI performance for a polymer class with varying cloud points when the size of the groups for interaction with hydrate cages are not optimal. Two polymer classes where large (octyl) groups were placed as terminal groups, namely *N*-octylmethacrylamide/*N*-methylolmethacrylamide and an amine oxide polymer, hyperbranched polyethyleneimine with a mix of octyl and ethyl groups, were deliberately synthesized. Two ratios of *N*-octylmethacrylamide/*N*-methylolmethacrylamide (OctylMAm/MMAm) copolymers were synthesized and the other polymer had a pentylene group with a terminal hydroxyl group, poly(*N*-hydroxypentylacrylate) (pM$_5$). Both of these polymer classes had a low cloud point, but the KHI performance was poor.

3. Do polymers with the same $M_w$ and same number of optimum-sized hydrophobic groups but with different cloud points have similar KHI performance?

The copolymer VP with *n*-butyl acrylate (BuA) in a 12:1 ratio was synthesized and it had a low cloud point. The KHI performance of this copolymer was much better than PVP, which indicates that lowering the cloud point is beneficial if it involves addition of the correct size hydrophobic groups. Polyglycol chains as polyglycol(9) methacrylate (PEG9MA) monomer units was added to PVCap, synthesizing VCap/PEG9MA in both 19:1 and 9:1 ratio. By adding hydrophilic polyglycol groups as side chains the KHI performance was not improved.

4. Can we take a high cloud point KHI polymer and improve the performance by adding a few hydrophobic groups to reduce the cloud point?

Blocks of the hydrophobic monomer methyl methacrylate (MMA) was added in two different ways to VIMA/VCap and PVP, respectively. The two methods of adding MMA were either in a mixture with VIMA and KHI monomers or after polymerizing VIMA and KHI monomers for 1 h. Both methods gave copolymers with considerably lower cloud points, but the KHI performance was essentially unchanged compared to VIMA/VCap, with perhaps a slight improvement in the KHI performance for PVP. These results indicates that if the hydrophobic monomer does not possess the correct size hydrophobic groups the decrease in cloud point is not beneficial with regards to the KHI performance.

## 4.2 Paper II: Reliability and Performance of Vinyl Lactam-Based Kinetic Hydrate Inhibitor Polymers after Treatment under a Range of Conditions[211]

A range of treatments have been applied to well-known kinetic hydrate inhibitors (KHIs) such as poly(*N*-vinylcaprolactam) (PVCap), poly(*N*-vinylpyrrolidone) (PVP) and 1:1 *N*-vinylcaprolactam:*N*-vinylpyrrolidone (VCap:VP) copolymer in order to determine their reliability and whether the treatment conditions could affect the KHI performance. Further, the effect of these conditions could either increase or decrease the KHI performance. The treatment utilized include thermal aging (at varying temperatures, at varying pH and in monoethylene glycol (MEG) solvent), treatment with microwave or ultrasound, ball-milling and oxidizing agents (household bleach or hydrogen peroxide, also with heat).

The long-term reliability of both PVCap (about 41 wt.% in MEG) and 1:1 VP:VCap copolymer (53.8 wt.% in water) were investigated (Table 4.1).

Table 4.1. Slow constant cooling tests on 2500 ppm active polymer. Standard deviations are given in parentheses.

| **Polymer** | **$T_o$ (°C)** | **$T_a$ (°C)** |
|---|---|---|
| No additive | 16.8 (0.5) | 16.7 (0.4) |
| PVCap 2004 | 10.0 (0.3) | 7.9 (0.2) |
| PVCap 2010 | 9.7 (0.4) | 7.8 (0.5) |
| PVCap 2016 | 10.2 (0.2) | 7.5 (0.4) |
| 1:1 VP:VCap 2004 (immediate testing) | 7.3 (0.5) | 6.0 (0.5) |
| 1:1 VP:VCap 2004 | 7.4 (0.6) | 6.5 (0.4) |
| 1:1 VP:VCap 2010 | 8.5 (0.7) | 5.8 (0.7) |
| 1:1 VP:VCap 2016 | 8.2 (0.6) | 5.8 (0.3) |
| 1:1 VP:VCap 2020 | 8.1 (0.4) | 5.4 (0.4) |

All samples were kept in screw-lid-sealed plastic bottles in the laboratory at 20.5 °C and only occasionally briefly opened. Hence the samples were stored aerobically but without loss of solvent. Within a confidence interval of 95 % there were no significant difference in the performance for neither PVCap nor 1:1 VP:VCap copolymer at different manufacturing years. In addition, a solution of 1:1 VP:VCap (2004) copolymer were prepared and tested immediately as well as after stirring overnight at 20.5 °C. The results were almost identical, indicating that there is no difference in waiting approximately 24 h before testing the polymer solution.

The potential effect pH, heat, microwave, ultrasonic and the addition of monoethylene glycol (MEG) have on the performance of PVCap and 1:1 VP:VCap copolymer was investigated and summarized (Table 4.2).

Table 4.2. Slow constant cooling KHI results for 2500 ppm KHI polymer. MEG concentration 2500 ppm. With the effect of pH, heating, microwave, ultrasonic and addition of MEG. Standard deviations are given in parentheses.

| **Polymer** | **$T_o$ (°C)** | **$T_a$ (°C)** |
|---|---|---|
| No additive | 16.8 (0.5) | 16.7 (0.4) |
| PVCap $M_w$ = 7-12 kg/mol | 10.4 (0.3) | 8.9 (0.3) |
| PVCap + MEG | 9.2 (0.4) | 8.8 (0.3) |
| PVCap (pH 3.9) | 10.2 (0.2) | 9.6 (0.2) |
| PVCap (pH 3.9, heat 90 °C for 20 h) | 10.6 (0.3) | 9.8 (0.3) |
| 1:1 VP:VCap 2004 | 7.4 (0.6) | 5.6 (0.4) |
| 1:1 VP:VCap 2004 (heat 80 °C for 20 h) | 7.5 (0.4) | 5.6 (0.3) |
| 1:1 VP:VCap 2004 + MEG | 7.1 (0.5) | 5.7 (0.3) |
| 1:1 VP:VCap 2004 + MEG (immediate testing) | 7.0 (0.5) | 5.5 (0.4) |
| 1:1 VP:VCap 2004 + MEG (after 160 °C for 1 h) | 7.4 (0.6) | 6.3 (0.5) |
| 1:1 VP:VCap 2004 (pH 3.9) | 7.8 (0.5) | 5.5 (0.4) |
| 1:1 VP:VCap 2004 (pH 3.9, heat 80 °C for 20 h) | 8.0 (0.4) | 5.6 (0.4) |
| 1:1 VP:VCap 2004 (microwave treatment) | 7.1 (0.4) | 5.9 (0.4) |
| 1:1 VP:VCap 2004 (ultasonic treatment) | 7.3 (0.5) | 5.7 (0.5) |

The 1:1 VP:VCap copolymer solution was heated to 80 °C anaerobically for 20 h in a sealed tube. Then another solution of 1:1 VP:VCap copolymer was deliberately acidified to pH 3.9 by adding hydrochloric acid. An identical sample was in addition heated to 80 °C anaerobically for 20 h in a sealed tube. The same pH with PVCap both with and without heating anaerobically in a sealed tube to 90 °C for 20 h was also conducted. Within a 95 % confidence level, there were no statistically difference in the performance between the unaltered polymer, heated,

acidified and acidified as well as heated samples of the respective KHI polymers. A 1:1 VP:VCap copolymer solution was microwaved at 780 W until the solution boiled (4-5 min). Another solution was ultrasound treated at 40 kHz for 5 min at 20.5 °C. There were no statistically difference in the performance between the unaltered copolymer, and the copolymer treated with microwave and ultrasound, respectively. MEG was added to a solutions of 1:1 VP:VCap copolymer and one solution was stirred for 24 h before testing, one tested immediately and one heated to 160 °C for 1 h, with no statistically difference in results. Only when MEG was added to PVCap there were a slight increase in performance.

The impact mechanical stress makes on KHI polymers were investigated by using ball-milling apparatus equipped with zirconium(IV) oxide balls on KHI powders. The KHI polymer powders were ball-milled for 60 min (10 min with 2 min cooling intervals in-between) at 700 rpm, during which the temperature can reach up to 70 °C.[212] (Table 4.3).

Table 4.3. Slow constant cooling KHI test results for the ball-milled polymers at 2500 ppm. PVP 120*k* insoluble in DMF, manufacturer gives $M_w = 3 \times 10^6$ g/mol. Standard deviations are given in parentheses.

| **Polymer** | **$M_n$ (g/mol) / PDI** | **$T_o$ (°C)** | **$T_a$ (°C)** |
|---|---|---|---|
| No additive | - | 16.8 (0.5) | 16.7 (0.5) |
| PVP 120*k* ($M_w = 3 \times 10^6$ g/mol) | - | 13.7 (0.4) | 11.2 (0.3) |
| PVP 120*k* after 60 min ball-milling | 10000 / 2.57 | 12.8 (0.5) | 10.5 (0.5) |
| PNIPMAM | 19000 / 12.1 | 10.5 (0.5) | 10.1 (0.4) |
| PNIPMAM after 60 min ball-milling | 7000 / 1.47 | 9.8 (0.4) | 9.4 (0.3) |

Within the 95 % confidence level there were no statistically significant difference between the original PVP 120*k* and the original PNIPMAM compared to the ball-milled version of the respective polymers. The results from PVP and PNIPMAM indicate the KHI polymers may degrade to some degree under very harsh mechanical conditions. If the molecular weight rage is reduced to a more optimal shorter polymer chains this could improve the KHI performance of the polymers. Ball-milling was tried as a mean to make polymer via vinyl polymerization of classic monomers found in KHIs with a radical initiator. Both VCap and NIPMAM was ball-milled separately with 1 wt.% AIBN for 3 × 10 min periods. The same procedure was repeated but with 2-propanol added as solvent. In both situation no polymerization appeared to have taken place by $^1$H NMR analysis.

Oxidation agents were investigated as the last chemical treatment in this study. The two oxidizing agents used in this study were the biocides sodium hypochlorite and hydrogen peroxide (Table 4.4).

Table 4.4. Slow constant cooling KHI result for 2500 ppm polymer after treating with oxidizing agents. Standard deviations are given in parentheses.

| **Polymer** | ***T<sub></sub>*** |  |
|---|---|---|

*Some precipitate in the sample, removed before KHI performance testing.

1 Mole equivalent of sodium hypochlorite was added to PVCap, and only when the solution was heated to 90 °C for 20 h there were a difference in performance. The performance decreased, but this is obviously caused by lower polymer concentration due to some undissolved portions after heating. But some of the remaining PVCap could have been oxidized. The same conditions was used for 1:1 VP:VCap copolymer, resulting in no statistical differences in performance. 1 Mol and 2 mol equivalent of 30 wt.% hydrogen peroxide solution was added to separate solutions of PVCap. In both cases there were an increase in performance. The solution with 1 mol equivalent $H_2O_2$ was in addition stirred for 20 h at 20.5 °C, and this one gave the best performance of the two. Thus, it seems that the hydrogen peroxide is able to affect the solubility of the

PVCap polymer. The formation of a PVCap·$H_2O_2$ adduct cannot be ruled out since the PVP·$H_2O_2$ adduct is known.[213]

## 4.3 Paper III: Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly(*N*-vinylcaprolactam)[169]

Poly(*N*-vinylcaprolactam) (PVCap) is one of the most well-known KHI polymers and is often used as a benchmark for comparison of other potential KHI polymers (Figure 4.3).[140,166,172,214–218] The largest constituent of a KHI formulation is the carrier solvent, and it would be beneficial if this solvent also acted as a synergist with the KHI polymer. A range of solvents have been reported to function as synergist with PVCap. These includes glycol ethers particularly with three to four carbon atoms in the alkyl chain in addition to phenylpropylene glycol[171–173] and alcohols containing three to five carbon atoms.[171,174] It have also been shown that not only does the molecular weight affect the synergetic performance of alcohols, so does also the branching of the molecule.[175] Different solvent were tested for their potential synergetic effect with poly(*N*-*iso*-propyl methacrylamide) (PNIPMAM),[168] and this parallel study complements this by investigating the synergetic effect on another polymer namely PVCap. Different length, branching and cyclic alkyl “tails” of alcohols, glycol ethers and ketones implements were investigated as solvent synergists. Throughout this study, PVCap ($M_w$ = 10 000 g/mol) was used as the KHI polymer where different solvent synergists were added. The concentrations used was 2500 ppm of KHI polymer and 5000 ppm of synergist. Different classes of chemicals were investigated as synergist, including glycol ethers, aliphatic alcohols (acyclic and cyclic) and ketones.

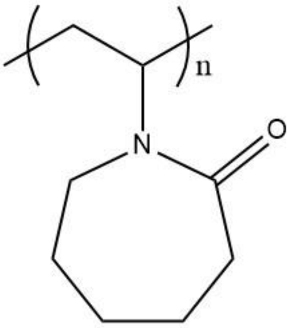


Figure 4.3. Schematic of poly(*N*-vinylcaprolactam) (PVCap).

Slow constant cooling KHI experiments (SCC) were utilized to examine the potential synergistic effect of the solvents on PVCap (Table 4.5).

Table 4.5. Summarized results for SCC KHI tests of 2500 ppm PVCap with 5000 ppm of different solvents.

| **Additive** | **$T_o$ (°C)** | **$T_a$ (°C)** |
|---|---|---|
| D.I. water | 17.2 | 16.6 |
| PVCap | 10.4 | 8.9 |
| **Synergist** | | |
| Monoethylene glycol (MEG) | 9.2 | 8.8 |
| *n*-Butyl glycol ether (nBGE) | 7.3 | 3.8 |
| *iso*-Butyl glycol ether (iBGE) | 5.7 | 2.5 |
| *tert*-Butyl glycol ether (tBGE) | 6.2 | <3.7* |
| Monoethylene glycol mono-n-hexyl ether | 10.2 | 9.9 |
| 2-(Cyclopentyloxy)ethanol | 4.7 | 2.1 |
| 2-(Cyclohexyloxy)ethanol | 4.2 | 2.3 |
| Diethylene glycol monoethyl ether (DEGEE) | 9.5 | 8.5 |

| | | |
|---|---|---|
| Butyl diglycol ether | 5.5 | 2.9 |
| Diethylene glycol mono-*n*-hexyl ether | 7.3 | 5.8 |
| Triethylene glycol monobutyl ether | 5.3 | 3.2 |
| 2-Propanol (*iso*-propanol) | 9.5 | 6.6 |
| 1-Butanol | 7.5 | 4.8 |
| 2,2-Dimethyl-1-propanol (neopentyl alcohol) | 5.8 | 3.9 |
| 3-Methyl-1-butanol (*iso*-amylalcohol) | 5.6 | 2.0 |
| 3-Methyl-2-butanol | 6.4 | 3.4 |
| 1-Pentanol | 7.4 | 2.5 |
| 4-Methyl-1-pentanol | <3 | <3 |
| 1-Hexanol** | 5.8 | 3.3 |
| 2-Ethyl-1-hexanol*** | 10.8 | 10.4 |
| Furfuryl alcohol | 9.7 | 7.5 |
| Tetrahydrofurfuryl alcohol | 9.5 | 6.4 |
| Cyclopentanol | 6.8 | 5.1 |
| Cyclohexanol | 6.8 | 3.4 |
| 4-Methylcyclohexanol (cis and trans mixture) | 5.9 | 3.1 |
| Cycloheptanol | 6.2 | <3 |
| 2-Methyl-3-pentanone | 10.3 | 8.8 |
| 3,3-Dimethyl-2-butanone | 7.4 | 4.3 |
| 4-Methyl-2-pentanone | 5.7 | 3.4 |
| 5-Methyl-2-hexanone | 7.5 | 4.3 |

*Cooling stopped at 3.7 °C. **Cloudy solution. ***Solvent synergist was not totally dissolved.

From Table 4.5 it can be observed that addition of the various solvents to PVCap gave a wide range of results. Most worked as synergists with PVCap, while a few impaired the KHI performance of PVCap. Monoglycol ethers are well-known for their proven synergetic effect on various KHI polymers, including poly(*N*-vinyl lactam)s and poly(*N*-alkyl(meth)acrylamide)s and they have been investigated as synergists for PNIPMAM.[13,18,147,159,168,171,219] To follow up this research we started by investigating a rage of glycol ethers for their potential synergetic effect with PVCap. Besides monoethylene glycol (MEG) which only had a minimal synergetic effect with PVCap at the tested concentration, all other alkyl glycol ethers had at least four carbon alkyl group, because they have better performance than smaller alkyl groups as suggested by previous work.[172] It was found that for the acyclic monoglycol ethers the synergistic effect improved in the sequence monoethylene glycol mono-n-hexyl ether < MEG < nBGE < tBGE ~ iBGE. Two monoglycol ethers containing cyclic alkyl groups, as performed in previous work on PNIPMAM,[168] namely 2-(cyclopentyloxy)ethanol and 2-(cyclohexyloxy)ethanol was investigated for their potential synergy with PVCap. The latter having the best synergy with PVCap, but both these cyclic monoglycol ethers had a better performance compared to the acyclic monoglycol ethers investigated in this study. This indicates that if the alkyl group is of the correct size, monoglycol ethers containing branched or cyclic alkyl groups appears to have a better synergy with PVCap than monoglycol ethers with straight-chain alkyl group. These findings have a good correlation with the results for the same monoglycol ethers tested with PNIPMAM.[168] The impact on the synergetic properties of glycol ethers by adding more oxyethylene (glycol ether) groups into the alkyl "tail" was investigated. In total three diglycol ethers were investigated with ever increasing alkyl "tail", diethylene glycol monoethyl ether (DEGMEE), butyl diglycol ether and diethylene glycol mono-*n*-hexyl ether in addition to one ether with three oxyethylene groups, butyl triglycol ether. Of these few diglycol ethers, the best synergy was achieved with butyl diglycol ether and further extension of the oxyethylene groups did not improve the synergistic performance.

The impact of the functional groups of the molecule were investigated by comparing the glycol functional group to the original alcohol. Of the acyclic alcohols the synergistic effect improved in the sequence 2-ethyl-

1-hexanol < 2-propanol < 1-butanol ~ 1-pentanol < 3-methyl-2-butanol < 2,2-dimethyl-1-propanol ~ 1-hexanol ~ 3-methyl-1-butanol << 4-methyl-1-pentanol. The same trend as found for the glycol ethers was found for the alcohol analogues as well, branching of the alkyl "tail" was beneficial for better synergetic performance with PVCap. 4-Methyl-1-pentanol gave a superb synergetic effect with PVCap, and was the best synergistic result, significantly better than all the other compounds tested in this study (Figure 4.4). We believe that in addition to both the shape and size of the alkyl group being important factors for synergy, the fact that the alcohol is close to its solubility limit may also be a factor.

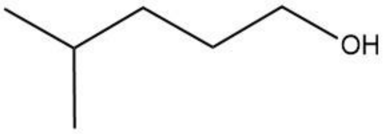


Figure 4.4. Schematic of 4-methyl-1-pentanol.

The synergistic potential of some cyclic alcohols with PVCap were studied. Adding heteroatoms to the cyclic groups to make them more polar than cycloalkyl groups is not beneficial, like it is in furfuryl alcohol and tetrahydrofurfuryl alcohol as they only gave weak synergy with PVCap. Both cyclopentanol and cyclohexanol had comparable results, the latter slightly better at delaying catastrophic hydrate growth. For the cyclic alcohols, branching of the alkyl "tail" was not found to be beneficial as the result for 4-methylcyclohexanol (*cis* and *trans* mixture) was more or less identical to that of the cyclohexanol. The least water-soluble cyclic alcohol tested, cycloheptanol, had the best synergistic performance with PVCap of all the cyclic alcohols tested.

Some water-soluble ketones as functional groups were the last ones to be investigated for their potential synergy with PVCap in this study. The four ketones tested had branched alkyl "tails" since this was shown to be beneficial for both glycol ethers and alcohols. 2-Methyl-3-pentanone had no synergy with PVCap, the three other ketones gave synergy with PVCap. 3,3-Dimethyl-2-butanone and 4-methyl-2-pentanone gave equal results while 5-methyl-2-hexanone had the best synergy with PVCap. This is the ketone with the furthest spacing between the branching and the ketone group, resulting in less sterically hindering.

## 4.4 Paper IV: Further Investigation of Solvent Synergists for Improved Performance of Poly(*N*-vinylcaprolactam)-Based Kinetic Hydrate Inhibitors[170]

KHI formulations contain water-soluble polymers and carrier solvent. This carrier solvent can also act as a synergist with the KHI polymer, thus enhancing the hydrate-inhibiting properties of the polymer. Together with poly(*N*-vinylcaprolactam) (PVCap) glycol ethers, particularly with three to four carbon atoms in the alkyl chain and phenylpropylene glycol have shown good synergy in laboratory studies (Figure 4.5).[171–173] In the first part of this study it was showed that glycol ethers with five to six carbon atoms also possessed good synergy with PVCap.[169] For the alcohols, reports on alcohols containing from three to five carbon atoms was beneficial for synergy with PVCap, although not as powerful as monoglycol ethers.[171,174] Antagonistic effect on the performance of PVCap have been shown for the smaller alcohols. In addition, not just the molecular weight of the alcohol but also the branching of the molecule affects the synergistic performance.[175]

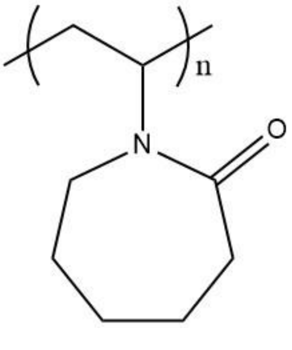


Figure 4.5. Schematic of poly(*N*-vinylcaprolactam) (PVCap).

In the previous study,[169] a wide range of alcohols, glycol ethers and ketones were investigated as synergetic solvents with PVCap. In that study, outstanding synergetic effect was achieved by 4-methyl-1-pentanol (iHexOl) (Figure 4.6). This report builds on that study, by investigating iHexOl in more detail as well as some newly synthesized solvents predicted by the first study to have good synergism. Both slow constant cooling (SCC) and isothermal KHI experiments were conducted.

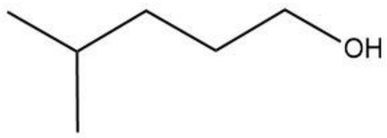


Figure 4.6. Schematic of 4-methyl-1-pentanol (iHexOl).

The results of the effect of varying the concentration of 4-methyl-1-pentanol have on the synergistic effect on PVCap, which concentration was held constant in addition to polymerize PVCap in 4-methyl-1-pentanol, are summarized (Table 4.6).

Table 4.6. Summarized results for SCC tests containing constant concentration of PVCap with varying concentrations of 4-methyl-1-pentanol.

| **Substance** | | **Concentration (ppm)** | | ***$T_o$* (°C)** | ***$T_a$* (°C)** |
|---|---|---|---|---|---|
| **KHI polymer** | **Synergist** | **KHI Polymer** | **Synergist** | | |
| DIW | | - | - | 17.2 | 16.6 |
| - | iHexOl | - | 5000 | 15.3 | 14.2 |
| PVCap | - | 2500 | - | 10.4 | 8.9 |
| PVCap made in iHexOl | iHexOl | 2500 | 5000 | 11.8 | 8.9 |
| PVCap | iHexOl | 2500 | 1000 | 7.1 | 4.6 |
| PVCap | iHexOl | 2500 | 2500 | 4.1 | 1.7 |
| PVCap | iHexOl | 2500 | 5000 | <3 | <3 |
| PVCap | iHexOl | 2500 | 10000 | 7.2 | 6.0 |

Alone, 4-methyl-1-pentanol had almost no KHI effect compared to deionized water, so it is only effective when used together with KHI polymers. PVCap polymerized in 4-methyl-1-pentanol gave somewhat poorer KHI result than pure PVCap polymer. One possible reason for this result could be coupled to the low water-solubility of the PVCap polymerized in 4-methyl-1-pentanol. When the concentration of 4-methyl-1-pentanol was increased from 1000 ppm up to 5000 ppm, the KHI performance was also increased. The concentration of 5000 ppm 4-methyl-1-pentanol achieved the best synergistic performance. At a concentration of 10000 ppm 4-methyl-1-pentanol, the synergistic effect with PVCap was negative compared to 5000 ppm. A possible reason is again linked to the solubility of the solvent.

Different solvents were investigated for their potential synergistic effect with PVCap using slow constant cooling KHI experiments (SCC) (Table 4.7).

Table 4.7. Summarized results for SCC tests on 2500 ppm PVCap with 5000 ppm of different solvents.

| **Additive** | **$T_o$ (°C)** | **$T_a$ (°C)** |
|---|---|---|
| DIW | 17.2 | 16.6 |
| PVCap | 10.4 | 8.9 |
| **Synergist** | | |
| 2-Methyl-1-pentanol | 5.6 | 3.6 |
| 3-Methyl-1-pentanol | 5.9 | 3.5 |
| 4-Methyl-1-pentanol (iHexOl) | <3 | <3 |
| 2-((4-Methylpentyl)oxy)ethane-1-ol (iHex(EO)Ol) | 5.2 | 4.3 |
| Phenol | 17.0 | 16.4 |
| 2-Phenoxyethanol | 10.3 | 6.7 |
| Cyclohexanol | 6.8 | 3.4 |
| 4-Methylcyclohexanol (*cis* and *trans* mixture) | 5.9 | 3.1 |
| 4-Methylcyclohexanol (*cis* and *trans* mixture) + 1EO | 5.4 | 2.6 |
| 4-Methylcyclohexanol (*cis* and *trans* mixture) + 2EO | 6.4 | 3.7 |
| 4-Methylcyclohexanone | 7.8 | 6.9 |
| Cycloheptanol | 6.4 | <3 |
| Cycloheptanone | 5.5 | 3.8 |
| *n*-Butyl glycol ether (BGE) | 7.3 | 3.8 |
| Butyl diglycol ether (DBGE) | 5.5 | 2.9 |
| Di(propylene glycol)butyl ether (DPGBE) isomer mix | 5.5 | <3 |
| 2-*n*-Butoxyethyl acetate | 5.5 | <3 |

None of the isomers of 4-methyl-1-pentanol, namely 1-hexanol, 2-methyl-1-pentanol and 3-methyl-1-pentanol, had a performance as good as 4-methyl-1-pentanol. For both 2-methyl-1-pentanol and 3-methyl-1-pentanol the branching can potentially cause a steric hindering for the hydroxyl group. The monoglycol ether 2-((4-methylpentyl)oxy)ethane-1-ol (iHex(EO)Ol) was synthesized, but the result with PVCap was not as good as the alcohol analogue 4-methyl-1-pentanol. No statistically significant difference at the 95 % confidence level between the three solvents were found when adding glycol ether groups, 4-methylcyclohexanol (*cis* and *trans* mixture), adding one oxyethylene (glycol ether) group making 4-methylcyclohexanol + 1EO and adding two oxyethylene (glycol ether) group making 4-methylcyclohexanol + 2EO. The branched analogue of butyl diglycol ether (DBGE), di(propylene glycol)butyl ether (DPGBE) was investigated, and it gave similar results as the linear ethylene glycol DBGE. Phenol ruined the performance of PVCap completely, and 2-phenoxyethanol, which has a much less acidic proton than phenol, although the performance was not ruined, it is on level with pure PVCap polymer. It is believed that the properties of the aromatic ring is what causes this poor performance, with its six π-electrons in the cloud circulate in regions both above and below the plane of the ring making *p* orbitals. It is these *p* orbitals that could interact with the PVCap polymer. The cyclic ketones, 4-methylcyclohexanone and cycloheptanone, were investigated for their potential synergetic effect with PVCap polymer, but there appears to be no substantial benefit of ketones over alcohols. 2-*n*-Butoxyethyl acetate, which is *n*-butyl glycol ether (BGE) with an acetate ester functional group, the results parallels those of the alcohols, glycol ethers and ketones, in that making the molecule more hydrophobic (compared to BGE) without losing water-solubility was beneficial for the synergetic performance with PVCap.

Isothermal KHI tests on PVCap together with some of the best solvent synergist from the SCC test are summarized (Table 4.8).

Table 4.8. Isothermal tests conducted on PVCap and synergist solvents, (n/r = not reached).

| **Substance** | | **Concentration (ppm)** | | ***$t_o$* (min)** | ***$t_a$* (min)** |
|---|---|---|---|---|---|
| **Polymer** | **Synergist** | **Polymer** | **Synergist** | | |
| PVCap | - | 2500 | - | 0 | 0 |
| PVCap | iHexOl | 2500 | 1000 | 166 | 176 |
| PVCap | iHexOl | 2500 | 2500 | 270 | 1711 |
| PVCap | iHexOl | 2500 | 5000 | 352 | 2807 |
| PVCap | iHexOl | 2500 | 10000 | 293 | 1059 |
| PVCap | iHexOl | 5000 | 5000 | 604 | n/r |
| PVCap | iHexOl | 5000 | 10000 | 1145 | n/r |
| PVCap | iHexOl | 7500 | 5000 | 1531 | n/r |
| PVCap | iHexOl + BGE | 5000 | 10000 + 5000 | 869 | 3060 |
| PVCap | Cycloheptanol | 2500 | 5000 | 149 | 210 |
| PVCap | TBGE | 7500 | 5000 | 262 | 336 |

As seen for the SCC tests, when the concentration of PVCap was held constant at 2500 ppm, the performance increased as the concentration of 4-methyl-1-pentanol increased from 1000 ppm to 5000 ppm, but was worsened when the concentration was 10000 ppm 4-methyl-1-pentanol. When the concentration of PVCap was increased to 5000 ppm, the performance increased as the 4-methyl-1-pentanol concentration increased from 5000 ppm to 10000 ppm. A combination of 7500 ppm PVCap and 5000 ppm 4-methyl-1-pentanol gave the best performance while rendering the solution completely water-soluble. Neither cycloheptanol nor triethylene glycol monobutyl ether (TBGE) had nearly as good synergistic performance with PVCap as 4-methyl-1-pentanol in these isothermal tests. The same was found when BGE was added in addition to 4-methyl-1-pentanol.

In the next isothermal KHI tests, 4-methyl-1-pentanol was used with both PVCapBGE which is PVCap 50 wt.% in BGE and PVCapEND which is PVCap polymer where mercaptosuccinic acid was used as a chain transfer agent (Table 4.9).

Table 4.9. Isothermal tests conducted on PVCapEND and PVCapBGE with synergists, n/r = not reached.

| **Substance** | | **Concentration (ppm)** | | **$t_o$ (min)** | **$t_a$ (min)** |
|---|---|---|---|---|---|
| **Polymer** | **Synergist** | **Polymer** | **Synergist** | | |
| PVCapEND | iHexOl | 5000 | 5000 | 463 | n/r |
| PVCapEND | iHexOl + BGE | 5000 | 5000 + 5000 | 1239 | n/r |
| PVCapEND | iHexOl + BGE | 7500 | 5000 + 5000 | 1315 | 1818 |
| PVCapBGE | BGE | 2500 | 2500 | 146 | 200 |
| PVCapBGE | iHexOl + BGE | 2500 | 2500 + 2500 | 163 | 172 |
| PVCapBGE | iHexOl + BGE | 2500 | 5000 + 2500 | 789 | 3360 |
| PVCapBGE | iHexOl + BGE | 5000 | 5000 + 5000 | 1352 | 1638 |
| PVCapBGE | iHexOl + BGE | 5000 | 10000 + 5000 | 2194 | 2949 |
| PVCapBGE | iHexOl + BGE | 7500 | 5000 + 7500 | 1606 | 1613 |
| PVCapBGE w/o BGE | iHexOl | 7500 | 5000 | 1354 | 1741 |

When the results for the same conditions for PVCapBGE were compared to PVCap, both with and without 4-methyl-1-pentanol, BGE had a little improvement in performance for PVCapBGE but with 4-methyl-1-pentanol added the PVCap had the best performance. When BGE was removed from 7500 ppm PVCapBGE with 5000 ppm 4-methyl-1-pentanol, the solubility of the polymer decreased to about 90 %, but as seen by the standard deviation the results were not statistically significant different compared to when BGE was precent. When the same concentrations were used with PVCapEND with 4-methyl-1-pentanol and BGE, the results were similar, but in this case the added BGE aided the solubility of the polymer and 4-methyl-1-pentanol.

Two solvents synergists with very different water-solubility, namely 4-methyl-1-pentanol which has a limited water-solubility and TBGE which is very water-soluble, was used in the following isothermal tests (Table 4.10).

Table 4.10. Isothermal tests on PVCapEND and PVCapBGE with iHexOl and TBGE as synergists and 0.5 wt.% NaCl and/or 1 mL decane, n/r = not reached.

| **Substance** | | **Concentration (ppm)** | | **Additive** | **$t_o$ (min)** | **$t_a$ (min)** |
|---|---|---|---|---|---|---|
| **Polymer** | **Synergist** | **Polymer** | **Synergist** | | | |
| PVCap | TBGE | 7500 | 5000 | NaCl | 178 | 220 |
| PVCap | TBGE | 7500 | 5000 | NaCl+decane | 213 | 246 |
| PVCapEND | iHexOl + BGE | 7500 | 5000 + 5000 | - | 1315 | 1818 |
| PVCapEND | iHexOl + BGE | 7500 | 5000 + 5000 | NaCl | 548 | 1190 |
| PVCapEND | iHexOl + BGE | 7500 | 5000 + 5000 | NaCl+decane | 172 | n/r |
| PVCapBGE | iHexOl + BGE | 5000 | 5000 + 5000 | - | 1352 | 1638 |
| PVCapBGE | iHexOl + BGE | 5000 | 5000 + 5000 | NaCl | 1706 | n/r |
| PVCapBGE | iHexOl + BGE | 5000 | 5000 + 5000 | NaCl+decane | 274 | n/r |
| PVCapBGE | iHexOl + BGE | 7500 | 5000 + 7500 | NaCl | 523 | 843 |
| PVCapBGE | iHexOl + BGE | 7500 | 5000 + 7500 | NaCl+decane | 204 | n/r |

When a concentration of 5000 ppm was used for both the polymer and the solvent synergist, the results was improved when NaCl was added to the PVCapBGE with 4-methyl-1-pentanol system, but it was worsened when the KHI polymer was PVCapEND. When the liquid hydrocarbon phase in the form of decane was added, the hold time ($t_o$) was reduced but the time for catastrophic hydrate growth ($t_a$) was increased, for both systems. The decane has two main effects. Firstly, it lowers the equilibrium temperature, in this case by about 0.3 °C.[220] Secondly, it can become a solvent for the KHI formulation, in particular 4-methyl-1-pentanol in this study. Removal of the 4-methyl-1-1pentanol from the water phase to the decane phase appears to have a significant effect on the $t_o$ value but not on the $t_a$ value. When decane was added to the system containing the more water-soluble TBGE, there was an observed improvement in the performance, which indicated that the TBGE was not partitioning into the decane phase.

Some of the conditions used in the isothermal tests were used in the SCC tests, such as the use of 3.5 wt.% NaCl + 0.2 wt.% $CaCl_2$, liquid hydrocarbon phase (decane) or varying the aqueous solution volume. The same concentrations of 2500 ppm KHI polymer and 5000 ppm solvent synergist (Table 4.11).

Table 4.11. Summarized results for SCC experiments for 2500 ppm PVCap with 5000 ppm of iHexOl or TBGE under harsher conditions.

| Substance | | Concentration (ppm) | | Additive | $T_o$ (°C) | $T_a$ (°C) |
|---|---|---|---|---|---|---|
| **KHI polymer** | **Synergist** | **KHI Polymer** | **Synergist** | | | |
| DIW | | - | - | - | 17.2 | 16.6 |
| PVCap | - | 2500 | - | - | 10.4 | 8.9 |
| PVCap | - | 2500 | - | 3.5 wt.% NaCl + 0.2 wt.% $CaCl_2$ | 8.2 | 6.2 |
| PVCap* | - | 2500 | - | 1mL Decane | 9.5 | 8.8 |
| PVCap | iHexOl | 2500 | 5000 | - | <3 | <3 |
| PVCap | iHexOl | 2500 | 5000 | 3.5 wt.% NaCl + 0.2 wt.% $CaCl_2$ | <3 | <3 |
| PVCap* | iHexOl | 2500 | 5000 | - | 4.1 | <3 |
| PVCap* | iHexOl | 2500 | 5000 | 1mL Decane | 5.4 | 2.2 |
| PVCap | TBGE | 2500 | 5000 | - | 5.3 | 3.2 |
| PVCap* | TBGE | 2500 | 5000 | - | 6.9 | 4.5 |
| PVCap* | TBGE | 2500 | 5000 | 1mL Decane | 5.8 | 4.8 |

*15 mL Volume in cells.

For systems containing either PVCap polymer alone or PVCap with 4-methyl-1-pentanol, the inhibition performance improved when salts were added. This was not the case when the liquid volume was reduced for systems containing PVCap with 4-methyl-1-pentanol or TBGE. When decane was added to a system consisting of only PVCap the performance increased, but when 4-methyl-1-pentanol also were present, the addition of decane lowered the performance. The opposite was the case when TBGE was the solvent synergist, then the addition of decane improved the performance.

## 4.5 Paper V: Powerful Synergy of Acetylenic Diol Surfactants with Kinetic Hydrate Inhibitor Polymers - Choosing the Correct Synergist Aqueous Solubility[220]

The KHI formulation consists of one or more water-soluble polymers dissolved in one or more solvents. In addition, both the solvent and various classes of non-polymeric synergists can be added to improve the performance. Thus, by judicious choice of the polymer solvent system the injected KHI polymer solution can be considerably enhanced. Earlier study determined that alcohols and glycols with the correct-size hydrophobic groups and with their solubility limit close to that of typical KHI dosages, had good synergistic performance with PVCap.[169] Another class of synergist, those of ethoxylated acetylenic diols, have recently been shown to have good synergy with 1:1 VP:VCap copolymer.[221] This study investigates the synergistic properties of 5-methyl-1-hexyn-3-ol (5-MH), 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD) and 2,4,7,9-tetramethyl-5-decyne-4,7-diol decaethoxylate (TMDD-EO10) with PVCap, VP/VCap and PNIPMAM (Figure 4.7).

The results from the slow constant cooling KHI tests (SCC) are summarized (Table 4.12). All polymers have a concentration of 2500 ppm. Deionized water, PVCap ($M_w$ = 8-10 kg/mol) tested by itself in addition to synergistic tests with *n*-butyl glycol ether (BGE), *iso*-butyl glycol ether (iBGE), butyl diglycol ether (BDGE) and 4-methyl-1-pentanol (iHexOl) were included for comparison purposes.[169]

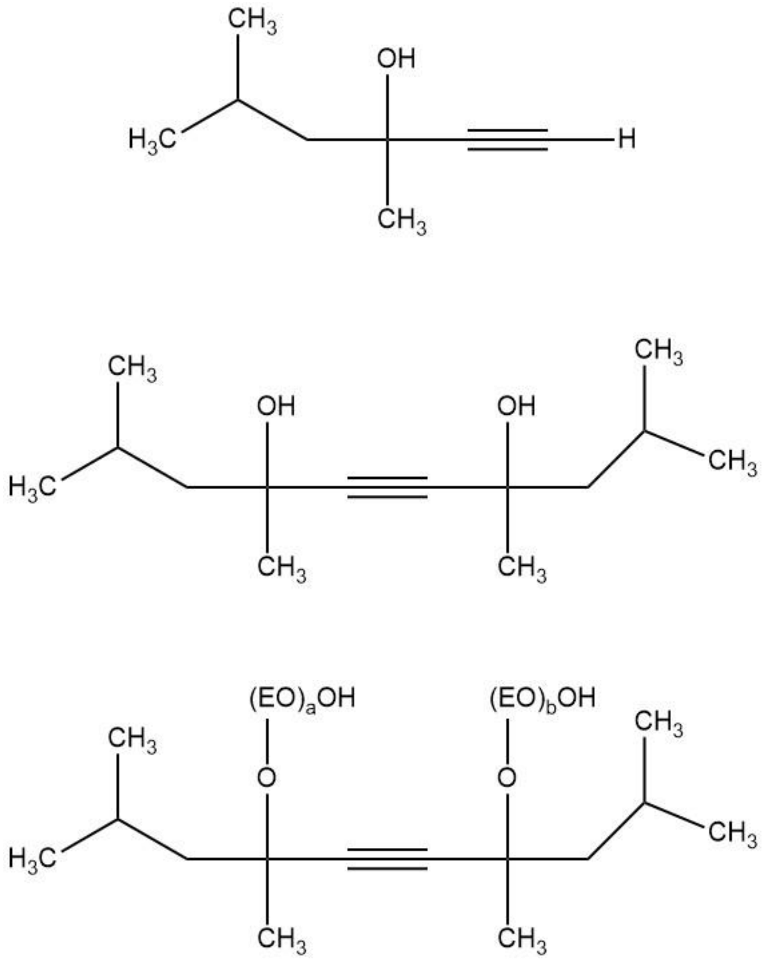


Figure 4.7. Schematic of the nonionic surfactants used in this research: From the top 5-methyl-1-hexyn-3-ol (5-MH), 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD) and 2,4,7,9-tetramethyl-5-decyne-4,7-diol decaethoxylate (TMDD-EO10) where a + b = 10.

Table 4.12. Summary of the SCC KHI tests, all polymers with a concentration of 2500 ppm.

| **Polymer** | **Synergist** | **[Synergist] ppm** | **$T_o$ (av.) ± deviation [°C]** | **$T_a$ (av.) ± deviation [°C]** | **$T_o$ (av.) – $T_a$ (av.) [°C]** |
|---|---|---|---|---|---|
| DIW | - | - | 17.2 ± 0.6 | 16.7 ± 0.5 | 0.5 |
| - | 5-MH | 5000 | 16.7 ± 0.4 | 16.1 ± 0.5 | 0.6 |
| - | TMDD | 5000 | 15.6 ± 0.4 | 15.2 ± 0.4 | 0.4 |
| - | TMDD-EO10 | 5000 | 15.7 ± 0.3 | 15.5 ± 0.3 | 0.2 |
| PVCap | - | - | 10.2 ± 0.3 | 8.8 ± 0.5 | 1.4 |
| PVCap | - | - | 10.6 ± 0.5 | 9.3 ± 0.1 | 1.3 |
| PVCap | - | - | 9.5 ± 0.2 | 8.8 ± 0.2 | 0.7 |
| PVCap | BGE | 5000 | 7.3 ± 0.4 | 3.8 ± 0.4 | 3.5 |
| PVCap | BDGE | 5000 | 5.5 ± 0.4 | 2.9 ± 0.4 | 2.6 |
| PVCap | iBGE | 5000 | 5.7 ± 0.4 | 2.5 ± 0.3 | 3.2 |
| PVCap | iHexOl | 5000 | <3.0 | <3.0 | - |
| PVCap | 5-MH | 5000 | 5.4 ± 0.4 | 3.9 ± 0.3 | 1.5 |
| PVCap | TMDD | 2500 | 4.3 ± 0.5 | 3.0 ± 0.3 | 1.3 |
| PVCap | TMDD | 5000 | <2.0 | <2.0 | - |
| PVCap | TMDD | 5000 | 2.8 ± 0.2 | 2.2 ± 0.2 | 0.6 |
| PVCap | TMDD | 5000 | 5.9 ± 0.5 | 4.8 ± 0.5 | 1.1 |
| PVCap | TMDD-EO10 | 2500 | 8.8 ± 0.3 | 7.8 ± 0.2 | 1.0 |
| PVCap | TMDD-EO10 | 5000 | 8.3 ± 0.4 | 8.0 ± 0.3 | 0.3 |
| VP/VCap | - | - | 8.1 ± 0.9 | 5.7 ± 0.4 | 2.4 |
| VP/VCap | BDGE | 5000 | 6.8 ± 0.4 | 4.2 ± 0.3 | 2.6 |
| VP/VCap | 5-MH | 5000 | 7.0 ± 0.6 | 4.5 ± 0.4 | 2.5 |

| | | | | | |
|---|---|---|---|---|---|
| VP/VCap | TMDD | 5000 | 5.5 ± 0.4 | 3.7 ± 0.3 | 1.8 |
| VP/VCap | TMDD-EO10 | 5000 | 8.2 ± 0.6 | 5.9 ± 0.2 | 2.3 |
| PNIPMAM | - | - | 10.5 ± 0.8 | 10.2 ± 0.6 | 0.3 |
| PNIPMAM | BGE | 5000 | 6.2 ± 0.8 | 5.0 ± 0.3 | 1.2 |
| PNIPMAM | iBGE | 5000 | 5.5 ± 0.5 | 4.2 ± 0.2 | 1.3 |
| PNIPMAM | iHexOl | 5000 | 4.6 ± 0.8 | 2.9 ± 0.3 | 1.7 |
| PNIPMAM | 5-MH | 5000 | 7.2 ± 0.2 | 5.5 ± 0.2 | 1.7 |
| PNIPMAM | TMDD | 5000 | 5.8 ± 0.4 | 3.2 ± 0.4 | 2.6 |
| PNIPMAM | TMDD-EO10 | 5000 | 8.8 ± 0.4 | 8.2 ± 0.2 | 0.6 |

By themselves, 5-MH, TMDD and TMDD-EO10 showed no KHI effect. Together with PVCap, TMDD-EO10 had a synergy little weaker than that obtained with BGE, it showed only weak synergy with PNIPMAM and negligible synergy with VP/VCap copolymer. When TMDD was used in combination with the KHI polymers tested in this study, the synergy was amongst the best and much better than TMDD-EO10. TMDD had best synergy with PVCap, and the result can only be compared to that of PVCap with 4-methyl-1-pentanol. TMDD and ethoxylated derivatives are exceptionally small di amphiphiles that have a triple bond in the middle of the molecule. The alkyne triple bond may be a reason for the good synergy observed, by having no rotation and thus fixing the two *iso*-butyl end groups to be kept away from each other. Other important factors may be the water-solubility, dual hydrophobic end groups as well as both optimum size and shape of these *iso*-butyl groups. 5-MH which is close to half the molecule compared to TMDD with only one *iso*-butyl end group, was investigated to determine the significance of the twin hydrophobic end groups in TMDD. Together with PVCap, 5-MH gave good synergy. The results were on par with both iBGE and BDGE, but far from as good as either TMDD or 4-methyl-1-pentanol. For both VP/VCap copolymer and PNIPMAM the synergy with 5-MH was better than for TMDD-EO10, but weaker than TMDD. When decane was added as the model liquid hydrocarbon phase, the performance of the PVCap with TMDD decreased. The poor KHI performance is thought to be related to the partitioning of the sparingly water-soluble TMDD to the liquid hydrocarbon phase.

The last test done in this study was by utilizing isothermal test to further confirm the powerful synergy of TMDD with PVCap (Table 4.13).

Table 4.13. Isothermal test results for PVCap with synergist and cooling to 4 °C unless otherwise stated.

| **Polymer** | **Conc. ppm** | **Synergist** | **Conc. ppm** | **ΔT °C** | **Hold time ($t_o$) min** | **Fast growth time ($t_a$) min** |
|---|---|---|---|---|---|---|
| PVCap[f] | 2500 | - | - | 13.8 | 80-90[a] | 80-100[a] |
| PVCap[f] | 2500 | iBGE | 5000 | 13.8 | 117, 119, 148, 128, 123 (av.127) | 421, 398, 465, 476, 487 |
| PVCap | 2500 | TMDD | 5000 | 15.8 | 523, 826, 716, 679, 572 (av. 663) | 763, 1180, 1063, 968, 899 (av. 974) |
| PVCap | 2500 | TMDD[b] | 5000 | 15.5[c] | 95-100[d] | 95-100 |
| PVCap | 7500 | | | 15.8[e] | 100-150 | 100-155 |
| PVCap | 7500 | TMDD | 5000 | 15.8[e] | 624, 366, 348, 371, 286 (av. 398) | <1 bar drop due to hydrates in 3600 min |
| PVCap | 7500 | TMDD | 5000 | 15.5[bce] | 324, 279, 282, 263, 272 (av. 284) | <1 bar drop in 3600 min |

[a]Hydrates formed before reaching 4 °C. [b]1 mL Decane was added. [c]Calculated.[28] [d]Hydrate formation started in all cells on reaching approximately 4 °C. [e]15 mL Of aqueous solution. [f]Cooling to 6 °C.

TMDD had a performance significantly better than iBGE, further underlining the powerful synergy of TMDD. The addition of decane was used as the artificial liquid hydrocarbon phase. The isothermal test indicated the same trend as seen in the standard constant cooling test, with the performance being significantly hampered when the liquid hydrocarbon phase was introduced. It is believed that the same is taking place in these isothermal tests, that TMDD is partitioning into the liquid hydrocarbon phase.

## 4.6 Paper VI: Boronic and Organic Acids as Synergists for a Poly(*N*-vinylcaprolactam) Kinetic Hydrate Inhibitor[222]

Kinetic hydrate inhibitors (KHIs) formulation consists of two parts, the main active components being one or more specifically designed water-soluble polymers, in addition the carrier solvent system which synergists and enhancers can make up. Non-ionic boronic acids have been reported to be used as anti-agglomerants (AAs).[223] Some of the boronic acids were found to be extremely hydrate-philic (attracted to hydrate surfaces) and able to strongly reduce the surface oil-hydrate interfacial tension, even lower than the threshold observed for industry standard AAs. Boronic acids are based on boric acid [$B(OH)_3$] on which one of the hydroxyl groups is replaced by either an alkyl or aryl group.[224] Due to the hydrate-philic nature of boronic acids it is quite possible that they might act as synergist with KHI polymers. Thus, in this study reports for the first time on the synergistic behavior of a range of alkyl and aromatic boronic acids together with the KHI polymer poly(*N*-vinylcaprolactam) (PVCap) (Figure 4.8).

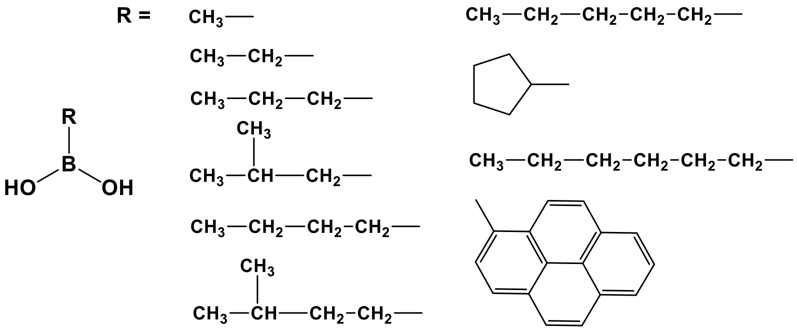


Figure 4.8. Schematic of the boronic acids used in this study.

The result from the slow constant cooling KHI test (SCC) for the boronic acids are summarized (Table 4.14).

Table 4.14. SCC KHI test results with PVCap alkylboronic acids, organic acids and alkyl carboxylates.

| **PVCap Conc. ppm** | **Synergist** | **Conc. ppm** | **$T_o$ (av.)°C** | **$T_a$ (av.)°C** |
|---|---|---|---|---|
| - | - | - | 17.2 | 16.7 |
| 2500 | - | - | 10.4 | 8.9 |
| | **Alkylboronic acid** | | | |
| 2500 | Methyl | 5000 | 10.0 | 9.1 |
| 2500 | Ethyl | 5000 | 10.5 | 9.0 |
| 2500 | *n*-Propyl | 5000 | 7.4 | 4.1 |
| - | *iso*-Butyl | 5000 | 16.8 | 15.8 |
| 1000 | *iso*-Butyl | 5000 | 7.1 | 4.4 |
| 2500 | *iso*-Butyl | 1000 | 9.2 | 8.1 |
| 2500 | *iso*-Butyl | 2500 | 8.4 | 5.9 |
| 2500 | *iso*-Butyl | 5000 | 6.4 | 3.3 |
| 2500 | *iso*-Butyl | 5000 * | 5.3 | 3.0 |
| 2500 | *n*-Butyl | 5000 | 8.7 | 5.2 |
| 2500 | *iso*-Pentyl | 5000 | 8.3 | 2.9 |
| 2500 | *n*-Pentyl | 5000 | 12.5 | 12.1 |
| 2500 | Cyclopentyl | 5000 | 7.2 | 4.1 |
| 2500 | Cyclopentyl | 5000 * | 7.2 | 2.3 |
| 2500 | *n*-Hexyl | 5000 | 14.6 | 14.3 |
| 2500 | Pyrenyl | 5000 | 12.4 | 11.9 |
| | **Organic Acids and salts** | | | |
| 2500 | 2-Methylpropanoic acid | 5000 | 10.7 | 9.9 |
| 2500 | 3-Methylbutanoic acid | 5000 | 8.2 | 5.8 |
| 2500 | 4-Methylpentanoic acid | 5000 | 14.2 | 14.0 |
| 2500 | Sodium 4-Methylpentanoate | 5000 | 7.8 | 7.7 |
| 2500 | 3,3-Dimethylbutanoic acid | 5000 | 11.5 | 11.2 |
| 2500 | Sodium 3,3-dimethylbutanoate | 5000 | 5.1 | 5.0 |

*1mL Decane added.

At a concentration of 2500 ppm PVCap and 5000 ppm alkylboronic acid, the increase in synergistic effect improved in the sequence of the alkyl groups *n*-hexyl < *n*-pentyl ~ pyrenyl < ethyl ~ methyl < *n*-butyl ~ *iso*-pentyl < *n*-propyl ~ cyclopentyl < *iso*-butyl. Of these alkylboronic acids pyrenyl, *n*-pentyl and *n*-hexyl showed antagonistic behavior with PVCap, while methyl and ethyl had no significant effect on the performance of PVCap. The alkylboronic acids that improved the performance were *n*-butyl, *iso*-pentyl, *n*-propyl, cyclopentyl and *iso*-butyl. Because of that the best performing alkylboronic acid, *iso*-pentyl boronic acid, was not at the water-solubility limit, it is presumed that the optimal synergistic performance of *iso*-butylboronic acid have less to do with its water-solubility and is more due to the shape and size of the molecule.

The concentrations of both PVCap and the best performing alkylboronic acid, *iso*-pentyl boronic acid, was altered. Within the range of concentrations used in this study, an increase in concentration of either of these resulted in an improved performance. For the same system liquid hydrocarbon phase in the form of decane was added. This resulted in a statistically significant improvement over the system without decane. We presume that the performance improvement comes from the lowering of the hydrate equilibrium temperature (HET) of the system by adding decane, since *iso*-butylboronic acid is very water-soluble and probably does not partition into the decane phase. No statistically significant difference was found between the systems with and without decane when cyclopentylboronic acid was used. Of the two alkylboronic acid with added decane to the system, cyclopentylboronic acid is more hydrophobic than *iso*-butylboronic acid. This could explain the difference in result, since the equilibrium temperature is reduced in both systems, we presume that a little cyclopentylboronic acid may have partitioned to the decane phase.

The alkylboronic acids were compared with organic acids with regards to their synergistic effect, both with PVCap. As both organic acids and alkylboronic acids are weak acids, a minor percentage of them will be dissociated in water. The organic acids are a little stronger, so more of them will be dissociated in water. From studies with several other classes of synergist we were convinced that branched acids would be beneficial over straight chain acids, as such only branched acids were investigated in this study. 4-Methylpentanoic acid and 3,3-dimethylbutanoic acid had an antagonistic effect with PVCap, while 2-methylpropanoic acid which if anything worsened the performance compared to just PVCap alone. 3-Methylbutanoic acid had the best synergistic performance with PVCap of all the organic acids tested in this study. It is the equivalent organic acid of *iso*-butylboronic acid, since it has the same chain length between the OH group and the end of the alkyl group.

Finally, in order to enlarge the study of alkyl carboxylates, two more alkyl carboxylates were investigated.[225] From this study it is known that sodium salt of 3-methylbutanoic acid had negligible synergy with PVCap. Therefore, the carbon chain length was increased to five carbon atoms, 4-methylpentanoate, which showed adequate synergy with PVCap. Sodium 3,3-dimethylbutyrate had good synergy with PVCap, the best amongst the two alkyl carboxylates investigated.

## 4.7 Paper VII: Synthesis and Investigation of Polymers of 2-Methacrylamido-caprolactam as Kinetic Hydrate Inhibitors[226]

Poly(*N*-vinylcaprolactam) (PVCap) is one of the best KHIs currently available and several copolymers of VCap have also been applied in the field.[227] Compared to other KHI polymer classes such as polyalkyl(meth)acrylamides, VCap-based KHI polymers are known to be particularly good at inhibiting hydrate crystal growth. Therefore, this gave the incentive to explore alternate caprolactam-based polymers. The caprolactam ring in this new class of caprolactam-containing polymers synthesized, will be two atoms further away from the backbone then what is the case for PVCap. In addition, the use of methacylamido monomer unit was chosen as previous work have indicated that an extra methyl group in the polyvinyl backbone is favorable for KHI performance. This effect has been observed for *N*-alkyl acrylamide polymers and for poly(*N*,*N*-dimethylhydrazido methacrylamide) compared to poly(*N*,*N*-dimethylhydrazido acrylamide).[142–144] This new class of caprolactam-containing polymers are based on 2-methacrylamido-caprolactam (Figure 4.9).

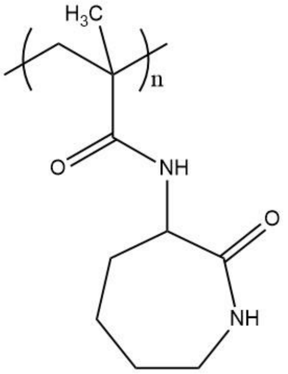


Figure 4.9. Structure of poly(2-methacrylamido-caprolactam) (poly(2-MACap)).

The 2-MACap homopolymer poly(2-MACap) was not water-soluble, so copolymers were made with *N*-vinyl-*N*-methylacetamide (VIMA), *N*-vinylpyrrolidone (VP), *N*-methylol methacrylamide (MOlMA) and *N*-methylmethacrylamide (MMA) (Figure 4.10).

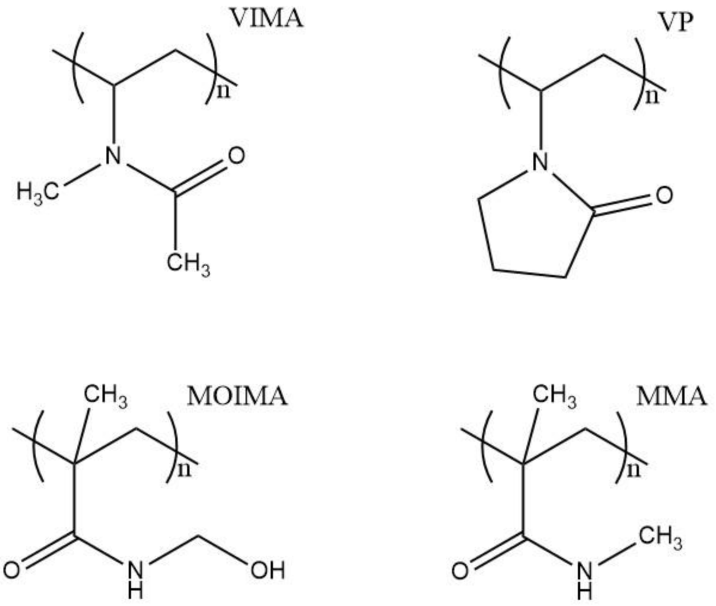


Figure 4.10. Structure of comonomer units used with 2-MACap copolymers: *N*-vinyl-*N*-methylacetamide (VIMA), *N*-vinylpyrrolidone (VP), *N*-methylol methacrylamide (MOlMA) and *N*-methylmethacrylamide (MMA).

All these copolymers were water-soluble and their cloud point ($T_{cl}$), molecular weight and PDI were measured (Table 4.15).

Table 4.15. Cloud point ($T_{cl}$), molecular weight and PDI for the polymers synthesized in this study.

| **Polymer** | **$T_{cl}$ (°C)** | **Molecular weight g/mol** | **PDI** |
|---|---|---|---|
| Poly(2-MACap) | < 0 | 12600 | 5.42 |
| 2-MACap:VP 1:1 copolymer | 27 | 99400 | 2.67 |
| 2-MACap:VIMA 1:1 copolymer | 28 | 61500 | 2.93 |
| 2-MACap:VIMA 1:2 copolymer | 35 | Aggregated | - |
| 2-MACap:VIMA 2:1 copolymer | 43 | Aggregated | - |
| 2-MACap:MOlMA 1:1 copolymer | > 95 | Not soluble in DMF | - |
| 2-MACap:MMA 1:1 copolymer | 58 | 2100 (major),<br>120800<br>(broad minor) | 1.16,<br>12.21 |

The copolymers were tested for their inhibition performance using slow constant cooling (SCC) KHI test. The results for PVCap ($M_w$ = 10000 g/mol),[169] PVP K-15 ($M_w$ = 8000 g/mol)[210] and PVIMA ($M_w$ = 12401 g/mol)[228] are also included. Both the onset temperature for hydrate formation ($T_o$) and the rapid hydrate growth temperature ($T_a$) are given for each polymer (Table 4.16).

Table 4.16. Summarized SCC KHI test results for the water-soluble polymers, also with synergist solvents. (iBGE = *iso*-butyl glycol ether, 4-MePeOl = 4-methyl-1-pentanol).

| **Copolymer** | **Solvent synergist** | **Concentration (ppm)** | | **$T_o$ (°C)** | **$T_a$ (°C)** |
|---|---|---|---|---|---|
| | | **Polymer** | **Synergist** | | |
| No additive | - | - | - | 17.2 | 16.6 |
| PVCap | - | - | - | 10.4 | 8.9 |
| PVP K-15 | - | - | - | 13.3 | 9.1 |
| PVIMA | - | - | - | 14.2 | 13.2 |
| 2-MACap:VP (1:1) | - | 2500 | - | 11.2 | 10.0 |
| | - | 5000 | - | 8.9 | 7.5 |
| | iBGE | 2500 | 5000 | 8.3 | 6.7 |
| | 4-MePeOl | 2500 | 5000 | 6.7 | 5.4 |
| 2-MACap:VIMA (1:1) | - | 2500 | - | 8.8 | 7.7 |
| | - | 5000* | - | 9.2 | 8.2 |
| | iBGE | 2500 | 5000 | 7.4 | 6.3 |
| | 4-MePeOl | 2500 | 5000 | 5.7 | 4.6 |
| 2-MACap:VIMA (1:2) | - | 2500 | - | 10.9 | 10.1 |
| | - | 5000 | - | 7.6 | 7.2 |
| 2-MACap:VIMA (2:1) | - | 2500 | - | 11.0 | 10.5 |
| 2-MACap:MOIMA (1:1) | - | 2500 | - | 14.7 | 14.5 |
| 2-MACap:MMA (1:1) | - | 2500 | - | 8.8 | 8.1 |
| | - | 5000 | - | 6.4 | 5.7 |
| | iBGE | 2500 | 5000 | 6.2 | 5.4 |
| | 4-MePeOl | 2500 | 5000 | 4.6 | 3.8 |

*97 +% Soluble.

All copolymers had an improved performance when the concentration was increased, except for 2-MACap:VIMA (1:1) which was not completely water-soluble at increased concentration. At a concentration of 2500 ppm of KHI polymer their performance increased in the following order 2-MACap:MOIMA (1:1) < 2-MACap:VP (1:1) ~ 2-MACap:VIMA (2:1) ~ 2-MACap:VIMA (1:2) < 2-MACap:MMA (1:1) ~ 2-MACap:VIMA (1:1).

The 2-MACap:MOIMA (1:1) was probably to hydrophobic to give good KHI result. For the 2-MACap:VP (1:1) the performance was somewhat poorer than pure PVCap, but significantly better than PVP K-15. This indicates that the VP monomer is not as an effective monomer for KHI polymers as the caprolactam group in the 2-MACap monomer is. 2-MACap:VIMA (1:1) had a better KHI performance than pure PVCap. The copolymers of 2-MACap:VIMA in the ratios 1:2 and 2:1 had a worse performance than the 1:1 ratio, which correlates well with results for VIMA:VCap copolymers, where it was shown that a 1:1 copolymer gave the best KHI performance.[147,227] The copolymer 2-MACap:MMA (1:1) gave a good KHI result, better than PVCap in addition to it having a more useful cloud point. Further, the average $T_o$ and $T_a$ values between 2-MACap:MMA (1:1) and 2-MACap:VIMA (1:1) were not found to be significantly different ($p > 0.05$). This indicates that although the molecular weights are clearly different, the performance of these copolymers are similar.

Previously it has been shown that *iso*-butyl glycol ether (iBGE) had a good synergistic effect on PVCap and PNIPMAM, and that 4-methyl-1-pentanol (4-MePeOl) had a very strong synergistic effect on PVCap.[168,169] Both iBGE and 4-MePeOl improved the KHI performance for 2-MACap:VP (1:1), 2-MACap:VIMA (1:1) and 2-MACap:MMA (1:1) copolymers, with the most pronounced improvement with 4-MePeOl. The best result was obtained for 2-MACap:MMA (1:1) with 4-MePeOl. The case for the good synergy between 2-MACap copolymers and 4-MePeOl could be the same reason for why it was such a good synergist with PVCap, that both the size and shape of the alkyl group is important for the synergy but also the fact that the alcohol is close to the solubility limit may also be a factor.[153]

## 4.8 Paper VIII: Alternative Lactam-Based Kinetic Hydrate Inhibitors - Investigation of Polymers of 2-Methacrylamido-caprolactam[145]

In this continuation of the 2-methacrylamido-caprolactam (2-MACap) work,[226] the research was continued on this new class of caprolactam-containing polymers to understand the structure-performance relationship better and to find further improvements. Moreover, 2-MACap was copolymerized with some new comonomers that was postulated could either enhance the performance or raise the cloud point to more useful levels. Polymers with a new monomer 2-acrylamido-caprolactam (2-ACap) was also investigated to determine if the extra methyl group in the polyvinyl backbone is favorable for KHI performance, as seen for *N*-alkyl methacrylamide polymers and poly(*N*,*N*-dimethylhydrazido methacrylamide) (Figure 4.11).[143,144,229] In addition, the synergetic properties of 2-MACap polymers with some molecules that are well-known synergists for PVCap was investigated, to see if the performance improvements are similar with our new class of caprolactam-based polymers.

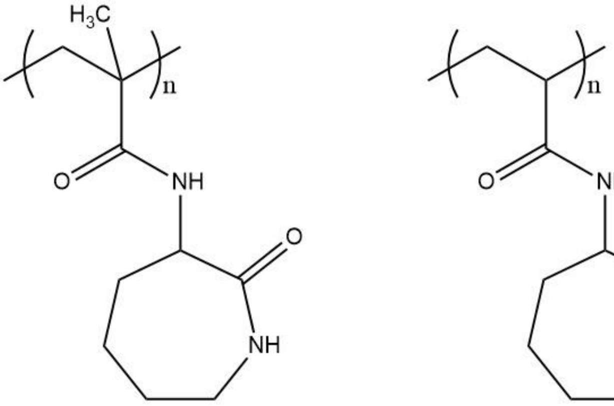


Figure 4.11. Poly(2-methacrylamido-caprolactam) (poly(2-MACap)) (left) and poly(2-acrylamido-caprolactam) (poly(2-ACap)) (right).

The comonomers used to make copolymers of 2-MACap were methacrylamide (MAm), *N*-methylmethacrylamide (MMA), *N*,*N*-dimethylmethacrylamide (DMMAm), *N*-*iso*-propylmethacrylamide (NIPMAm), *N*,*N*-dimethylhydrazidomethacrylamide (NDMHMAm), 1-acryloylpyrrolidine (APYD), *N*-methacryloylpyrrolidine (MAPYD), *N*-(pyrrolidine-1-yl)methacrylamide (NPyMA), poly(ethylene glycol) monoethyl methacrylate (PEGMA-9) and *N*-vinyl-*N*-methylacetamide (VIMA) (Figure 4.12).

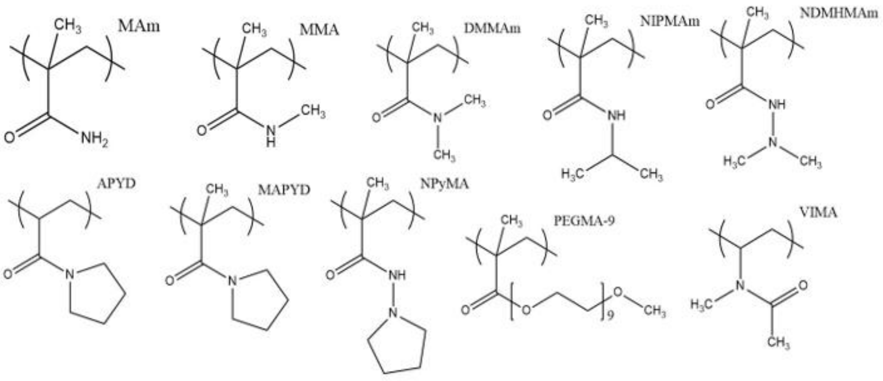


Figure 4.12. Structure of comonomer units used with 2-MACap copolymers: Methacrylamide (MAm), *N*-methylmethacrylamide (MMA), *N*,*N*-dimethylmethacrylamide (DMMAm), *N*-*iso*-propylmethacrylamide (NIPMAm), *N*,*N*-dimethylhydrazidomethacrylamide (NDMHMAm), 1-acryloylpyrrolidine (APYD), *N*-methacryloylpyrrolidine (MAPYD), *N*-(pyrrolidine-1-yl)methacrylamide (NPyMA), poly(ethylene glycol) methacrylate (PEGMA-9) and *N*-methyl-*N*-vinylacetamide (VIMA).

Slow constant cooling KHI experiments (SCC) was used to investigate the KHI potential for these copolymers, and their results are summarized (Table 4.17).

Table 4.17. Summarized SCC KHI test results for the copolymers with cloud points and GPC/SEC data. From the previous publications no additive, PVCap, 2-MACap:MMA (1:1) and 2-MACap:VIMA (1:1) are added for comparison.[169,226]

| **Copolymer** | **$T_{cl}$ (°C)** | **$M_w$ (g/mol)** | **PDI** | **Conc. (ppm)** | **$T_o$ (°C)** | **$T_a$ (°C)** |
|---|---|---|---|---|---|---|
| Poly(2-ACap) | < 0 | 9600 | 1.94 | - | - | - |
| Poly(2-MACap) | < 0 | 12600 | 5.42 | - | - | - |
| No additive | - | - | - | - | 17.2 | 16.6 |
| PVCap | - | 10000 | - | 2500 | 10.4 | 8.9 |
| 2-MACap:MAm (1:1) | 33 | Not soluble in DMF | | 2500 | 10.3 | 9.0 |
| 2-MACap:MMA (1:1) | 58 | 2100 (major), 120800 (broad minor) | 1.16, 12.21 | 2500 | 8.8 | 8.1 |
| | - | | | 5000 | 6.4 | 5.7 |
| 2-MACap:MMA (1:2) | 85 | Not soluble in DMF | | 2500 | 10.8 | 9.6 |
| 2-MACap:DMMAm (1:1) | < 2 | 2000 | 3.11 | 2500 | 10.7 | 9.9 |
| 2-MACap:NIPMAm (1:1) | 24 | 3200 | 5.01 | 2500 | 8.0 | 7.4 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2-MACap:NDMHMAm (1:1) | >100 | 500 | 1.25 | 2500 | 12.0 | 11.8 |
| | - | | | 5000 | 10.1 | 9.9 |
| 2-MACap:APYD (1:1) | 28 | 3300 | 4.39 | 2500 | 9.2 | 8.6 |
| | - | | | 5000 | 6.7 | 5.8 |
| 2-MACap:MAPYD (1:1) | 24 | 1300 | 2.42 | 2500 | 8.4 | 8.1 |
| 2-MACap:MAPYD (1:2) | 20 | 2500 | 3.25 | 2500 | 10.8 | 10.3 |
| 2-MACap:NPyMA (1:1) | >100 | 800 | 1.25 | 2500 | 11.8 | 10.8 |
| | - | | | 5000 | 9.4 | 8.3 |
| 2-MACap:PEGMA-9 (4:1) | 54 | 15900 | 8.74 | 2500 | 10.3 | 9.0 |
| | - | | | 5000 | 7.8 | 6.8 |
| 2-MACap:VIMA (1:1) | 28 | 61500 | 2.93 | 2500 | 8.8 | 7.7 |
| 2-MACap: NIPMAm:VIMA (1:1:0.5) | 30 | 7800 | 4.37 | 2500 | 9.4 | 8.5 |
| 2-ACap:MMA (1:1) | 60 | 22600 | 38.2 | 2500 | 9.7 | 8.8 |
| 2-ACap:MAPYD (1:1) | 24 | 4700 | 2.25 | 2500 | 10.4 | 10.0 |

The KHI performance of the copolymers at a concentration of 2500 ppm increased in the sequence 2-MACap:NDMHMAm (1:1) ~ 2-MACap:NPyMA (1:1) < 2-MACap:MAPYD (1:2) ~ 2-MACap:MMA (1:2) ~ 2-MACap:DMMAm (1:1) < 2-ACap:MAPYD (1:1) ~ 2-MACap:MAm (1:1) ~ 2-MACap:PEGMA-9 (4:1) < 2-ACap:MMA (1:1) < 2-MACap:NIPMAm:VIMA (1:1:0.5) < 2-MACap:APYD (1:1) < 2-MACap:MMA (1:1) ~ 2-MACap:VIMA (1:1) < 2-MACap:MAPYD (1:1) < 2-MACap:NIPMAm (1:1). When the concentration was increased for all the polymers the KHI performance was improved.

In this present discussion of the new copolymers tested, 2-MACap:MMA (1:1) from the previous study is used as the starting point as this gave best performance in that study.[226] The first structural aspect investigated was the importance of the backbone methyl group coming from both comonomers. 1-Acryloylpyrrolidine (APYD), which is an acrylamide with a pyrrolidine ring, was copolymerized with 2-MACap, making 2-MACap:APYD (1:1). This copolymer gave an adequate performance. The methylated version, *N*-methacryloylpyrrolidine (MAPYD) was copolymerized with 2-MACap, making the copolymer 2-MACap:MAPYD (1:1). This copolymer had an excellent KHI performance. Not only did this copolymer perform better than the non-methylated comonomer, but it had a performance amongst the best of the comonomers tested. However, both the $T_o$ value and the $T_a$ value between 2-MACap:MAPYD (1:1) and 2-MACap:MMA (1:1) was not found to be significantly different ($p > 0.05$ in a statistical *t*-test). 2-MACap:MMA (1:2) and 2-MACap:MAPYD (1:2) copolymers were synthesized and the results from both were clearly worse than the 1:1 ratio copolymers with the same monomers, and now on the same performance level with PVCap. Here the ratio between the monomers were not optimal, and the hydrophilic to hydrophobic moiety of the copolymer was imbalanced.

2-ACap was synthesized and copolymerized with the good performing comonomers MMA and MAPYD, respectively. Both 2-ACap:MMA (1:1) and 2-ACap:MAPYD (1:1) had a poorer result than their methylated counterparts indicating that adding a methyl group improved the inhibition performance. The steric effect of the methyl group opens the polymer structure and increasing the surface-to-volume ratio, which is presumed to be the cause of the improved KHI effect. Further, it is essential for a good functionality of a KHI polymer that the bulk of the polymer has a low molecular weight.

The copolymer 2-MACap:MAm (1:1) had a performance that was not found to be significantly different ($p > 0.05$ in a statistical $t$-test) from the PVCap results. This copolymer was not totally dissolved (< 95 %) at a concentration of 2500 ppm. 2-MACap:DMMAm (1:1) copolymer also had limited solubility in water which would explain why it gave lower performance compared to the 1:1 copolymer with MMA as the comonomer. The KHI performance of 2-MACap:NIPMAm (1:1) was in accordance with the good performing copolymers of MMA and MAPYD. The results for 2-MACap:NIPMAm (1:1) and 2-MACap:MMA (1:1) both the $T_o$ value and the $T_a$ value were found to be significantly different ($p < 0.05$ in a statistical $t$-test). But for 2-MACap:NIPMAm (1:1) and 2-MACap:MAPYD (1:1) only the $T_a$ value between them was found to be significantly different ($p < 0.05$ in a statistical $t$-test). The cloud point of 24 °C was still too low for practical application. The terpolymer 2-MACap:NIPMAm:VIMA (1:1:0.5) had a slight increase in cloud point to 30 °C, but the KHI effect for the terpolymer was less than the copolymers 2-MACap:NIPMAm (1:1) and 2-MACap:VIMA (1:1). Two hydrazide comonomers were copolymerized with 2-MACap, 2-MACap:NDMHMAm (1:1) and 2-MACap: NPyMA (1:1), they had no cloud point but their KHI performance were clearly worse than PVCap. This could be related to their molecular weight being too low or possibly caused by the increased hydrophilicity of these hydrazide-based polymers. 2-MACap:PEGMA-

9 (4:1) showed an inhibition effect similar to PVCap and 2-MACap:MAm (1:1). In fact both the $T_o$ value and the $T_a$ values between 2-MACap:PEGMA-9 (4:1), PVCap and 2-MACap:MAm (1:1) were not found to be significantly different ($p > 0.05$ in a statistical *t*-test). The PEGMA comonomer had a strong effect on the hydrophilicity of the copolymer with 2-MACap. Just 20 mol% PEGMA turned an insoluble homopolymer into a water-soluble copolymer with cloud point 54 °C, also considerably higher than PVCap.

From the previous publications it have been shown that the acyclic aliphatic alcohol 4-methyl-1-pentanol (4-MePeOl) gave a good synergetic performance with the caprolactam-based KHI polymers PVCap and 2-methacrylamido-caprolactam (2-MACap).[169,170,226] In this study the field of potential synergist using mixtures have been broadened with 2-MACap:MMA (1:1) and 2-MACap:MAPYD (1:1). The synergists investigated were hexabutylguanidinium chloride (HBuGCl), tetrabutylphosphonium bromide (TBPB), tetrabutylammonium bromide (TBAB), tetrapentylammonium bromide (TPAB), sodium 4-methyl pentanoate (iPeCOONa) and 4-methylvaleric acid (iPeCOOH) (Table 4.18).

The onium salts (quaternary ammonium or phosphonium salts, TBAB, TPAB and TBPB) synergists gave little performance enhancement to 2-MACap:MMA (1:1) copolymer with only TBAB giving a significant improvement. In contrast, the copolymer 2-MACap:MAPYD (1:1) gave good synergetic effect with all three onium salts, significantly decreasing both the average $T_o$ and $T_a$ values. With the addition of TPAB giving the best results. The onium salts are thought to exhibit good synergy with PVCap because of their different geometries (alkyl vs. ring structure respectively). This means that the copolymer and the synergist operate on different aspects on the hydrate formation, thereby optimizing their combined inhibition. 2-MACap:MMA (1:1) does not have the extra pyrrolidine ring, so its mode of action might be too similar to TPAB and they end up outcompeting themselves for the same $5^{12}6^4$ cavity on the 1,1,1 Structure II hydrate surface.

Table 4.18. SCC test results with 2-MACap:MMA (1:1) and 2-MACap:MAPYD (1:1) with different synergists. Results with 2-MACap:MMA (1:1) with *iso*-butyl glycol ether (iBGE) and 4-methyl-1-pentanol (4-MePeOl) taken from the first study are added for comparison.[226]

| **Copolymer** | **Solvent synergist** | **Concentration (ppm)** | | ***T<sub>o</sub>* (℃)** | ***T<sub>a</sub>* (℃)** |
|---|---|---|---|---|---|
| | | **Polymer** | **Synergist** | | |
| 2-MACap:MMA (1:1) | - | 2500 | - | 8.8 | 8.1 |
| | TBAB | 2500 | 5000 | 7.8 | 6.6 |
| | TPAB | 2500 | 5000 | 9.7 | 7.0 |
| | TBPB | 2500 | 5000 | 8.8 | 7.3 |
| | HBuGCl | 2500 | 5000 | 6.4 | 4.5 |
| | iBGE | 2500 | 5000 | 6.2 | 5.4 |
| | 4-MePeOl | 2500 | 5000 | 4.6 | 3.8 |
| | iPeCOOH | 2500 | 5000 | 7.3 | 6.2 |
| | iPeCOONa | 2500 | 5000 | 6.9 | 5.9 |
| 2-MACap:MAPYD (1:1) | - | 2500 | - | 8.4 | 8.1 |
| | TBAB | 2500 | 5000 | 6.4 | 5.2 |
| | TPAB | 2500 | 5000 | 3.4 | 2.0 |
| | TBPB | 2500 | 5000 | 4.8 | 3.0 |
| | HBuGCl | 2500 | 5000 | 3.1 | 2.0 |
| | iPeCOOH | 2500 | 5000 | 11.9 | 11.2 |
| | iPeCOONa | 2500 | 5000 | 8.1 | 7.3 |

These multiple alkyl groups in these quaternary ammonium or phosphonium salts could be increased by introducing them on guanidinium salts, which have three nitrogen atoms in the cationic center. The guanidinium salt HBuGCl increased the performance for both copolymers, with most pronounced improvement for 2-MACap:MAPYD (1:1).

From the previous study it was shown that 4-MePeOl had an excellent synergistic effect with 2-MACap:MMA (1:1).[226] To get a better understanding of the role the of the functional group, we changed the functional group from alcohol to a carboxylic acid in the compound iPeCOOH, in addition to the carboxylate form iPeCOONa and tested it with the 2-MACap:MMA (1:1) and 2-MACap:MAPYD (1:1) copolymers. For 2-MACap:MMA (1:1) the performance was worse than with the alcohol as the functional group. Both iPeCOOH and iPeCOONa were antagonistic with 2-MACap:MAPYD (1:1). The synergy KHI test results highlight the difficulty in pre-determining which molecules will enhance the performance of a given KHI polymer. Exactly what is happening in solution to cause these differences is hard to say, but it may be a combination of polymer-synergist interactions as well as competitive interactions to prevent hydrate nucleation and crystal growth.

## 4.9 Paper IX: High Cloud Point Polyvinylaminals as Non-Amide-Based Kinetic Gas Hydrate Inhibitors[230]

The main constituents of kinetic hydrate inhibitor (KHI) formulations used in the petroleum industry are water-soluble polymers,[147,159,166,231,232] and the majority of these are polyamides based on vinylic monomers such as *N*-vinyl lactams and *N*-alkyl(meth)acrylamides. When hyperbranched polyester amides are included, these three classes represent the most of the commercially available KHI polymers. Non-amide-based KHI polymers, including poly(amine oxides), polyvinyloxazolines and polyquaternaries, have been investigated. This study investigates a new class of nonamide KHI polymer, namely polyvinylaminals with the focus to determine whether nonamide polymers can perform as good as classic amide-based polymers. Polyvinylaminals contain cyclic aminal (or aminoacetal) groups with two nitrogen atoms. A series of polyvinylaminals was synthesized by the reaction of varying molecular weight polyvinylamines with alkylamines (Figure 4.13). They were tested in two different experiments, THF hydrate crystal growth-inhibition experiment and high-pressure slow constant cooling gas hydrate KHI experiment.

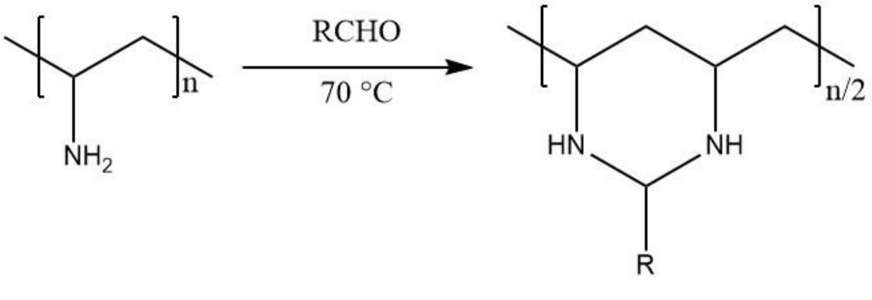


Figure 4.13. Schematic over the general synthesis of polyvinylaminals.

Since the possibility of the amine groups to be quaternized is present, it is reasonable that the polyvinylaminals may be good at inhibiting hydrate crystal growth. The results from the THF hydrate crystal growth inhibition experiments are summarized (Table 4.19).

In these experiments, the results are average from six tests per chemical. Since we were investigating protonated polyvinylaminals two different pH of 3 and 7 were used. At pH 3 the THF hydrate crystal growth was in general less than at pH 7. Presumably, larger protonated water clusters found in the acidic solution and a higher concentration of hydronium ions ($H_3O^+$) slow down the hydrate growth rate. In addition, possibly the water molecules at the THF hydrate crystal surface are also protonated, aiding in slowing down the growth rate. At pH 7 some polyvinylaminals gave comparable performance to tetrabutylammonium bromide (TBAB) but none of them performed as well as tetrapentylammonium bromide (TPAB). The *n*-pentanal and cyclohexane carboxyaldehyde derivatives obtained the best result in this study. A small but not major improvement in the performance was observed for some of the polyvinylaminals that were tested at pH 3. This indicates that for this type of polymer class protonation of some of the amine groups to give quaternary ammonium groups is only a minor advantage for hydrate growth inhibition.

Table 4.19. The summarized results from the THF hydrate crystal growth experiments.

| **Polyvinylaminal** | **Conc. (ppm)** | **pH** | **g/h** | **Crystal shape** |
|---|---|---|---|---|
| No additive | - | 7 | 1.59 | Rhombic |
| | | 3 | 1.30 | Rhombic |
| Tetrabutylammonium bromide | 4000 | 7 | 0.45 | Distorted rhombic |
| Tetrapentylammonium bromide | 4000 | 7 | 0.04 | V. distorted |
| Polyvinylamine, $M_w$=10000 g/mol | 4000 | 7 | 1.81 | Rhombic |
| Polyvinylaminal/n-butanal | 4000 | 6.5 | 0.72 | Rhombic |
| Polyvinylaminal/n-pentanal | 2000 | 3 | 0.80 | Mostly rhombic |
| | 4000 | 7 | 0.34 | Hexagonal plates |
| | | 3 | 0.23 | Hexagonal plates |
| Polyvinylaminal/n-hexanal | 2000 | 3 | 1.25 | Rhombic crystals + hexagonal plates |
| | 4000 | 7 | 0.65 | Rhombic crystals + hexagonal plates |
| | | 3 | 0.38 | Hexagonal plates |
| Polyvinylaminal/cyclopentane carboxaldehyde | 4000 | 7 | 0.58 | Rhombic crystals + hexagonal plates |
| Polyvinylaminal/cyclohexane carboxaldehyde | 4000 | 7 | 0.39 | Hexagonal plates |
| | | 3 | 0.33 | Hexagonal plates |

The next part of the study is devoted to the results from the slow constant cooling gas hydrate KHI experiments (SCC) (Table 4.20).

Table 4.20. Summarized results from the high-pressure slow constant cooling gas hydrate KHI experiments.

| **Polyvinylaminal** | **Conc. (ppm)** | **pH** | $T_o$ **(°C)** | $T_a$ **(°C)** | **Cell type** |
|---|---|---|---|---|---|
| No additive | - | 7.0 | 17.1 | 16.6 | Steel |
| | | | 16.8 | 16.4 | Sapphire |
| PVP-K15 $M_w$ = 8000 g/mol | 2500 | 7.0 | 11.6 | 10.9 | Sapphire |
| | | | 11.1 | 9.9 | Steel |
| PVCap, $M_w$ = 10 000 g/mol | 2500 | 7.0 | 9.6 | 9.2 | Steel |
| | | | 9.9 | 8.9 | Sapphire |
| Polyvinylamine, $M_w$=10000g/mol | 2500 | | 16.9 | 16.8 | Sapphire |
| Polyvinylaminal/butanal | 2500 | 6.5 | 15.1 | 15.0 | Sapphire |
| Polyvinylaminal/*iso*-pentanal (3-methylbutanal) | 2500 | 6.5 | 11.6 | 11.2 | Steel |
| | | | 11.8 | 11.5 | Sapphire |
| | 5000 | | 10.0 | 9.7 | Sapphire |
| Polyvinylaminal/pivaldehyde (2,2-dimethylpropanal) | 2500 | 6.5 | 15.2 | 15.1 | Sapphire |
| Polyvinylaminal/*n*-pentanal | 2500 | 6.5 | 11.8 | 11.7 | Sapphire |
| | | 2.9 | 11.5 | 11.4 | Sapphire |
| Polyvinylaminal/*n*-hexanal | 2500 | 6.5 | 11.9 | 11.8 | Sapphire |
| Polyvinylaminal/*iso*-hexanal (4-methylpentanal) in iPrOH[#] | 2500 | 6.5 | 10.3 | 10.0 | Steel |
| Polyvinylaminal/cyclopentane carboxaldehyde | 2500 | 6.5 | 11.6 | 11.5 | Sapphire |
| Polyvinylaminal/cyclohexane carboxaldehyde | 2500 | 6.5 | 9.8 | 9.4 | Steel |
| | | | 10.4 | 10.2 | Sapphire |
| | | 3.1 | 11.2 | 10.8 | Sapphire |
| | 5000 | 6.5 | 7.0 | 6.5 | Steel |
| | | | 7.6 | 7.1 | Sapphire |

[#] 8 Tests.

As expected for a very hydrophilic polymer without pendant hydrophobic groups, polyvinylamine did not show any KHI activity in these tests. All the polyvinylaminals derived from polyvinylamine on the other hand, showed some KHI activity which increased with the size of the pendant alkyl or cycloalkyl groups as long as water solubility was not lost. The butanal and the pivaldehyde polyvinylaminals had the poorest KHI performance of the ones made and tested in this study. When the butanal derivative was branched at the end using 3-methylbutanal (*iso*-pentanal) the hydrophobicity increased as did also the KHI effectivity. The same trend was observed when 4-methylpentanal (*iso*-hexanal) was used. This also had the best KHI activity of all polymers made and tested with acyclic groups. The reason for this is believed to be caused by the alkyl branching giving an end group that results in better van der Waals interaction with the open hydrate cavities than what the straight-chain alkyl group can provide, as seen in previous studies.[162,169]

Cycloalkyl groups are another class of hydrocarbyl fragments that possesses good van der Waals interactions either with hydrate cavities or creating cavities in the water solution. Two polymers with cycloalkyl groups were made by reacting the base polyvinylamine with cyclopentane carboxaldehyde or cyclohexane carboxaldehyde. The five-ring polyvinylaminal had a similar KHI performance as the pentanal derivative while the six-ring polyvinylaminal with pendant cyclohexyl groups had the pest KHI performance of all the polyvinylaminals synthesized and tested in this study. Previous results from our group suggests that increased hydrophobicity with hydrocarbyl groups of the correct size and shape can indeed improve the KHI performance as long as sufficient water solubility is maintained.[153]

# 5 Main Conclusions

The main conclusions from this PhD study can be summarized in the following:

For many KHI polymer classes there is a correlation between a low cloud point and the hydrate inhibition performance. There are some exceptions to this, shown experimentally by poor KHI performance of polymers with low cloud points when they possessed very small or very large hydrophobic groups on the side chains. The optimum size of these groups was found to be about three to six carbon atoms depending on the type of hydrophilic functional group to which they are attached and their position. The benefit of a low cloud point was allocated to three theories:

1. The surface area/hydrodynamic volume ratio of the polymer is maximized.
2. The hydrophobic interactions of the polymer is maximized at a temperature when hydrogen-bonding is about to break down.
3. The concentration of polymer is greater at interfacial regions (gas-water of oil-water) where formation of hydrate first occurs.

The well-known kinetic hydrate inhibitors (KHIs) such as poly(*N*-vinylcaprolactam) (PVCap), poly(*N*-vinylpyrrolidone) (PVP) and 1:1 *N*-vinylcaprolactam:*N*-vinylpyrrolidone (VCap:VP) copolymer showed good robustness when a range of treatments have been applied, thermal aging (at varying temperatures, at varying pH and in monoethylene glycol (MEG) solvent), treatment with microwave or ultrasound, ball-milling and oxidizing agents (household bleach or hydrogen peroxide, also with heat). Oxidizing agents were the only treatment that affected the KHI performance. Bleach (aqueous sodium hypochlorite) worsened the performance of PVCap but only at elevated temperatures and in basic solution. The performance of PVCap improved upon addition of hydrogen peroxide. This may be due to formation of a $PVCap \cdot H_2O_2$ adduct or a synergistic effect.

From the KHI experiments on PVCap with different synergists, several structure-activity observations were made.

- Generally better synergetic effect is achieved by cyclic alkyl "tail" than an acyclic "tail" containing the same number of carbon atoms.
- Better synergetic effect is achieved with end-tail branching (one or two methyl groups) of the alkyl "tail" than a straight-chain alkyl "tail".
- The synergetic effect relates to the hydrophobicity/water solubility limit of the solvent as well as to the shape.

The branching and placement of the alkyl "tail" were found to be important structural features to optimize in alcohols and glycol ether synergists. Two isomers of iHexOl (2-methyl-1-pentanol and 3-methyl-1-pentanol) showed good but poorer synergetic performance than iHexOl. For the glycol ethers it was showed that di(propylene glycol)butyl ether (DPGBE) (methyl branches) gave a better synergetic performance than butyl diglycol ether (DBGE) (no branching).

The experimental research also indicates that for the same number of carbon atoms, compounds with glycol functional groups generally have better synergetic performance than compounds with alcohol as functional group. Further, primary alcohols have better synergetic performance than secondary alcohols. Compounds with ketone as the functional group can have adequate synergy, with the best ketone having the largest end-branched alkyl group as long as sufficient water-solubility is maintained.

For the compounds containing an ether functional group, cyclic alcohol and ketone, the synergetic effect was best for 2-(cyclohexyloxy)ethanol, cycloheptanol and 4-methyl-2-pentanone, respectively. Aromatic compounds did not give good synergy. Outstanding synergetic effect was achieved with 4-methyl-1-pentanol (iHexOl). However when PVCap were polymerized in 4-methyl-1-pentanol the synergetic effect was not as good, possibly caused by the initiator incorporating *iso*-hexyl groups from the solvent into the polymer, changing the polymer conformation. The glycol ether version of iHexOl, iHex(EO)Ol did not give better synergetic performance than iHexOl. The experimental research highlights the importance of finding the right concentrations combinations of both PVCap and iHexOl in order for maximizing the synergetic effect. Indications that cosolvents is beneficial for improved synergetic effect was observed in a system with iHexOl and BGE, possibly by BGE improving the solubility of the sparingly soluble iHexOl. When a liquid hydrocarbon phase was introduced to the system, the KHI performance decreased significantly when using iHexOl but improved a little when TBGE was added. Speculations that this is caused by the difference in the hydrophilicity between the solvents. The less water-soluble iHexOl partitions far more to the decane phase (rendering it unavailable for hydrate inhibition), than for TBGE. This was also observed for the less water-soluble TMDD. The optimal molecular weight distribution for the KHI polymer when used with a solvent synergist is not the same as the optimum distribution when using the polymer alone. This may be because the low $M_w$ polymer fraction (closer to the synergist size) prevents smaller gas hydrate particle growth (nucleation), whereas the higher $M_w$ fraction prevents growth more of larger particles.

For alkylboronic acids used as synergist with PVCap, the ideal chain length from the boron atom appears to be three carbon atoms, and it improves if the tail is branched (*iso*-butyl) or if it is cycloalkyl group of a similar shape. Longer alkyl tails could make the alkylboronic acids antagonistic. This is different than the optimum chain length of five and four carbon atoms for the best synergetic performing ammonium salts and alcohols.

Both 2-ACap and 2-MACap copolymers had KHI effect, some had better performance that exceeded PVCap of similar molecular weight. Especially the 2-MACap showed strong KHI potential. The copolymers that had the worst inhibition effect were also the most hydrophilic with no cloud point. As has been observed in previous methacrylamido-based polymers, a high percentage of backbone methyl groups led to improved performance. This was experimentally observed for 2-MACap:MAPYD (1:1) vs. 2-MACap:APYD (1:1), as well as for 2-MACap:MAPYD (1:1) vs. 2-ACap:MAPYD (1:1) and 2-MACap:MMA (1:1) vs. 2-ACap:MMA (1:1). The best inhibition results was found for 2-MACap:MMA (1:1), 2-MACap:NIPMAm (1:1) and 2-MACap:MAPYD (1:1). The results for 2-MACap:MMA (1:1) and 2-MACap:MAPYD (1:1) with synergist highlight the difficulty in pre-determining which molecules will enhance the performance of a given KHI polymer, without doing the necessary experimental work, since some of them were antagonistic with one of the copolymers while giving synergy with the other.

The non-amide-based polyvinylaminals with the best KHI performance were pentanal and cyclohexanecarboxyaldehyde derivatives. As seen for the synergists, branching of the end of the pendant alkyl groups improved the inhibition performance. In THF tests, the polyvinylaminal with pendant cyclohexyl groups had the best performance.

# 6 Future Work

Based on the obtained results and conclusions presented in this thesis, it would be interesting to conduct more work on these topics:

Further investigations of the importance of low cloud point on more polymer classes could be carried out, with systematic increase in the size of the pendant hydrophobic groups on the side chains. Also, different hydrophobic groups and the effect on the cloud point with respect to their placement and attachment and the polymer could be investigated.

Solvent synergism includes a whole range of possible further studies. A broader range of molecular weight and different classes of polymers could be investigated. In addition, based on the findings different functional groups and branching of the solvent could be further investigated. Also blends of solvent synergists and the effect of introducing salts and/or liquid hydrocarbon phase to the system could be investigated in more detail. Moreover, different KHI monomers could be polymerized in a range of solvent synergists.

The molecular weight of 2-MACap copolymer could be optimized, both for better comparison but also for improved KHI performance. It would be interesting to make block copolymers instead of statistical (random) copolymers. Different end-caps could also be investigated, and using chain transfer agents to reduce the molecular weight. Further, different comonomers could be used for copolymerization, preferably backbone methylated. More potential synergists with the better performing 2-MACap copolymers could be investigated. Moreover, it would be interesting to investigate further the effect of having comonomers with different geometries compared to the geometry of the solvent synergist in case there is competition for site-adsorption on hydrate particle surfaces. The lactam ring could also be placed on other backbones.

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# Appendices

**Paper I.** Does the Cloud Point Temperature of a Polymer Correlate with Its Kinetic Hydrate Inhibitor Performance?

**Paper II.** Reliability and Performance of Vinyl Lactam-Based Kinetic Hydrate Inhibitor Polymers after Treatment under a Range of Conditions

**Paper III.** Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly(*N*-vinylcaprolactam)

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# Paper I

Does the Cloud Point Temperature of a Polymer Correlate with Its Kinetic Hydrate Inhibitor Performance?

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# Paper II

Reliability and Performance of Vinyl Lactam-Based Kinetic Hydrate Inhibitor Polymers after Treatment under a Range of Conditions

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# Reliability and Performance of Vinyl Lactam-Based Kinetic Hydrate Inhibitor Polymers after Treatment under a Range of Conditions

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**ABSTRACT:** Well-known kinetic hydrate inhibitors (KHIs) such as poly(*N*-vinylcaprolactam) (PVCap), poly(*N*-vinylpyrrolidone) (PVP), and 1:1 *N*-vinylcaprolactam:*N*-vinylpyrrolidone (VCap:VP) copolymer have been subjected to a range of treatments to determine their reliability and whether the treatment conditions could affect the KHI performance, both positively or negatively. This included thermal aging (at varying temperatures, at varying pH, and in monoethylene glycol (MEG) solvent), treatment with microwaves or ultrasound, ball-milling, and oxidizing agents (household bleach or hydrogen peroxide, also with heat). In addition, samples of commercial polymer solutions kept for up to 15 years were also tested for KHI performance to determine their long-term reliability. Testing was carried out using a synthetic natural gas mixture in steel rocking cells using slow constant cooling starting at ca. 76 bar. All samples of PVCap and 1:1 VP:VCap showed good KHI performance to the first sign of hydrate formation, but older samples showed a better ability to inhibit crystal growth. KHI polymer testing after treatment with microwaves or ultrasound, or thermal aging (at varying temperatures, varying field pH, and in MEG solvent up to 160 °C) showed little loss of performance. Oxidizing agents, particularly sodium hypochlorite solution, worsened the KHI performance.

## 1. INTRODUCTION

One of the chemical methods used to prevent gas hydrate formation in oil and gas field production flow lines is injection of kinetic hydrate inhibitors (KHIs).[1−7] The main active ingredient in KHIs is a water-soluble polymer, but deployed formulations usually contain organic solvents or other molecules that can act as synergists. KHI polymers usually contain amphiphilic groups. The mechanism of KHIs is still the subject of debate, but it appears several of these amphiphilic groups (i.e., in oligomers or polymers) are needed to prevent gas hydrate nuclei and/or crystals from growing into macroscopic size and subsequently blocking flow lines.[8−10]

Well-known classes of KHI polymers that have been applied in the field include various *N*-vinyllactam homopolymers and copolymers and poly(*N*-alkyl(meth)acrylamides) (Figure 1).[7] KHI polymers may be subjected to a range of field conditions. First, before injection they may be stored in tanks for long periods at temperatures up to 40 °C. Later, the polymer will be injected into a hot well stream usually at the well head, where the fluids may reach 80−100 °C. Some polymers may thermally degrade at these temperatures.[11−13]

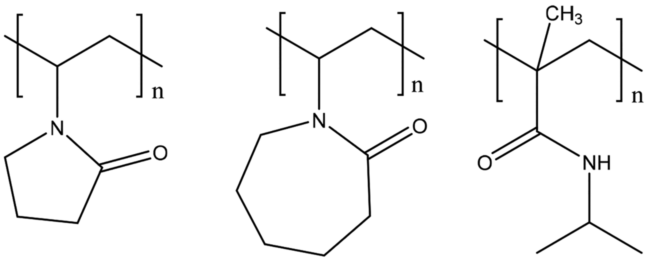

Figure 1. KHI polymers, left to right: poly(*N*-vinylpyrrolidone) (PVP), poly(*N*-vinylcaprolactam) (PVCap), and poly(*N*-isopropylmethacrylamide) (PNIPMAm).

In addition, the pH of the produced water (i.e., aqueous phase from an unprocessed well stream) under pressure will be quite acidic due to dissolved carbon dioxide and often hydrogen sulfide, as well as organic acids from the liquid hydrocarbon phase. The pH is usually around 4−6 but can occasionally be even lower. Thus, the KHI polymer must be able to survive hot acidic conditions for a time and still inhibit hydrate formation when the fluids cool inside the hydrate-forming region.

The KHI may also be injected along with a thermodynamic inhibitor (THIs) to boost the hydrate inhibition.[14−17] The commonest THIs used in production flow lines are methanol and monoethylene glycol (MEG), but ethanol is also sometimes used. Due to the volumes and costs, methanol and MEG are often regenerated and reused. If the THI is injected with KHI and is regenerated on site, the KHI polymer will be subjected to elevated temperatures; this can be up to 160 °C if the THI is MEG.[18,19] It is important that the KHI polymer in the MEG does not cause fouling and is not degraded by this thermal treatment as the whole formulation is to be reinjected.

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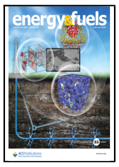

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If the KHI polymer is not to be recycled, it may be preferable in some regions if the polymer is destroyed before it is discharged in the produced water into the environment. Several methods have been proposed recently.[20−22] One method to destroy the polymer is oxidation with common oxidizing agents such as bleach solution (aqueous sodium hypochlorite) or hydrogen peroxide. In the field, this oxidation treatment may be the last one to be encountered by the KHI polymer but, in this case, it is preferable if the polymer is not preserved but is degraded as much as possible.

In this report we have investigated typical conditions encountered by the KHI polymer as well as some other nonfield conditions simply to observe the effect on the polymer. These include

1. aging for up to 15 years
2. thermal treatment—at varying temperatures, varying pH, and in MEG solvent
3. microwave treatment
4. ultrasound
5. ball-milling
6. oxidizing agents with or without heat treatment—household bleach or hydrogen peroxide

The KHI polymer was tested before and after these different treatment conditions.

## 2. EXPERIMENTAL METHODS

**2.1. Chemicals Used and KHI Polymer Treatment Equipment.** Batches of poly(*N*-vinylcaprolactam) (PVCap; $M_w$ 3000−4000 and 7000−12000 g/mol) and 1:1 *N*-vinylcaprolactam:*N*-vinylpyrrolidone (VCap:VP; $M_w$ 2000−4000 g/mol) were supplied by BASF, Germany between 2004 and 2016. PVCap samples were approximately 41 wt % solution in MEG. For all experiments except the long-term stability study, the MEG was removed by triple precipitation of the polymer, followed by removal of residual solvents under vacuum. The VCap:VP copolymer was 53.8 wt % in water and was used as supplied. Poly(*N*-vinylpyrrolidones) (PVP K15, 8000 g/mol; PVP 120*k*, $M_w$ $3 \times 10^6$ g/mol) pure powders were obtained from Ashland Chemical Co. All of these lactam-based KHI polymers had pH about 7−8 as 2500 ppm aqueous solutions. MEG solvent (99%) and acetic acid (99+%), aqueous hydrogen peroxide (30 vol %), and aqueous hydrochloric acid (37 wt %) were supplied by VWR (Avantor). Sodium hypochlorite ("Klor" bleach solution, approximately 5 wt % NaOCl) was supplied by Coop Mega, Norway.

Microwaving of polymer solutions was carried out using a Miele microwave oven. A 100 mL aliquot of a 2500 ppm solution of KHI polymer was placed in the oven in a glass vessel and subjected to microwaves at 780 W until the solution boiled (4−5 min). Ball-milling on solid KHI polymer samples was carried out using a Pulverisette 7, from Fritsch GmbH, Germany. Zirconium(IV) oxide balls were used in containers of the same material. Solids were milled for 10 min periods (with 2 min cooling periods in-between) at 700 rpm.

Ultrasound treatment of KHI polymer solutions was carried out using a Branson 2510 ultrasonic cleaner at 40 kHz with 2.8 L bath from Emerson, USA. A 2500 ppm solution of KHI polymer was placed in the sonic bath and subjected to ultrasound for 5 min at ca. 20.5 °C.

**2.2. KHI Equipment and Experimental Methods.** We carried out high-pressure KHI performance tests using a multisteel rocking cell apparatus, supplied by PSL Systemtechnikk, Germany (Figure 2). The cells themselves were made by Svafas, Norway, and each has an internal volume of 40 mL. Five cells were used for our study placed in a water bath. A steel ball is placed in each cell which runs smoothly back and forth when the cells are rocked. Each cell was filled with 20 mL of aqueous KHI solution.

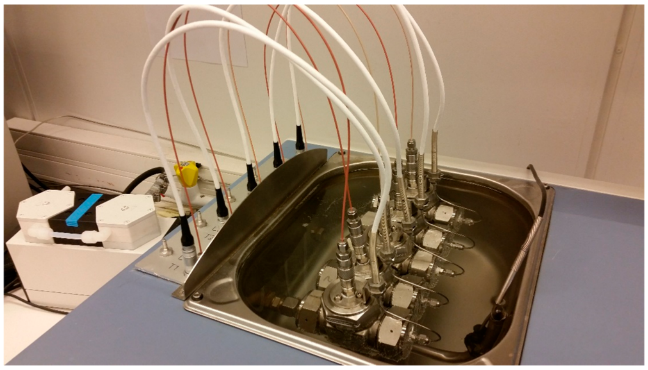

**Figure 2.** Rocking cell rig showing the five steel cells in upright position.

The test method in both rigs was our standard "slow constant cooling" test method described previously.[23,24] The rest of the test method was as follows: Air in the sapphire or steel cells was removed using a vacuum pump, and then the cells were filled with 2−3 bar of synthetic natural gas (SNG; Table 1). The cells were briefly rocked, and the procedure pump−fill was repeated twice except on the last fill the cells were then charged with 79 bar of SNG. This gas mixture preferentially forms structure II hydrates as the most thermodynamically stable phase. A computer logged the pressure, and temperature for each cell as well as the temperature in the cooling bath. The cells were cooled at a rate of 1.0 °C/h from 20.5 to 2.0 °C while rocking at 15 rocks per minute at an angle of 40°.

**Table 1. Composition of Synthetic Natural Gas**

| component | mol % |
|---|---|
| methane | 80.67 |
| ethane | 10.20 |
| propane | 4.90 |
| isobutane | 1.53 |
| *n*-butane | 0.76 |
| $N_2$ | 0.10 |
| $CO_2$ | 1.84 |

In this type of test, we first observe a pressure drop of 1.5−2 bar due to gas dissolution in the aqueous phase. Thereafter a linear pressure decrease is observed as the temperature decreases in a closed system. The first deviation from this linear pressure decrease is taken as the first sign of hydrate formation in the system. We call this the onset temperature (To) although true nucleation could have taken place at an earlier stage. The second parameter obtained from these experiments is the temperature for rapid hydrate formation (Ta), which is found where the pressure drop is at its steepest (meaning the inflection point of the pressure curve). This gives an indication of when the KHI is no longer able to confine the growth of hydrates. Some KHIs give very rapid hydrate growth once nucleation has begun while others, such as many *N*-vinylcaprolactam-based polymers, are able to slow the crystal growth process for long periods.

At the end of the slow constant cooling experiment, we plot a graph of pressure and temperature vs time for each cell. These graphs are essentially identical in form for both the steel and sapphire cells. Up to 10 individual tests were carried out on each sample. An example of a typical set of pressure and temperature vs time data for one sample is given in Figure 3. This is a graph from two sets of five tests giving a total of 10 tests. The closeness of the pressure and temperature traces gives some visual idea of the reproducibility of the test. In Figure 4 we show a graphical example, demonstrating how we determine To and Ta. The test is for PVCap (2020 sample). In this test, To was found to be 10.3 °C and Ta is found to be 8.6 °C. Due to the stochastic nature of hydrate formation, the data scattering is 10−15%.[25,26] A full set of To and Ta values from eight blank tests and 10 tests on a

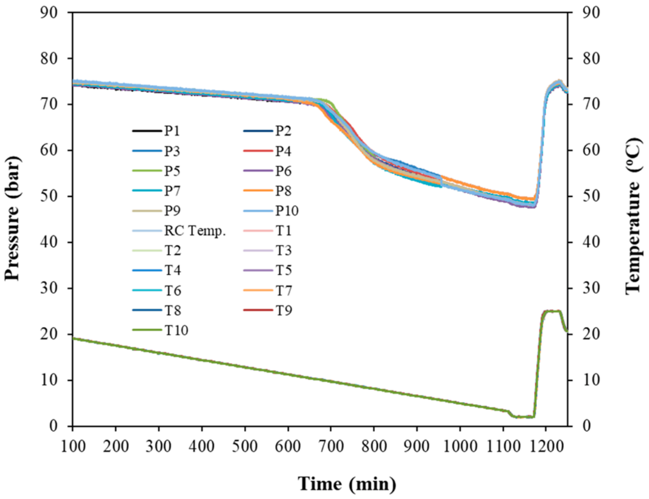

**Figure 3.** Example of pressure and temperature vs time graph for a set of 10 slow constant cooling tests. (RC Temp. is the temperature given on the cooling bath display.)

PVCap sample are given in Table 2. In addition, we give the average and standard deviations (population type). No systematic errors leading to consistently better or worse results for any of the cells were observed. Temperatures in the cells and the water bath were observed to be homogeneous. The two methods that we used to determine the hydrate equilibrium temperature (HET) for high-pressure gas hydrate systems are calculations using Calsep's PVTSim and laboratory experiments by standard slow hydrate dissociation.[27,28] Previous experiments conducted by our group using a SNG−water system agreed very well with the calculated value (accuracy within 1 °C).[29]

**2.3. Results and Discussion.** *2.3.1. Long-Term Aging.* All polymer solutions were tested 8−10 times to get reasonably reliable To and Ta values. Standard deviations were no more than 0.7 °C. Each solution was prepared the day before testing unless otherwise stated. The first part of the study was to check the long-term reliability of commercial KHIs. We had obtained samples of PVCap (ca. 41 wt % in MEG) and 1:1 VP:VCap copolymer (53.8 wt % in water) from the supplier at four times, in 2004, 2010, 2016, and 2020. All samples were kept at the laboratory temperature of 20.5 °C the whole time in screw-lid-sealed plastic bottles which were only opened occasionally and briefly. Thus, the samples were stored aerobically but without loss of solvent. Both types of these VCap-based polymers are known to be very poorly biodegraded in the OECD306 seawater test over 28 days.[2,7] Samples were used as received; no solvents were removed for these long-term aging studies.

The KHI performance results for tests at 2500 ppm active polymer were carried out in the steel multicell rocking equipment and are summarized in Table 3. 8−10 tests were conducted on each polymer solution. Tests were carried out in 2019 so that the oldest samples were approximately 15 years old at that time. Although the lowest average To value (7.3 °C) was found for the oldest batch (2004), at the 95% confidence level ($p > 0.05$ from statistical $t$ test), there was no significant difference between the To values performances of each group of polymers supplied at the three dates. However, there is a trend to higher Ta values as the polymers get older. This is for both PVCap and 1:1 VP:VCap copolymer. We are not sure of the reason for this trend. Since operators wish to keep their flow lines completely hydrate free, the time to first hydrate crystal formation is usually regarded as the more important parameter. Therefore, we conclude that on the basis of To values both polymers give reliable KHI performance even after a 15 year storage period. Other commercial KHI polymers such as hyperbranched poly(esteramide)s or poly(*N*-alkylmethacrylamide)s were not investigated as we had not stored them for such a long time.

Usually, we make up 2500 ppm polymer aqueous solutions the day before the test to allow the polymer chains to be fully hydrated by the water and come to their equilibrium structure.[9,23,24,26] To check if this is necessary, we prepared solutions of 1:1 VP:VCap copolymer (2004 batch) at 2500 ppm and tested them immediately as well as after stirring overnight at 20.5 °C. Both solutions gave almost identical average To and Ta values, indicating that there was no difference in waiting approximately 24 h before testing the polymer solution. We also carried out the same procedure with this polymer but with added 2500 ppm MEG, i.e., immediate testing with a freshly made solution and testing after stirring 24 h. The results are summarized in Table 4 but discussed later in this study.

*2.3.2. Thermal Aging at Normal pH.* Some KHI storage facilities, for example in the Middle East, might keep concentrated KHI solutions for many months at up to 40+ °C, especially during the summer. We have not kept any of our laboratory samples at these temperatures for long periods, so instead we decided to investigate heating the samples to even higher temperatures for short periods, which might be typical of well head temperatures. The PVCap used in this study had a higher molecular weight range (7−12 kg/mol) than

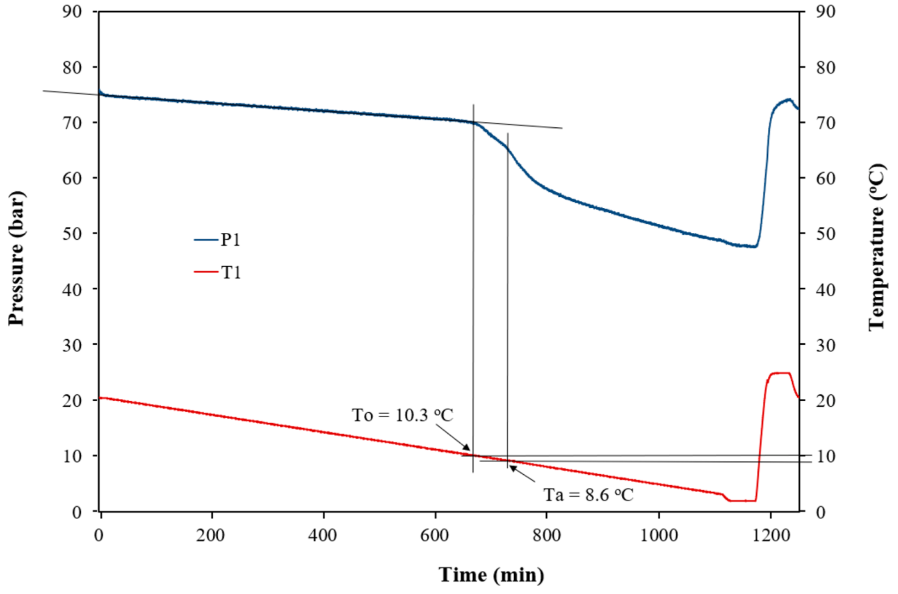

**Figure 4.** Example of To and Ta determination for one of the steel rocking cells in a slow constant cooling test.

Table 2. Examples of the Range of To and Ta Values for Blank Tests and PVCap ($M_w$ = 7−12*k*)

| | To values, °C | Ta values, °C | To(av), °C | SD, °C | Ta(av), °C | SD, °C |
|---|---|---|---|---|---|---|
| blank test | 16.8, 17.2, 17.3, 17.0, 16.0, 17.1, 17.8, 16.7 | 16.8, 17.1, 17.1, 17.0, 15.9, 16.9, 17.6, 16.7 | 17.0 | 0.49 | 16.9 | 0.45 |
| PVCap(7−12*k*) | 10.3, 10.3, 10.5, 10.3, 9.8, 10.6, 10.2, 11.2, 10.4, 10.3 | 9.9, 9.9, 10.1, 9.8, 9.6, 10.1, 9.9, 10.0, 9.8, 9.9 | 10.4 | 0.34 | 9.9 | 0.14 |

Table 3. Slow Constant Cooling Tests on 2500 ppm Active Polymer[a]

| polymer | To(av), °C | Ta(av), °C |
|---|---|---|
| no additive | 16.8 (0.5) | 16.7 (0.4) |
| PVCap 2004 | 10.0 (0.3) | 7.9 (0.2) |
| PVCap 2010 | 9.7 (0.4) | 7.8 (0.5) |
| PVCap 2016 | 10.2 (0.2) | 7.5 (0.4) |
| 1:1 VP:VCap copolymer 2004 (immediate testing) | 7.3 (0.5) | 6.0 (0.5) |
| 1:1 VP:VCap copolymer 2004 | 7.4 (0.6) | 6.5 (0.4) |
| 1:1 VP:VCap copolymer 2010 | 8.5 (0.7) | 5.8 (0.7) |
| 1:1 VP:VCap copolymer 2016 | 8.2 (0.6) | 5.8 (0.3) |
| 1:1 VP:VCap copolymer 2020 | 8.1 (0.4) | 5.4 (0.4) |

[a] To and Ta are the average of 8-10 individual experiments. Standard deviations are given in parentheses.

those used in Table 2. The MEG solvent was removed before testing. PVCap homopolymer is less likely to be injected at high well head temperatures as it has a cloud and deposition point of about 30−40 °C as a 2500 ppm solution in deionized water. Therefore, we concentrated on heating the 1:1 VP:VCap copolymer in aqueous solution, which has cloud and deposition points of about 70 and 85 °C, respectively.[30] We found that heating a 2500 ppm aqueous solution of this polymer to 80 °C for 20 h gave no visual change in the solution, when cooled back to room temperature, and no significant change in the KHI performance (Table 4). Photographs of the 2500 ppm solution of this copolymer at 20 °C (after heating) and at 80 °C are given in Figure 5.

*2.3.3. Thermal Aging with MEG.* KHIs can be used as a retrofit solution, to replace some or all of the injected thermodynamic hydrate inhibitor (THI), in a field application.[31] MEG is often regenerated and reinjected. Therefore, it is important to know if the KHI would survive the MEG regeneration processing where the temperature of the fluids can reach as high as 160 °C.[32−36]

First, we checked if MEG was a synergist for the 1:1 VP:VCap copolymer 2004 batch. A mixture of 2500 ppm of both chemicals gave average To and Ta values (10 tests) of 7.1 and 5.7 °C, respectively (Table 4). The To value is a little lower but is not statistically significantly different from the copolymer alone ($p < 0.05$ for statistical *t* test). MEG has been reported to be a weak synergist with PVCap.[37] Sometimes synergy is reported between KHI and THI, but often this is just an additional effect and not true synergy; i.e., the KHI gives extra inhibition on top of the THI inhibition but not more than the full effect of each when mixed.[38−40] At best, MEG is a poor synergist. Etherification (ethoxylation) of alcohols to form alkyl glycol ethers produces much more powerful synergists.[41]

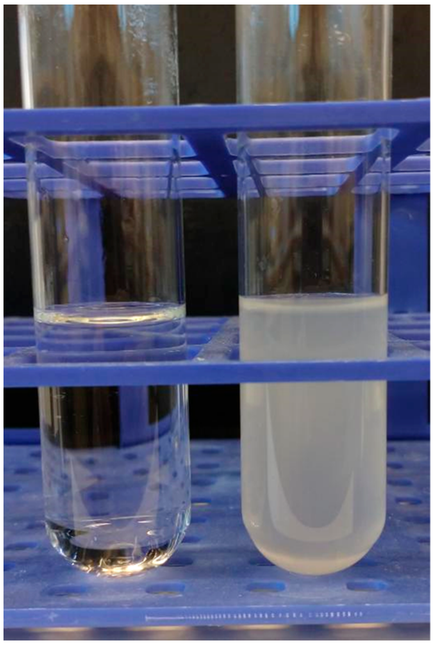

Figure 5. 2500 ppm solutions of 1:1 VP:VCap copolymer at 20 °C after first heating to 80 °C (left) and at 80 °C (right).

Next, we heated a solution of 1:1 VP:VCap copolymer (2004 batch) with an equivalent weight (based on active copolymer) of MEG to 160 °C for 1 h under an anaerobic atmosphere in a sealed stirred vessel. The pH was still about 7 after this treatment. When we

Table 4. Effect of Thermal Aging in MEG, pH, Ultrasonic and Microwave Treatment[a]

| polymer | To(av), °C | Ta(av), °C |
|---|---|---|
| no additive | 16.8 (0.5) | 16.7 (0.4) |
| PVCap ($M_w$ = 7−12 kg/mol) | 10.4 (0.3) | 8.9 (0.3) |
| PVCap + MEG | 9.2 (0.4) | 8.8 (0.3) |
| PVCap (pH 3.9) | 10.2 (0.2) | 9.6 (0.2) |
| PVCap (pH 3.9, heat 90 °C for 20 h) | 10.6 (0.3) | 9.8 (0.3) |
| 1:1 VP:VCap copolymer 2004 | 7.4 (0.6) | 5.6 (0.4) |
| 1:1 VP:VCap copolymer 2004 (heat 80 °C for 20 h) | 7.5 (0.4) | 5.6 (0.3) |
| 1:1 VP:VCap copolymer 2004 + MEG | 7.1 (0.5) | 5.7 (0.3) |
| 1:1 VP:VCap copolymer 2004 + MEG (immediate testing) | 7.0 (0.5) | 5.5 (0.4) |
| 1:1 VP:VCap copolymer 2004 + MEG (after 160 °C for 1 h) | 7.4 (0.6) | 6.3 (0.5) |
| 1:1 VP:VCap copolymer 2004 (pH 3.9) | 7.8 (0.5) | 5.5 (0.4) |
| 1:1 VP:VCap copolymer 2004 (pH 3.9, heat 80 °C for 20 h) | 8.0 (0.4) | 5.6 (0.4) |
| 1:1 VP:VCap copolymer 2004 (microwave treatment) | 7.1 (0.4) | 5.9 (0.4) |
| 1:1 VP:VCap copolymer 2004 (ultrasonic treatment) | 7.3 (0.5) | 5.7 (0.5) |

[a] 2500 ppm KHI polymer used in all tests. MEG concentration was 2500 ppm. Average of 5−10 tests.

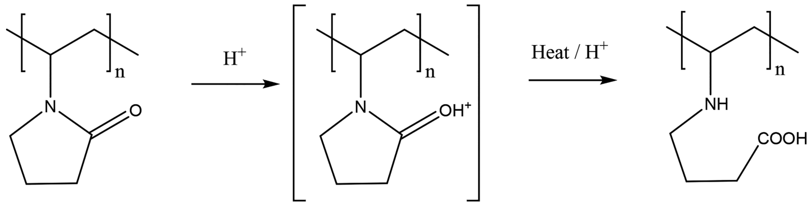

**Figure 6.** Hydrolysis of *N*-vinylpyrrolidone monomer units.

retested the solution at 2500 ppm active polymer, we observed an average To of 7.4 °C and Ta of 6.3 °C, i.e., the same KHI performance as before heat treatment at the 95% confidence level (Table 4). Therefore, since MEG was shown earlier to give no synergy, it appears this copolymer is able to survive the temperature and residence time experienced in MEG regeneration equipment.

*2.3.4. Effect of pH.* The motivation for this part of the study is unofficial reports from service companies that some KHI polymers perform differently at low produced water pH values. In this study we only investigated *N*-vinyllactam-based polymers. The pyrrolidone rings in PVP are reported to slowly ring-open hydrolyze under acidic conditions and elevated temperatures[42] (Figure 6). This may occur via the protonated monomer species, [VP-$H^+$], which will exist in solution at low pH before hydrolysis and could also affect the KHI performance. If these reactions also occur for caprolactam rings in VCap-containing polymers, it could also cause loss of KHI performance but might raise the polymer cloud point. Basic conditions can also cause hydrolysis of lactam rings, but alkyl substitution on the lactam nitrogen (as in VP or VCap-based polymers) makes the lactam more resistant against hydrolysis.[43] Degradation of *N*-vinyllactam polymers under basic conditions may be a relevant issue for their use in water-based drilling fluids which often have pH of 10−11.[30]

As explained earlier, the pH of the aqueous produced fluids from a gas or oilfield under pressure could be quite acidic due to the presence of dissolved $CO_2$ and $H_2S$, with the pH occasionally dropping below 4 for some fields. Although the $CO_2$ in our natural gas mixture would be expected to lower the pH of the KHI aqueous solution to about 5, we deliberately acidified a solution of 1:1 VP:VCap copolymer (2004 batch) to pH 3.9 by addition of hydrochloric acid. (A weak acid was not used as the amount needed for this pH could have an effect on the hydrate equilibrium temperature.)[44] Although we preacidified to pH 3.9, the actual pH at 70−80 bar from the partial pressure of $CO_2$ in the gas mixture, and its buffering effect, may raise the pH somewhat higher than 3.9 during the test.

The effect of preacidification (protonation) of KHI polymers has been reported previously, but usually in connection with quaternization of amine monomer units.[45,46] We maintained the final acidified VP:VCap polymer concentration at 2500 ppm. When this was tested the next day with no heating above room temperature, we obtained an average To of 7.8 ± 0.4 °C (Table 4). Then we heated an identical sample at pH 3.9 and 80 °C anaerobically for 20 h in a sealed tube. No deposition during the heating process was observed, and the sample was clear when cooled to room temperature. When we carried out new KHI tests, we observed an average To value of 8.0 ± 0.5 °C (10 tests), indicating no loss of performance at the 95% confidence level.

We also investigated a commercial PVCap under more acidic conditions with added hydrochloric acid. A 2500 ppm solution of this polymer at pH 3.9 gave the same KHI performance as the pure PVCap. We then heated an identical acidified polymer solution at pH 3.9 and 90 °C anaerobically for 20 h in a sealed tube. Surprisingly, this also did not affect the KHI performance (Table 4). This "stability" may be due to polymer precipitation above the cloud and deposition point of about 40 °C and therefore being less accessible for aqueous hydrolysis.

*2.3.5. Mechanochemical Treatment.* KHI polymers must survive rapid injection, movement through valves and the harsh physical flow environment in a multiphase flow line. To push this environment to an even more extreme physical condition, we investigated ball-milling of KHI polymers as powders using zirconium(IV) oxide balls. We wondered if this mechanical strain could cause cleavage of side groups on the polymer backbone or even the backbone itself. Mechanochemical solvent-free reactions by milling or grinding are becoming more popular as methods to do solvent-free reaction chemistry.[47] Mechanochemistry can even accomplish reactions and access molecules previously not accessible by solution chemistry. Ball-milling can also affect the microscopic and macroscopic properties of a material such as structure, morphology, crystallinity, and thermal stability.[48,49]

First, we presumed ball-milling might be able to break long polymer chains to shorter chains which would give improved KHI performance. Several studies suggest that very low molecular weight ranges (down to as little as 6−8 monomer units) give the best performance for KHI polymers when the distribution is monomodal.[2,8,50−52]

Some reports indicate substantial polymer degradation from ball-milling, e.g., for poly(methyl methacrylate).[53] However, other polymers such as polypropylene-ethylene copolymer or polyethylene homopolymer show a much slower degradation effect.[54] In addition, ball-milling of solutions of polymers are expected to give less chain breakage than powdered solids, so we used powdered polymers to ensure we would see an effect. For these reasons, we tested a high molecular weight polymer powder, PVP 120*k* ($M_w$ = 3 × $10^6$ g/mol given by the manufacturer; PDI not given), as VP monomer is known to polymerize to much higher molecular weights compared to VCap forming PVCap for example. We also knew that the KHI performance of PVP on our structure II hydrate-forming synthetic natural gas increases with decreasing molecular weight.[55]

We ball-milled PVP 120*k* powder for 60 min. The temperature during this type of milling can reach up to 70 °C.[56] GPC analysis of the milled polymer indicated a lower and broad molecular weight distribution ($M_n$ now 10000 g/mol with PDI = 12.1), so we expected a higher KHI performance, i.e., lower To value. We found that the average To value (six tests) of the PVP dropped from 13.7 °C before ball-milling to 12.8 °C after ball-milling, but the drop was only statistically significant at the 90% confidence level, giving $p = 0.09$ in a *t* test (Table 5).

We then ball-milled a sample of poly(*N*-isopropylmethacrylamide) (PNIPMAM) which had a much lower molecular weight ($M_n$) of 19000 g/mol (PDI = 2.6). After 60 min ball-milling the average To value had dropped from 10.5 to 9.8 °C but this was not statistically significantly different at the 95 or even 90% confidence level (Table

**Table 5. KHI Test Results for Ball-Milled Polymers (5−6 Tests on Each Polymer)**

| polymer | $M_n$ (g/mol)/PDI | To(av), °C | Ta(av), °C |
|---|---|---|---|
| no additive | | 16.8 (0.5) | 16.7 (0.5) |
| PVP 120*k* ($M_w$, 3 × $10^6$ g/mol) | [a] | 13.7 (0.4) | 11.2 (0.3) |
| PVP 120*k* after 60 min ball-milling | 10000/2.57 | 12.8 (0.5) | 10.5 (0.5) |
| PNIPMAM | 19000/12.1 | 10.5 (0.5) | 10.1 (0.4) |
| PNIPMAM after 60 min ball-milling | 7000/1.47 | 9.8 (0.4) | 9.4 (0.3) |

[a] Insoluble in DMF. Manufacturer gives $M_w$ as 3 × $10^6$ g/mol.

5). GPC analysis indicated a decrease in $M_n$ after ball-milling, dropping from 19000 to 7000 g/mol. These two results with PVP and PNIPMAM indicate that KHI polymers may degrade to some degree under very harsh mechanical conditions. However, this could improve the KHI performance if the molecular weight range is reduced to shorter, *but not too short*, polymer chains. Thus, ball-milling or some other kind of mechanical strain degradation might be a way to produce shorter and more optimal KHI polymers from larger polymer chains if they were not easily available by other means. An example might be natural polymers such as proteins and polysaccharides.

Ball-milling has recently been shown to convert monomers into polymers. This was demonstrated first for the conversion of phenylenevinylenes using a butoxide-based catalyst and ball-milling to poly(phenylenevinylenes) (PPVs).[57] Other polymers have been made, but as far as we know, classic radical polymerization has not been carried out for polyvinylation.[58] Therefore, we decided to try using ball-milling to form a polymer via vinyl polymerization of classic monomers found in KHIs with a radical initiator. We ball-milled both VCap and NIPMAM separately with 1% AIBN for 3 × 10 min periods. The resulting solid was analyzed by $^1$H NMR and shown to be monomer only with no broad peaks indicating polymer formation. The milling was repeated, this time with added 2-propanol as solvent. Again, no polymerization appeared to have taken place by NMR analysis.

*2.3.6. Treatment with Oxidizing Agents.* The final chemical treatment we investigated was oxidation. Oxidation processes have been proposed as a method to eliminate or reduce a KHI polymer in the produced water prior to discharge to an environmentally sensitive body of water.[59] There may also be a need to use an oxidizing biocide to treat injected water containing a KHI to prevent gas hydrate formation, for example in WAG or $CO_2$ injection. We have previously attempted to partially oxidize PVCap to convert the seven-ring caprolactam to a seven-ring adipimide (Figure 7).[60] We tried a variety of oxidizing agents, but none were able to accomplish the required oxidation, probably due to steric problems. (We are currently investigating oxidation of the caprolactam ring from the monomer, and we will report on this in a later study.) However, in that study we did not attempt the oxidation with the two biocides, sodium hypochlorite or hydrogen peroxide solution. Here we report these experiments for the first time.

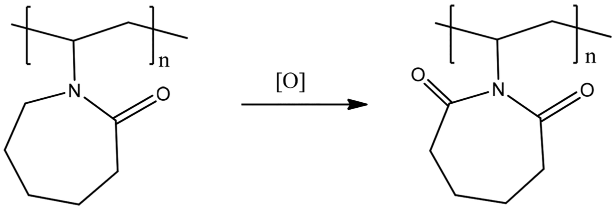

**Figure 7.** Oxidation of poly(*N*-vinylcaprolactam) to poly(*N*-vinyladipimide).

Addition of 1 mol equiv of sodium hypochlorite to a solution of PVCap ($M_w$ = 7−12 kg/mol; MEG removed), so that the polymer concentration was 2500 ppm, raised the pH to 9. This solution gave the same KHI performance as the untreated polymer (Table 6). However, when we heated the sodium hypochlorite/PVCap solution to 90 °C for 20 h (above the deposition point of PVCap) and cooled to room temperature, we observed a small amount of solid that would not dissolve, less than 10% of the polymer weight. After filtering, the filtrate was retested and the average To value had increased from 10.0 to 13.0 °C. This is obviously due to a lower concentration of polymer, but some of the remaining PVCap may have oxidized also, including degradation of the polymer chain, but remained water-soluble. The bleach-induced decomposition of other water-soluble polymers has been reported previously. For example, the molecular weight of poly(*N*-vinylpyrrolidone) decreased by a factor of 5 when exposed to sodium hypochlorite at pH 11.5.[61] The authors proposed that scission was initiated by free radical induced hydrogen abstraction of the proton $\alpha$ to the carbonyl. The polymer chain of poly(*N*-isopropylacrylamide) is degraded by sodium hypochlorite at pH 7−9 but the side chains are chlorinated to form a stable *N*-chloramide copolymer at higher pH.[62]

Attempted oxidation of VP:VCap copolymer with aqueous NaOCl (bleach) was also carried out for 20 h at 80 °C, just below the cloud point of the copolymer. This polymer appears to be quite robust. No visual change in the solution was observed, and as the results in the last two entries in Table 5 show, there was no significant change in the KHI performance of the polymer, assuming the small amount of bleach in solution did not interfere with the hydrate equilibrium temperature.

Hydrogen peroxide is a cheap oxidizing biocide which is known to form a solid 1:1 adduct with PVP.[63,64] However, we are unable to find a report of an adduct with PVCap. To a solution of PVCap we added 1 molar equiv (per VCap monomer) of 30 wt % hydrogen peroxide solution so the polymer concentration was 2500 ppm. The solution was stirred at 20.5 °C for 20 h with no sign of precipitation. We did not heat the solution as this would decompose the peroxide. When we tested the solution for KHI performance, we obtained an average To of 8.3 °C, which was significantly lower than the 10.2 °C value for the untreated polymer (statistically, $p$ value in $t$ test was $<0.05$). Interestingly, the cloud point was measured and it was found to have dropped by about 1 °C from about 39 to 38 °C (repeat tests). This seems to rule out oxidation to the adipimide ring as this is more hydrophilic than the caprolactam ring. We also found a 2 wt % solution of hydrogen peroxide decreased the cloud point to about 36 °C. Therefore, it seems the hydrogen peroxide is able to affect the solubility of PVCap. We can only speculate on the apparent synergistic effect of hydrogen peroxide on the PVCap KHI performance. For example, it is known that hydrogen bonds in pure hydrogen peroxide are weaker than those in water.[65] The presence of hydrogen peroxide in the PVCap solution may affect the rate of hydrate formation by weakening hydrogen bonding, or possibly the hydrogen bonding to PVCap is weakened allowing for better inhibition of growing hydrate clusters. Finally, since PVP·$H_2O_2$ is known, the formation of a PVCap·$H_2O_2$ adduct in solution cannot be ruled out.[64]

## 2.4. Conclusion.

*N*-Vinyllactam-based kinetic hydrate inhibitor polymers (KHIs) such as poly(*N*-vinylcaprolactam) (PVCap),

**Table 6. KHI Performance after Treatment with Oxidizing Agents**[a]

| polymer | To(av), °C | Ta(av), °C |
|---|---|---|
| no additive | 16.8 (0.5) | 16.7 (0.5) |
| PVCap ($M_w$ = 7−12 kg/mol) | 10.2 (0.5) | 9.0 (0.3) |
| PVCap +2500 ppm bleach (pH 9) | 10.0 (0.3) | 9.4 (0.3) |
| PVCap +2500 pm bleach (heat 90 °C for 20 h)[b] | 13.0 (0.4) | 9.5 (0.3) |
| PVCap + 10000 ppm $H_2O_2$ (20 °C for 20 h, pH 4.5) | 8.3 (0.3) | 7.6 (0.3) |
| PVCap + 20000 ppm $H_2O_2$ (immediate test, pH 4.3) | 9.5 (0.3) | 8.9 (0.2) |
| 1:1 VP:VCap copolymer 2016 | 8.2 (0.4) | 5.8 (0.3) |
| 1:1 VP:VCap copolymer 2016 + 2500 ppm NaOCl (pH 10.8, heat 80 °C for 20 h) | 8.1 (0.3) | 6.4 (0.3) |

[a] All KHI polymer concentrations are 2500 ppm. [b] Some precipitate in the sample, removed before KHI performance testing.

poly(*N*-vinylpyrrolidone) (PVP), and 1:1 *N*-vinylcaprolactam:*N*-vinylpyrrolidone (VCap:VP) copolymer were subjected to a range of treatments to determine their reliability and whether the treatment conditions could affect the KHI performance. Samples of PVCap and 1:1 VP:VCap up to 15 years old showed good performance regarding the onset of hydrate formation, but older samples showed a better ability to inhibit crystal growth. Various samples of VP:VCap copolymer of up to 15 years old showed no loss of performance after aerobic storage in plastic bottles at room temperature. KHI testing after thermal aging of PVCap or VP:VCap (at varying temperatures, at varying field pH, and in MEG solvent) showed little loss of performance, indicating good robustness for these polymers. Treatment with microwaves or ultrasound showed little change in the polymer performance. Harsh mechanical stress from ball-milling can reduce the polymer molecular weight to shorter chain lengths but might serve to improve the performance since it is known that low molecular weight polymers are most effective as KHIs. Oxidizing agents did affect the KHI performance. Bleach (aqueous sodium hypochlorite) worsened the performance of PVCap but only at elevated temperatures and in basic solution. The performance of PVCap improved upon addition of hydrogen peroxide. This may be due to formation of a PVCap·$H_2O_2$ adduct or a synergistic effect.

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### Notes

The authors declare no competing financial interest.

## NOMENCLATURE

AIBN = azobisisobutyronitrile
GPC = gel permeation chromatography
HET = hydrate equilibrium temperature
KHIs = kinetic hydrate inhibitors
MEG = monoethylene glycol
$M_n$ = number-average molecular weight
$M_w$ = weight-average molecular weight
NMR = nuclear magnetic resonance
PDI = polydispersity index
PNIPMAm = poly(*N*-isopropylmethacrylamide)
PVCap = poly(*N*-vinylcaprolactam)
PVP = poly(*N*-vinylpyrrolidone)
SNG = synthetic natural gas
Ta = temperature for the fastest hydrate formation rate
THI = thermodynamic inhibitor
To = onset temperature for first detection of hydrate formation
VCap:VP = *N*-vinylcaprolactam:*N*-vinylpyrrolidone
WAG injection = water and gas injection

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# Paper III

Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly(*N*-vinylcaprolactam)

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# Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly(*N*-vinylcaprolactam)

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**ABSTRACT:** The synergetic effect of a range of different solvents on the kinetic hydrate inhibitor (KHI) performance of poly(*N*-vinylcaprolactam) (PVCap) has been investigated. The equipment used was a high-pressure (76 bar) rocking cell apparatus using slow constant cooling (approximately 1 °C/h from 20.5 °C) and a synthetic natural gas mixture forming structure II hydrate. The synergetic effect was investigated by adding 5000 ppm of a range of alcohols, glycol ethers, and ketones to a solution of 2500 ppm of PVCap ($M_w$ = 10 000 g/mol). For many of the additives, the ranking of the synergetic effect can be explained with reference to the size, shape, and hydrophobicity of the main alkyl group ("tail") in the molecule as well as the presence of a glycol ether group. Among all of the solvents investigated, the best synergetic effect was achieved by 4-methyl-1-pentanol. When 5000 ppm of 4-methyl-1-pentanol was added to 2500 ppm of PVCap, no hydrate formation occurred down to the minimum test temperature of 3 °C (subcooling at ca. 16.3 °C) in 15 parallel experiments compared to 10.4 °C for pure PVCap. Predictions for improved glycol ether synergists are given.

## 1. INTRODUCTION

Gas hydrates are non-stoichiometric, snow-like, crystalline solids, where gases of certain molecular weight stabilize the hydrogen-bonded water molecular cages. Further, the guest molecules are small gas molecules entrapped within the cavities of the solid water molecule lattice. If certain low-molecular-weight hydrocarbons combine with water under specific conditions of temperature and pressure, gas hydrates will form. Typical favoring conditions of temperature and pressure are <20 °C and >30 bar, respectively.[1−4]

Many oil and gas operations meet the conditions needed for gas hydrate formation to occur. Gas hydrate formation can jeopardize oil and gas production if not treated.[4−12] One way of treating gas hydrates is by the utilization of low-dosage hydrate inhibitors (LDHIs) and, more specifically, the subgroup kinetic hydrate inhibitors (KHIs).[5]

The KHIs kinetically interact with the hydrate formation process and are believed to interfere with the hydrate nucleation step and/or the crystal growth processes. The KHI polymers are assumed to bind to the surface of hydrate particles at an early stage of nucleation and growth, thus preventing the particle from reaching the critical size for continuous growth.[13,14] The KHIs are added in relatively low concentrations, typically in the range of 0.1−1.0 wt %.[8,13−17] The main active compounds in KHIs are water-soluble polymers. The best of these polymers appear to need two essential structural features to be able to perform. First, the polymers need hydrophilic functional groups that can preferably hydrogen bond to water molecules. It is usually amide, imide, and amine oxide groups that accomplish this.[5,18,19] Second, a hydrophobic group must be present directly or adjacent to each of the hydrophilic groups for the polymers to have good performance.[20] Commercially available classes of KHIs with these structural properties include polymers and copolymers based on the monomers *N*-vinylcaprolactam, *N*-vinylpyrrolidone, and *N*-isopropylmethacrylamides as well as hyperbranched poly(ester amide)s based on diisopropanolamine and various cyclic anhydrides.[5] One of the most well-known KHI polymers is poly(*N*-vinylcaprolactam) (PVCap) (Figure 1).[20−27]

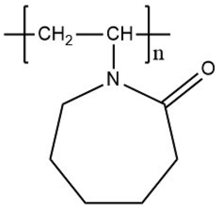

**Figure 1.** Structure of PVCap.

The polymer (or polymers) is by far the most expensive part of the injected KHI formulation. The active polymer typically makes up 10−30 wt % of the KHI formulation, with the remainder being carrier solvent. This low percentage is to keep the viscosity to a level that gives easy pumping of the fluid, often over long distances and low temperatures.[28] It is also possible to polymerize the KHI polymer in the solvent. This has been performed for both PVCap and poly(*N*-isopropylmethacrylamide) (PNIPMAM) with a range of different

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solvents.[29,30] The carrier solvent is often a low-molecular-weight alcohol, glycol, or glycol ether.[12] Examples of these solvents are methanol, ethanol, monoethylene glycol (MEG), and 2-*n*-butoxyethanol (nBGE). Another important aspect of the solvent is its potential to act as a synergist by enhancing the hydrate-inhibiting properties of the polymer. Therefore, it is of interest to find solvents that also perform as a synergist together with the KHI polymer. This could either increase the application performance window or, in some cases, reduce the needed KHI polymer dosage.[28]

Many solvents have been reported as beneficial regarding their synergetic effect on PVCap, including low-molecular-weight glycol ethers containing an alkoxy group having at least three carbon atoms.[31] A study on various glycol ethers and their synergy with PVCap was carried out, and it was shown that these glycol ether compounds prolong the nucleation time and extend the delay of catastrophic hydrate growth.[27] It has been reported that the most effective synergist within this class of compounds is monoglycol ethers containing 3−4 carbon atoms in the alkyl chain. Representative glycol ethers include 2-butoxyethanol (ethylene glycol monobutyl ether), 2-isopropoxyethanol, iso-2-butoxyethanol, propylene glycol butyl ether, and monobutyl ether diethylene glycol. Of these, 2-butoxyethanol (BGE) is often preferred because it is cheap, has a high flash point, is approved offshore, is used as a mutual solvent, and is a good synergist.[32] Higher homologues were found to be insoluble in saltwater (3.5%), and lower homologues were shown to exhibit low to no synergetic effect.[31]

The actual mechanism behind the synergism of the glycol ether compounds with the PVCap polymer is not known, and different claims regarding the mechanism have been presented. It has been claimed that they function by either stabilizing the KHI polymer at the hydrate−water interface or that the presence of glycol ether molecules enhance the absorption of the KHI polymer on hydrate growth sites more significantly than on hydrate nucleation sites.[27,33] Thus, the glycol ether molecules may associate themselves with the dissolved KHI polymer because of the hydrophobicity of the alkoxy group. This could, in turn, alter the conformation of the KHI polymer in solution. More of the KHI polymer length would be available for interaction with the hydrate crystal as the KHI polymer becomes extended.[31] Also, the molecular size of the glycol ether compounds is closely associated with the synergetic effect and independent of the “ethylene” or “propylene” series and primary or secondary hydroxyl groups.[27]

The effect of alcohols on PVCap has been reported to affect the performance both positively and negatively. Alcohols containing 3−5 carbon atoms have been reported to affect the performance of PVCap positively, although with a smaller positive effect than monoglycol ethers.[31,34] Lower alcohols, 1−3 carbon atoms, have been reported to affect the performance of PVCap negatively for a methane structure I hydrate system.[35] Another research group has used 1-octanol as a water-immiscible carrier solvent for PVCap, to aid recycling of the polymer. This alcohol showed comparable hydrate inhibition performance to aqueous PVCap, i.e., no synergy.[36] Another study using vinyl-lactam-based polymers and various solvent synergists showed that a lower interfacial tension corresponded to a longer onset time, i.e., a better kinetic inhibition performance.[37] They suggested the lowest gas/liquid interfacial tension rule for developing amide class KHIs or KHI synergists as well as determining their suitable applied dosages.

Another study claimed that the molecular weight of an alcohol alone is not the controlling factor on the synergetic influence of alcohol on the performance of PVCap.[35] Further, the length of the central alkyl “tail” in the alcohol exerts an effect on the hydrate crystal growth inhibition properties of PVCap. This could, in turn, be related to solubility parameters. The aqueous solubility of alcohols is affected by their hydroxyl group, and the effect is 2-fold. First, the formation of self-association hydrogen-bonded chains between the solute molecules in solution is caused by the hydroxyl group of the alcohols. These molecular associations leads to a decrease in the aqueous solubility of alcohols. A double positive influence on the aqueous solubility of alcohols is provided by the formation of mixed water−alcohol hydrogen-bond chains by the insertion of the hydroxyl groups into water: the alcohol molecules are stabilized in the hydrogen-bond chains, and the hydrophobic effect of water is reduced. Each of these influences alters the Gibbs free energy of the system differently.[38]

The mechanism behind the synergetic effect of alcohols on KHI polymers is not fully understood. One reported hypothesis is that alcohols increase the ability of the KHI polymers to adsorb on nucleation and/or growth sites.[27,33] Thus, it resembles the postulated synergetic mechanism for glycol ether compounds. One study on tetrahydrofuran (THF) hydrate suggests that, irrespective of the type of alcohol molecules present, a linear correlation between the inhibition performance and the ability of the synergist to adsorb on the hydrate surfaces was observed.[39] The alcohols are assumed to reduce the occupancy of THF, presumably as a result of the competition with the surrounding water molecules in the formation of hydrogen bonds. This will reduce the number of established water cages and the probability of guest molecule enclathration. The reduction in the number of water cages decreases the subsequent workload of the KHI polymer and enhances its effectiveness.[40] This corresponds well with the findings of another research group.[37] In their work, they tested the synergetic effect of different alcohols on vinyl-lactam-based polymers and found out that surface adsorption of KHI polymers is crucial for the inhibition of hydrate formation. Thus, lower gas/liquid interfacial tension correlates to stronger adsorption of the KHI polymers on the surface of the aqueous phase. Further, stronger or more hydrophobic groups lead to decreased solubility of the KHI polymer in water, but with the aid of alcohols, the KHI polymers will have a stronger surface adsorption. Therefore, stronger adsorption of KHI polymer molecules on the surface of the aqueous phase or stronger hydrophobic functional groups on the KHI polymers will produce a more resistant barrier between the liquid water molecules and the hydrate nuclei or particles. All of this takes place in the interface between the aqueous phase and the hydrate. This barrier increases the energy needed for the hydrate to grow.

Recently, we investigated the synergetic effect of a range of solvents on PNIPMAM.[30] In this parallel study, we have investigated a range of solvents on the KHI performance of PVCap using a structure II (sII)-forming gas system. Different length, branching, and cyclic alkyl “tails” of alcohol, glycol ethers, and ketones were tested for their synergetic effect on PVCap, with some surprising results. We chose 2500 ppm of

PVCap plus 5000 ppm of solvent, i.e., a 33.3 active wt % polymer solution, as our model KHI formulation.

## 2. EXPERIMENTAL SECTION

PVCap used in this study was obtained from BASF as Luvicap EG HM ($M_w$ = 10 000 g/mol). The ethylene glycol solvent was removed, leaving a dry powder of pure PVCap polymer. This PVCap powder was used throughout this study. All solvent synergists were sourced either from VWR, Merck, or TCI Europe with a minimum 99% purity.

The performance testing was conducted in a multi-rocking cell apparatus supplied by PSL Systemtechnik, Germany. The apparatus is capable of holding five high-pressure stainless-steel rocking cells. The cells have an internal volume of 40 mL and were supplied by Svafas, Norway. Within each cell is a stainless-steel ball for agitating the test solution. The gas used in the performance testing was a standard synthetic natural gas (SNG) mixture, which preferentially forms sII gas hydrates (Table 1).

**Table 1. Composition of the SNG Mixture Used in the Performance Testing**

| component | mol % |
|---|---|
| methane | 80.67 |
| ethane | 10.20 |
| propane | 4.90 |
| isobutane | 1.53 |
| *n*-butane | 0.76 |
| $N_2$ | 0.10 |
| $CO_2$ | 1.84 |

The procedure for high-pressure kinetic hydrate inhibition testing by the use of slow constant cooling is summarized in the following and has been described previously:[41,42] (1) At least 1 day in advance before initializing the test, the polymer and, if applicable, the synergist were dissolved to the desired concentration in deionized water. (2) To each of the five cells, 20 mL test solution was added. The test solution consisted of various additives dissolved in distilled water. (3) To replace the air with SNG in the cells, a sequence of vacuum and pressurizing with SNG was applied: first vacuum, then pressurizing with SNG to 3−5 bar, and then depressurizing before another round with vacuum. (4) After this, the system was pressurized with SNG to an experimental pressure of 76 bar. (5) The cells where cooled with a cooling rate of 1.0 °C/h from 20.5 to 2.0 °C, while they were rocking at a rate of 20 rocks/min at an angle of 40°.

Previously, the hydrate equilibrium temperature ($T_{eq}$) at 76 bar has been determined to be 20.2 ± 0.05 °C by standard laboratory dissociation experiments warming at 0.025 °C/h for the last 3−4 °C. This correlated well with calculations performed by the Calsep PVTSim software.[43,44]

During testing, the initial pressure is 76 bar and the temperature is decreased from 20.5 to 2.0 °C. Each cell is a closed system, and therefore, there will be a linear pressure decrease from which both the onset temperature for hydrate formation ($T_o$) and the rapid hydrate formation temperature ($T_a$) can be observed. The temperature at which the first observable deviation from the linear pressure decrease is defined as $T_o$. Because this is performed by an observation on a linear pressure decrease and is the first macroscopic observation of hydrate formation, it is quite possible that the hydrate nucleation initiated at a molecular level prior to this. However, these experiments are not capable of detecting this possible earlier nucleation. After $T_o$ has occurred, with a varying interval, a rapid pressure decrease can be observed. The temperature at which the pressure decrease is at its steepest or, in other words, the hydrate formation is at its fastest is defined as $T_a$. Figure 2 shows an example of a slow constant cooling experiment. In this experiment, five cells each containing 2500 ppm of PVCap together with 5000 ppm of cyclohexanol as the synergist were tested with slow constant cooling. The observed scattering in the values is believed to be related to the stochastic nature of the hydrate formation process. For each polymer or polymer/synergist mixture, at least eight individual experiments were carried out. Standard deviations for $T_o$ and $T_a$ were in the range of 0.2−0.8 °C. These variations as well as the average values for each "polymer and solvent" mixture are depicted the graphs in Figures 4, 6, 7, and 10.

Figure 3 shows how both $T_o$ and $T_a$ were determined from one of the cells in Figure 2. In this particular experiment, it was determined that $T_o$ had a value of 6.5 °C and that it occurred after 852.02 min. $T_a$ had a value of 3.4 °C and occurred after 1040.02 min.

## 3. RESULTS AND DISCUSSION

To investigate the synergetic effect on PVCap, results from standard cooling tests on PVCap alone were compared to the standard cooling test with PVCap with different additives. Further, in all tests, 2500 ppm of PVCap and 5000 ppm of additives were used. It should be noted that the additives have

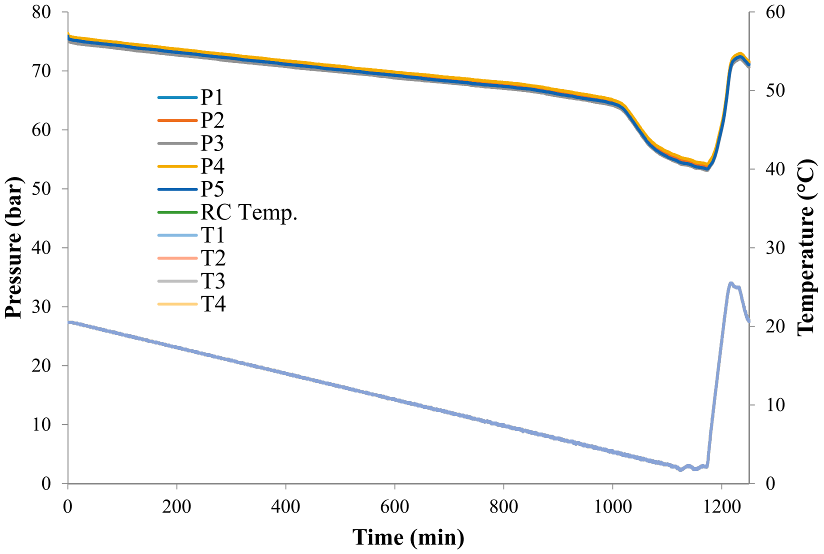

**Figure 2.** Results from five cells with 2500 ppm of PVCap and 5000 ppm of cyclohexanol as the synergist tested by the standard constant cooling experiment (RC Temp. = rocking cell bath temperature).

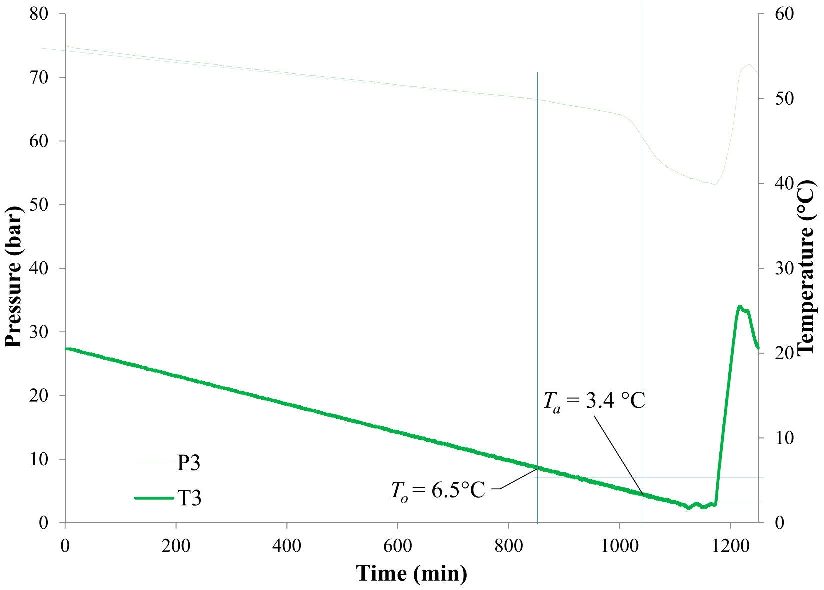

**Figure 3.** Standard constant cooling experiment for cell 3 containing 2500 ppm of PVCap and 5000 of ppm cyclohexanol as the synergist, where both $T_o$ and $T_a$ are determined.

different molecular weights; thus, the molar concentrations are not identical.

All of the results from the different additives used in this study, together with only deionized water (DIW) and PVCap alone, are summarized in Table 2. DIW gave hydrate formation at an average $T_o$ value of 17.2 °C. A total of 2500 ppm of PVCap alone gave an average onset temperature of $T_o$ = 10.4 °C. This $T_o$ value was used as the main comparative reference for all synergetic mixtures in this study.

From Table 2, it can be observed that the addition of the various solvents to PVCap gave a wide range of results. Most worked as synergists with PVCap, while a few impaired the KHI performance of PVCap (antagonism). We will discuss glycol ether solvents first, followed by aliphatic alcohols (acyclic and cyclic) and finally ketones.

Monoglycol ethers and especially *n*-butyl glycol ether (nBGE) are well-known for their proven synergetic effect on various KHI polymers, including poly(*N*-vinyl lactam)s and poly(*N*-alkyl(meth)acrylamide)s.[5,15,16,18,31,45] Recently, we investigated the synergetic effect of nBGE and other butyl glycol ethers on PNIPMAM, i.e., isobutyl glycol ether (iBGE) and *tert*-butyl glycol ether (tBGE).[30] We also varied the size of the hydrophobic tail on the glycol ethers. To follow up on this research, we investigated a range of glycol ethers for their synergetic effect on PVCap. The results are summarized in Table 2 and Figure 4.

First monoethylene glycol (MEG) was tested together with the PVCap polymer. MEG is a high-flash-point solvent commonly used in the petroleum industry. MEG showed only a weak synergetic effect on PVCap at our test concentration. MEG gave $T_o$ and $T_a$ values of 9.2 and 8.8 °C, respectively. The $T_o$ value was found to be significantly different ($p < 0.05$ in a statistical $t$ test) from the $T_o$ value for PVCap alone, but the $T_a$ values between them were not found to be significantly different ($p > 0.05$). At a higher concentration, the synergy is reported to increase.[35] All other alkyl glycol ethers had at least four carbon alkyl groups because previous work suggested that four carbon alkyls are better than smaller alkyl groups.[27]

**Table 2. Summarized Results from This Study**[a]

| synergist | $T_o$ (°C) | $T_a$ (°C) |
|---|---|---|
| DIW only | 17.2 | 16.6 |
| PVCap alone | 10.4 | 8.9 |
| monoethylene glycol (MEG) | 9.2 | 8.8 |
| *n*-butyl glycol ether (nBGE) | 7.3 | 3.8 |
| isobutyl glycol ether (iBGE) | 5.7 | 2.5 |
| *tert*-butyl glycol ether (tBGE) | 6.2 | <3.7[b] |
| monoethylene glycol mono-*n*-hexyl ether | 10.2 | 9.9 |
| 2-(cyclopentyloxy)ethanol | 4.7 | 2.1 |
| 2-(cyclohexyloxy)ethanol | 4.2 | 2.3 |
| diethylene glycol monoethyl ether (DEGMEE) | 9.5 | 8.5 |
| butyl diglycol ether | 5.5 | 2.9 |
| diethylene glycol mono-*n*-hexyl ether | 7.3 | 5.8 |
| triethylene glycol monobutyl ether | 5.3 | 3.2 |
| 2-propanol (isopropanol) | 9.5 | 6.6 |
| 1-butanol | 7.5 | 4.8 |
| 2,2-dimethyl-1-propanol (neopentyl alcohol) | 5.8 | 3.9 |
| 3-methyl-1-butanol (isoamyl alcohol) | 5.6 | 2.0 |
| 3-methyl-2-butanol | 6.4 | 3.4 |
| 1-pentanol | 7.4 | 2.5 |
| 4-methyl-1-pentanol | <3 | <3 |
| 1-hexanol[c] | 5.8 | 3.3 |
| 2-ethyl-1-hexanol[d] | 10.8 | 10.4 |
| furfuryl alcohol | 9.7 | 7.5 |
| tetrahydrofurfuryl alcohol | 9.5 | 6.4 |
| cyclopentanol | 6.8 | 5.1 |
| cyclohexanol | 6.8 | 3.4 |
| 4-methylcyclohexanol (*cis* and *trans* mixture) | 5.9 | 3.1 |
| cycloheptanol | 6.4 | <3 |
| 2-methyl-3-pentanone | 10.3 | 8.8 |
| 3,3-dimethyl-2-butanone | 7.5 | 4.3 |
| 4-methyl-2-pentanone | 7.4 | 4.3 |
| 5-methyl-2-hexanone | 5.7 | 3.4 |

[a] All tests with PVCap are at 2500 ppm, with the solvent concentration of 5000 ppm. [b] Cooling was stopped at 3.7 °C. [c] The solution was cloudy. [d] The solvent synergist was not totally dissolved.

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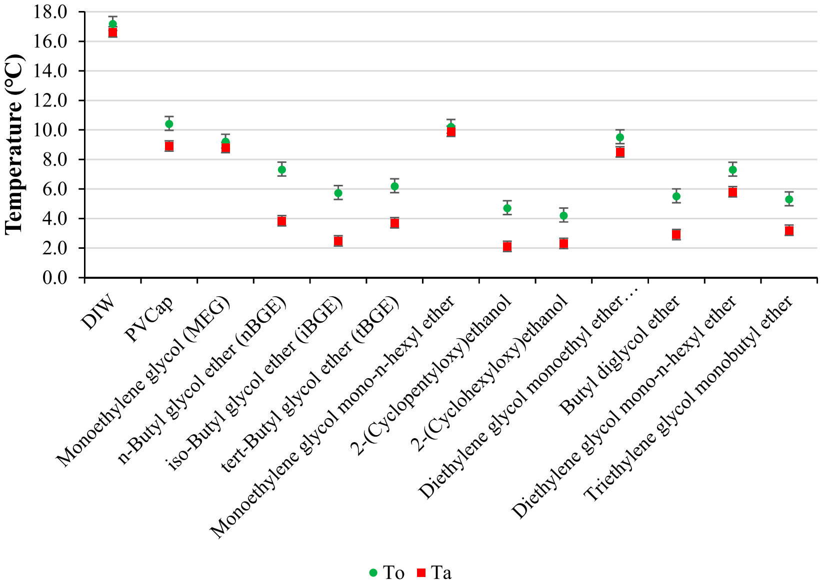

**Figure 4.** $T_o$ and $T_a$ values for PVCap (2500 ppm) with glycol ethers (5000 ppm).

From Table 2 and Figure 4 it can be observed that the addition of 5000 ppm of nBGE improved both the $T_o$ and $T_a$ values to 7.3 and 3.8 °C, respectively, compared to PVCap alone. The other butyl glycol ether isomers, iBGE and tBGE, further improved both the $T_o$ and $T_a$ values for PVCap relative to nBGE. The addition of 5000 ppm of iBGE decreased the $T_o$ value to 5.8 °C and the $T_a$ value to 2.6 °C. tBGE gave $T_o$ and $T_a$ values of 6.2 and <3.7 °C, respectively. These results correlate well with the reported results for the same butyl glycol ethers tested on PNIPMAM.[30] Here, the synergetic effect was greatest for tBGE, followed by iBGE and nBGE. However, both the iBGE and tBGE results were significantly different from the nBGE results ($p < 0.05$), but no significant difference was found between iBGE and tBGE ($p > 0.05$). One plausible explanation for this can be that the branched isomers of BGE are better at adhering to the hydrate surface and disturbing the surrounding water molecules. Similar observations were made for quaternary ammonium salts.[41,42]

Next, we wanted to examine how the presence of a more hydrophobic tail, i.e., larger alkyl group than butyl, would affect the synergetic performance of glycol ethers with PVCap. We tested monoethylene glycol mono-*n*-hexyl ether, and it gave a $T_o$ value of 10.2 °C and a $T_a$ value of 9.9 °C. The result for the $T_o$ value was not found to be significantly different ($p > 0.05$) from the $T_o$ value for PVCap alone. This indicates no synergetic effect on the crystal growth by monoethylene glycol mono-*n*-hexyl ether with PVCap polymer. The $T_a$ value, however, was found to be significantly different ($p < 0.05$) from the $T_a$ value for PVCap alone, indicating that monoethylene glycol mono-*n*-hexyl ether has some synergetic effect with the PVCap polymer on delaying catastrophic hydrate growth. The results clearly indicate that monoethylene glycol mono-*n*-hexyl ether is not as good a synergist with the PVCap polymer as any of the buylated glycol ethers. This could be caused by the fact that this glycol ether has no branching in the alkyl "tail" and, at the same time, the tail is too big for optimal interaction with open cages of growing hydrate particles.

We also tested monoglycol ethers containing cyclic alkyl groups, as performed in previous work on PNIPMAM.[30] In Table 2, the addition of 5000 ppm of 2-(cyclopentyloxy)-ethanol decreased both the $T_o$ and $T_a$ values to 4.7 and 2.1 °C, respectively. The addition of 2-(cyclohexyloxy)ethanol decreased the $T_o$ value to 4.2 °C and the $T_a$ value to 2.3 °C. Both solvents showed a significant improvement compared to the monoglycol ethers, nBGE, iBGE, and tBGE. The improvement between the two cyclic ethers was small, but it was found to be a significant difference ($p < 0.05$ in the statistical $t$ test) for both the $T_o$ and $T_a$ values. In summary, monoglycol ethers containing cyclic alkyl or branched alkyl groups appear to be better than straight-chain alkyl glycol ethers for improving the performance of PVCap, as long as the alkyl group is of the correct size. This also correlated well with the findings for the same monoglycol ethers tested on PNIPMAM.[30]

We thought it would be beneficial to investigate how extra oxyethylene (glycol ether) groups in the alkyl "tail" would affect the synergetic properties of glycol ethers. Extra glycol ether groups impart a higher flash point to the solvent, which can be useful for safety in the field. We started by testing PVCap with diethylene glycol monoethyl ether (DEGMEE), which has two glycol groups. The $T_o$ and $T_a$ values were 9.5 and 8.5 °C, respectively. These values indicate some synergetic effect with the PVCap polymer but less than all of the other monoglycol ethers investigated, except for monoethylene glycol mono-*n*-hexyl ether, both of which gave results similar to that of MEG. We believe that the ethyl tail in DEGMEE is too short for optimal synergy.

To see if a longer alkyl "tail" was beneficial for the synergetic effect, we then tested butyl diglycol ether. This glycol ether gave a $T_o$ value of 5.5 °C and a $T_a$ value of 2.9 °C, which indicate a clear improvement when the alkyl "tail" is increased by two carbon atoms. The results were similar to the results for iBGE, but both the $T_o$ and $T_a$ values were found to be significantly different ($p < 0.05$). On the basis of this result, we wanted to determine how an even longer alkyl "tail" would affect the synergetic properties of diglycol ether. We tested diethylene glycol mono-*n*-hexyl ether, which has six carbon atoms in the alkyl "tail", two more than butyl diglycol ether. Diethylene glycol mono-*n*-hexyl ether gave $T_o$ and $T_a$ values of 7.3 and 5.8 °C, respectively. Here, the alkyl "tail" may have become too dominant, because butyl diglycol ether had better synergy with the PVCap polymer. Still, the synergetic effect with the PVCap polymer was more prominent with diethylene glycol mono-*n*-hexyl ether than the glycol ether with a shorter alkyl "tail", diethylene glycol monoethyl ether. This again shows the importance of finding the proper length of the alkyl "tail" to obtain the good synergetic effect. $T_o$ for diethylene glycol mono-*n*-hexyl ether was not found to be significantly different from the $T_o$ value for nBGE. To summarize, of the few diglycol ethers tested, *n*-butyl diglycol ether had the best synergetic performance with the PVCap polymer.

We thought it would be useful to see the effect of extending the glycol chain. We therefore investigated *n*-butyl triglycol ether (triethylene glycol monobutyl ether) as the synergist for PVCap. We found that the blend with PVCap gave a $T_o$ value of 5.3 °C and a $T_a$ value of 3.2 °C. These values were similar to the butyl diglycol ether, i.e., no significant difference ($p > 0.05$) between the two solvents. We conclude that extending the ethoxylation from butyl diglycol ether to butyl triglycol ether does not aid the synergetic performance with the PVCap polymer. However, we stress that this study is limited; for example, no liquid hydrocarbons are present, deionized water is used, and only one gas composition is investigated. More varied studies on the best synergists will be reported later.

Next, we wanted to understand the importance of the glycol functional group compared to the original "unglycolated" alcohol; i.e., is ethoxylation of the alcohol beneficial for synergy with PVCap? Therefore, we investigated a range of alcohols with varying size and shape alkyl groups, some of which could be compared to glycols with the same alkyl groups. We begin with a discussion of the results with acyclic alcohols.

The structures of the acyclic alcohols can be found in Figures 5, and the KHI test results with acyclic alcohols are in Table 2 and shown graphically in Figure 6. All acyclic alcohols tested worked as synergists together with PVCap, except for 2-ethyl-1-hexanol, which had a slightly negative effect on the performance of the PVCap polymer. The results are discussed below, beginning with the smallest alcohols and increasing in size.

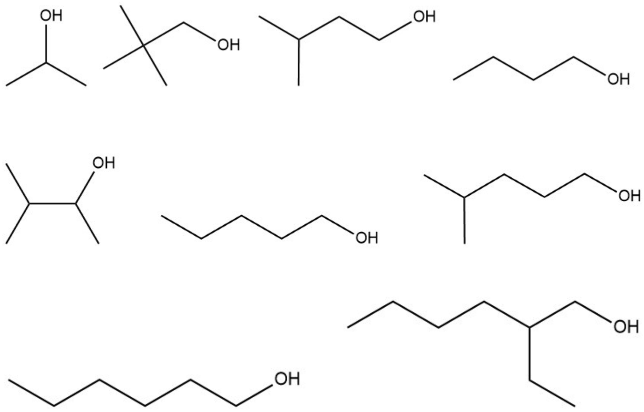

**Figure 5.** Structures for the acyclic alcohols investigated. From the top left to right: 2-propanol, 2,2-dimethyl-1-propanol, 3-methyl-1-butanol, 1-butanol, 3-methyl-2-butanol, 1-pentanol, 4-methyl-1-pentanol, 1-hexanol, and 2-ethyl-1-hexanol.

We did not investigate methanol and ethanol as synergists. Both solvents are used as thermodynamic hydrate inhibitors but are not good synergists at low concentrations.[18,35] Lower alcohols containing 1−3 carbon atoms have even been reported to affect the performance of PVCap negatively for a methane structure I hydrate system.[35] Further, it has been reported that alcohols containing 3−5 carbon atoms improve the KHI performance of PVCap positively, although they gave a smaller positive effect than monoglycol ethers with the same alkyl tail.[31,34]

In this research, the smallest alcohol investigated as a potential synergist for PVCap was 2-propanol, a solvent commonly used in our polymerization reactions. 2-Propanol had a weak synergetic effect on PVCap, with a $T_o$ value of 9.5 °C. After this, we increased the size of the alkyl group in the alcohol, also wanting to find out if more branching on the alkyl "tail" had a better synergetic effect on the PVCap polymer. The straight-chain alcohol 1-butanol showed some synergy, with an average $T_o$ value of 7.5 °C and a $T_a$ value of 4.8 °C. 2,2-Dimethyl-1-propanol performed significantly better and gave $T_o$ and $T_a$ values of 5.8 and 3.9 °C, respectively. Here, the branching is at carbon two in the alkyl "tail". Then, we tested an isomer of 2,2-dimethyl-1-propanol, 3-methyl-1-butanol. This alcohol gave a $T_o$ value of 5.6 °C, and thus, it was not found to be significantly better than 2,2-dimethyl-1-propanol ($p > 0.05$ from a *t* test). These results indicate the importance of the branching of the alkyl "tail" of the alcohol for better synergist performance with PVCap (this also fits with the glycol ether results for nBGE, iBGE, and tBGE). Interestingly, the average $T_a$ values for 2,2-dimethyl-1-propanol and 3-methyl-1-butanol were significantly different, 3.9 and 2.0 °C, respectively. This indicates that 3-methyl-1-butanol with the PVCap polymer could be better at inhibiting hydrate crystal growth than PVCap with 2,2-dimethyl-1-propanol.

Because branching of the alcohols appeared to give better synergetic properties, we tested another branched version, 3-methyl-2-butanol. This alcohol gave a $T_o$ value of 6.7 °C and a $T_a$ value of 3.4 °C. These values are better than the values for 1-butanol but not as good as the values for both 2,2-dimethyl-1-propanol and 3-methyl-1-butanol. Because 3-methyl-1-butanol and 3-methyl-2-butanol are both isomers, the only difference between the structures is the placing of the hydroxyl group. In 3-methyl-1-butanol, the hydroxyl group is on the end of the alkyl chain, while it is on carbon atom number two in 3-methyl-2-butanol, making it a secondary alcohol. This indicates that the placing of the hydroxyl group also plays an important part in determining if the alcohol will work well as a synergist with the PVCap polymer and not just the length of the alkyl "tail" or the branching of it.

To further investigate the role of the length and shape of the alkyl "tail", we then tested an alcohol with a longer alkyl "tail", i.e., 1-pentanol. It gave a $T_o$ value of 7.4 °C and a $T_a$ value of 2.5 °C. Thus, increasing the alkyl "tail" of the alcohol by one carbon atom did not give a significant difference in the $T_o$ value compared to 1-butanol ($p > 0.05$). There was, however, a significant difference in the $T_a$ values between 1-butanol and 1-pentanol, which indicates that increasing the straight alkyl "tail" from 4 to 5 carbon atoms makes the alcohol better at delaying hydrate crystal growth in blends with PVCap. A similar improvement was seen for PVCap blended with tetra-*n*-pentylammonium bromide (TPAB) compared to tetra-*n*-butylammonium bromide (TBAB).[15,18,41]

The next alcohol tested was 4-methyl-1-pentanol, which is 1-pentanol with an added methyl group to cause branching at the end of the alkyl tail. Another name for this molecule is isohexyl alcohol. Surprisingly, this alcohol gave a superb synergetic effect with PVCap, with no hydrates detected by the pressure

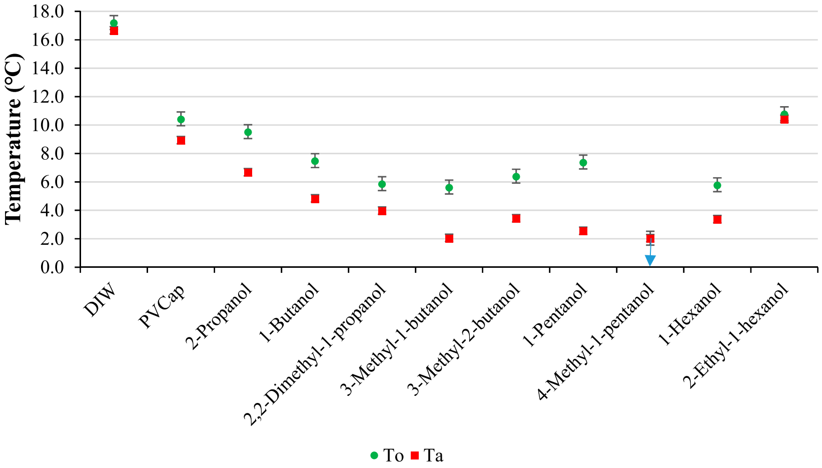

**Figure 6.** Graphical display of the synergetic effect of different acyclic alcohols (5000 ppm) with PVCap (2500 ppm).

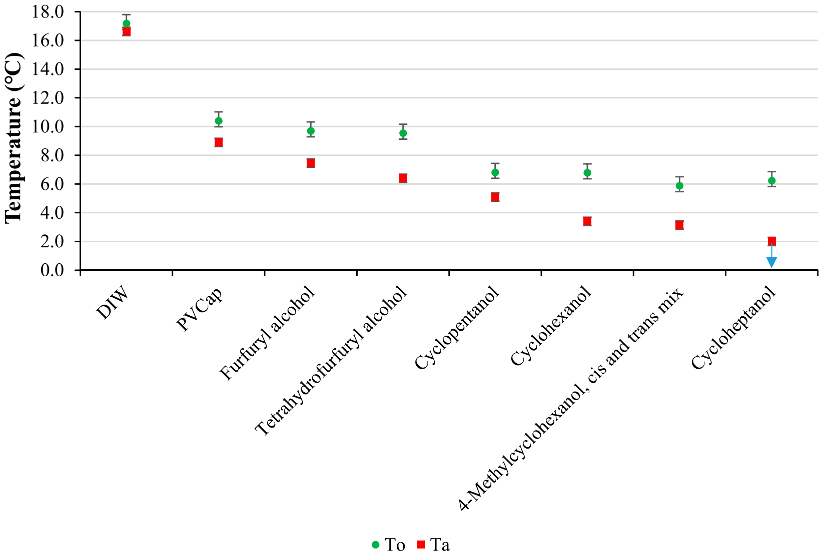

**Figure 7.** Graphic presentation of the performance of the cyclic alcohols, tetrahydrofurfuryl alcohol, and furfuryl alcohol (5000 ppm) as a potential synergist on the $T_o$ value of PVCap (2500 ppm).

drop down to 3 °C in all tests (this temperature was the minimum set temperature for the cooling cycle). We were so surprised by this result that we carried out 15 tests in all, and each of them gave $T_o$ and $T_a$ values of <3 °C together with the PVCap polymer. 4-Methyl-1-pentanol was also tested by itself at 5000 ppm (i.e., without PVCap) to give average $T_o$ and $T_a$ values of 15.3 and 14.2 °C, respectively. Thus, the alcohol by itself at this concentration has almost no effect compared to tests with just deionized water.

4-Methyl-1-pentanol has a flash point of 57 °C and water solubility of 7.6 g/L (i.e., 7600 ppm) at 20 °C, not much more than the test concentration of 5000 ppm. We believe both the shape and size of the alkyl group are important for synergy, but also the fact that the alcohol is close to its limit of solubility may also be a factor. This is reminiscent of our study on the effect of the cloud point on KHI polymer performance.[46] Here, we showed that polymers with low cloud points (i.e., close to their solubility limit at the test temperature) gave the best performance if they had the correct size and shape of the side groups. The “isohexyl” group in 4-methyl-1-pentanol has been investigated before in tetraalkylammonium bromide synergists. Tetra(isohexyl)ammonium bromide (TiHexAB) was synthesized and shown to outperform the related tetrabutyl and tetrapentyl salts.[41] This, in turn, led to a hypothesis that adsorption onto the hydrate crystal surface may not be the only synergetic mechanism operating but that the more hydrophobic TiHexAB is perturbing the nucleation of hydrate more than the less hydrophobic quaternary ammonium salts.

The result with 4-methyl-1-pentanol was significantly better than any of the alcohols or glycol ethers tested in this study. Because 4-methyl-1-pentanol is an isomer of 1-hexanol, we also tested this straight-chain alcohol for its potential as a synergist with the PVCap polymer. The solution of the PVCap polymer and 1-hexanol made a solution that became a little cloudy at room temperature, indicating limited solubility of this alcohol. The literature gives a solubility value of 5.9 g/L (i.e., 5900 ppm) at 20 °C in deionized water; therefore, we assume that, with added PVCap, the solubility must be even lower.[47] Like the other straight alkyl chain alcohols, 1-hexanol had a higher $T_o$ value than its branched analogues, including 4-methyl-1-pentanol. The $T_o$ and $T_a$ values for 1-hexanol with PVCap were 5.8 and 3.3 °C, respectively, indicating reasonable synergy and, therefore, that most if not all of 1-hexanol was properly dissolved in the test temperature range. The $T_o$ value for 1-

hexanol was not found to be significantly different ($p > 0.05$) from the $T_o$ values for both 2,2-dimethyl-1-propanol and 3-methyl-1-butanol. The same was found for the $T_a$ values for 1-hexanol and 2,2-dimethyl-1-propanol.

We also tested another branched version of 1-hexanol, the alcohol 2-ethyl-1-hexanol. This alcohol made a cloudy dispersion in water with the PVCap polymer, indicating poor solubility. This is not unexpected for an eight-carbon alcohol. As a result, there was negligible synergy for 2-ethyl-1-hexanol with PVCap, with average $T_o$ and $T_a$ values of 10.8 and 10.4 °C, respectively. For this reason, we did not test 1-octanol, also with eight carbon atoms, which has similar poor water solubility. It has been proposed as a solvent for removal and recovery of KHI polymers, such as PVCap.[36]

The next part of the study on solvent synergists for PVCap concerned cyclic alcohols. Figure 7 shows the synergist results for a series of cyclic alcohols, also summarized in Table 2. All of them were found to be soluble in water at 5000 ppm together with 2500 ppm of PVCap. Figure 8 shows the structure of the cyclic alcohols that was performance-tested for their potential synergetic effect on PVCap. The monoglycol ether derivatives of cyclopentanol and cyclohexanol were discussed earlier and are shown in Figure 4.

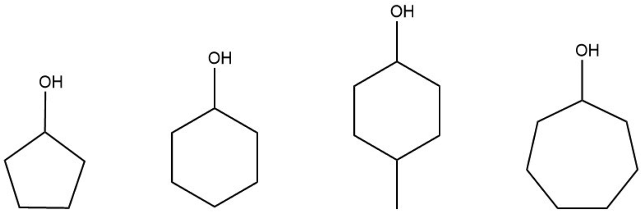

**Figure 8.** Structures of the cyclic alcohols tested as a potential synergist in this study. From left to right: cyclopentanol, cyclohexanol, 4-methylcyclohexanol, and cycloheptanol.

Furfuryl alcohol and tetrahydrofurfuryl alcohol gave only weak synergy with PVCap. This indicates that adding heteroatoms to the cyclic groups to make them more polar than cycloalkyl groups is not beneficial. Cyclopentanol gave $T_o$ and $T_a$ values of 6.8 and 5.1 °C, respectively. The average $T_o$ value for cyclohexanol was the same, i.e., no significant difference ($p > 0.05$). The $T_a$ value, however, was much lower for cyclohexanol, 3.4 °C. This could indicate that a larger alkyl ring helps to delay the catastrophic hydrate growth together with PVCap.

To see if branching the alkyl "tail" would also benefit the performance of the cyclic alcohols as it had on the straight acylic alcohols, 4-methylcyclohexanol (*cis* and *trans* mixture) was investigated. This alcohol had a $T_o$ value of 5.9 °C and a $T_a$ value of 3.1 °C. The $T_o$ value was found to be significantly different ($p < 0.05$) than the $T_o$ value for cyclohexanol, but the $T_a$ values between the two were not found to be significantly different ($p > 0.05$). The lower $T_o$ value for 4-methylcyclohexanol may be related to its higher hydrophobicity and ability to perturb the water phase to prevent nucleation. This supposition is backed up by results with 4-methyl-1-pentanol (discussed earlier) and cycloheptanol. Cycloheptanol is the least water-soluble of the cyclic alcohols tested but, nevertheless, gave a clear solution at 5000 ppm with 2500 ppm of PVCap. This alcohol gave average $T_o$ and $T_a$ values of 6.4 and <3 °C, respectively. This is the biggest synergetic effect observed with the PVCap polymer of all of the cyclic alcohols tested. The very low $T_a$ value may seem surprising considering that seven-ring molecules are not known to form clathrate hydrates, but we do know that seven-ring groups in polymers, such as PVCap, can strongly inhibit hydrate crystal growth.[1−5]

As mentioned earlier, the glycol ethers of both cyclopentanol and cyclohexanol gave lower $T_o$ and $T_a$ values than their related parent cyclic alcohols. Because glycolation (ethoxylation) imparts greater water solubility, solvent solubility is not such an important factor for optimal synergy as it is when comparing alcohols. Somehow, adding a glycol ether group gives an extra benefit to the synergy of an alcohol. It has been speculated that this is due to the glycol ether having more surfactant-like properties than the parent alcohol.[31] Interactions of the glycol ether with PVCap could affect the conformation of the polymer in solution, perhaps increasing its surface/volume ratio, which, in turn, could improve the KHI performance. The glycol ether for seven-ring and larger ring alcohols was not commercially available for testing. On the basis of the trends seen, we speculate that cycloheptyl glycol ether might be expected to perform better as a synergist for PVCap than the smaller cyclic glycol ethers.

To further investigate the impact of alkyl "tail" length and branching, we looked beyond alcohols and investigated some water-soluble ketones. The structures are shown in Figure 9, and their performance as synergists is shown graphically in Figure 10. Because the results for alcohols showed that branching of the alkyl "tail" is beneficial for their performance as a synergist with PVCap, we chose ketones that had branched alkyl "tails". As far as we are aware, this is the first study of the synergism of a range of ketones with PVCap.

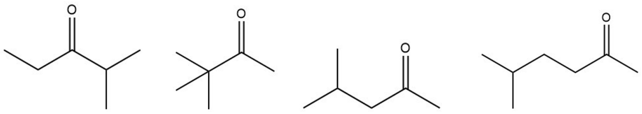

**Figure 9.** Structure of the various ketones investigated. From left to right: 2-methyl-3-pentanone, 3,3-dimethyl-2-butanone, 4-methyl-2-pentanone, and 5-methyl-2-hexanone.

The four ketones have a range of different alkyl groups bonded to either side of the carbonyl group. The choice was limited to what was commercially available and provided sufficient water solubility. 2-Methyl-3-pentanone gave a $T_o$ value of 10.3 °C and a $T_a$ value of 8.8 °C, which were not significantly different from the $T_o$ and $T_a$ values for PVCap alone; i.e., 2-methyl-3-pentanone possessed no synergetic effect on the PVCap polymer. This particular ketone, 2-methyl-3-pentanone, has the smallest alkyl group (isopropyl) compared to the others tested, which may be the reason for the lack of synergy. Isopropyl alcohol (2-propanol) also gave poor synergy with PVCap (Table 2).

The other three ketones all showed good synergy with PVCap. 3,3-Dimethyl-2-butanone gave an average $T_o$ value of 7.5 °C and an average $T_a$ value of 4.3 °C. The larger *tert*-butyl group on one side of the ketone is probably the reason for this, which is also not sterically hindered by the methyl on the other end of the ketone. As seen with the secondary alcohols, if the branching comes too close to the hydrophilic part of the molecule, in this case, the ketone group, the alkyl "tail" will hinder the hydrophilic group from interacting with the surrounding water molecules. Therefore, we tested a ketone with its hydrophilic group one carbon atom further away from

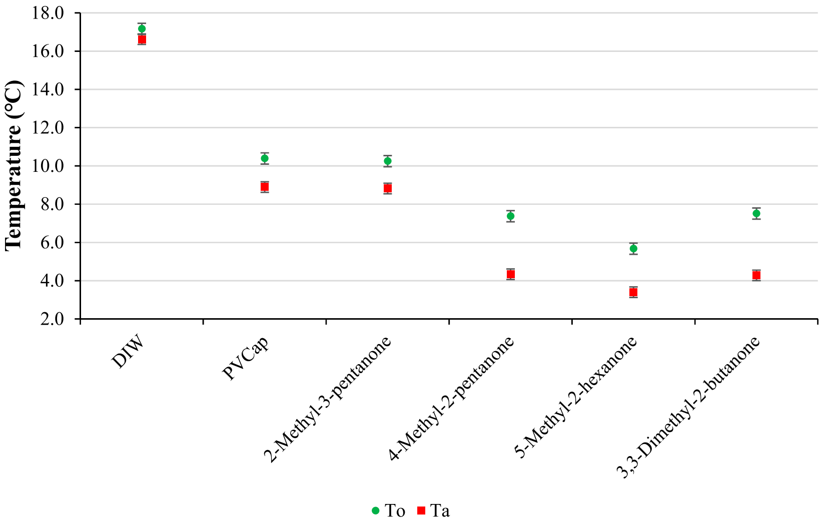

**Figure 10.** Graphical interpretation of the potential synergetic effect of different ketones (5000 ppm) on the $T_o$ and $T_a$ values of PVCap (2500 ppm).

the branching, namely, 4-methyl-2-pentanone. This ketone performed better than 2-methyl-3-pentanone, having $T_o$ and $T_a$ values of 7.4 and 4.3 °C, respectively, but there was no significant difference ($p > 0.05$) to the synergy of 3,3-dimethyl-2-butanone.

We were interested to see how a ketone with more spacing between the ketone group and the branching would perform as a synergist with the PVCap polymer. Thus, we tested 5-methyl-2-hexanone, which has two carbon atoms between the ketone group and the branching in the alkyl group. The result was better than the other ketones investigated, giving a $T_o$ value of 5.7 °C and a $T_a$ value of 3.4 °C. This improved synergy in the ketone series is probably due to this ketone being the most hydrophobic (and least water-soluble) but also indicates the importance of not having the alkyl branching too close to the hydrophilic part of the molecule.

## 4. CONCLUSION

In this study, we have investigated a range of monoglycol ethers, glycol ethers, acyclic alcohols, cyclic alcohols, and ketones for their potential as synergist solvents at 5000 ppm with 2500 ppm of PVCap. This was performed by carrying out slow constant cooling high-pressure KHI experiments with a sII hydrate forming SNG. The best synergist of all of the solvents tested was the acyclic aliphatic alcohol 4-methyl-1-pentanol, which was the only solvent to consistently give $T_o$ values of less than 3 °C. For the compounds containing an ether functional group, the synergetic effect was best for 2-(cyclohexyloxy)ethanol; for cyclic alcohols, the best solvent was cycloheptanol; and for the ketones, the best solvent was 4-methyl-2-pentanone.

We have made several structure−activity observations from the KHI test results. First, a cyclic alkyl "tail" generally gives a better synergetic effect than an acyclic "tail" containing the same number of carbon atoms. Second, end-tail branching (one or two methyl groups) of the alkyl "tail" gives better synergy than a straight-chain alkyl "tail". Further, the synergetic effect relates to the shape as well as the hydrophobicity/water solubility limit of the solvents. Our research also indicates that, for the same number of carbon atoms, compounds with glycol functional groups have generally better synergetic performance than compounds with alcohol as a functional group. In addition, secondary alcohols have a poorer synergetic effect than primary alcohols. We also found that compounds containing ketone as the functional group can indeed give reasonable synergy and that the best ketone has the largest end-branched alkyl group as long as it is sufficiently water-soluble.

On the basis of the trends seen, we speculate that the mono- or diglycol ethers of 4-methyl-1-pentanol and cycloheptanol, which are not commercially available, might be expected to perform better than any of the solvents in this study. We are currently in the process of exploring these new synergists. In addition, further research is planned on the solvents showing the best synergetic effect in this study, for example, by altering the concentration, combining different solvents, varying the solution salinity, varying the gas composition, using different KHI polymers, and using other KHI test methods, such as isothermal experiments.

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### Notes

The authors declare no competing financial interest.

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# Paper IV

Further Investigation of Solvent Synergists for Improved Performance of Poly(*N*-vinylcaprolactam)-Based Kinetic Hydrate Inhibitors

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# Further Investigation of Solvent Synergists for Improved Performance of Poly(*N*-vinylcaprolactam)-Based Kinetic Hydrate Inhibitors

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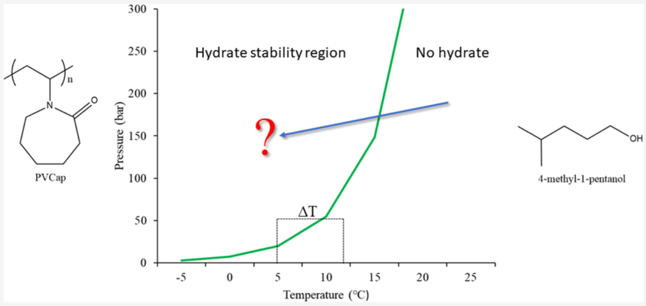

**ABSTRACT:** Poly(*N*-vinylcaprolactam) (PVCap) and related copolymers have been used as kinetic hydrate inhibitors (KHIs) to combat gas hydrate formation in oil and gas field production flow lines. It is known that the addition of certain solvents to the KHI polymer can enhance its ability to hinder gas hydrate formation. In an earlier study, a wide range of alcohols, glycol ethers, and ketones were investigated as synergetic solvents with PVCap. In that study, an outstanding synergetic effect was achieved by 4-methyl-1-pentanol (iHexOl). This report builds on that study by investigating iHexOl in more detail as well as some newly synthesized solvents predicted by the first study to have good synergism. Both slow constant cooling (SCC) and isothermal KHI experiments were conducted in high-pressure steel rocking cells using a structure II-forming natural gas mixture. The KHI polymer concentration, solvent concentration, and mixed solvent systems were investigated. The solvent synergist water solubility, also in brines, and partitioning to the liquid hydrocarbon phase are shown to be important factors to consider for optimizing KHI performance. Further, it was observed that the optimal molecular weight distribution for the KHI polymer when used with a solvent synergist is not the same as the optimum distribution when using the polymer alone.

## 1. INTRODUCTION

Gas hydrates are nonstoichiometric crystalline solids with many similarities with ice. In gas hydrates, gases of certain molecular weight stabilize hydrogen-bonded molecular water cages. Thus, if suitable low-molecular weight hydrocarbon gases combine with water under specific conditions of temperature and pressure, typically favoring conditions at temperature and pressure in the ranges of <25 °C and >30 bar, respectively, gas hydrates will form.[1−4] These requirements are not uncommon to encounter when producing or transporting oil and gas, and if it is left untreated, formation of gas hydrate plugs can occur, potentially jeopardizing operations and posing health hazards.[4−12] Therefore, it is important to treat the system in such a manner that the risk for forming gas hydrate plugs is eliminated. There exist multiple measures to handle and treat gas hydrate; one of them is the utilization of chemicals, more specifically, low-dosage hydrate inhibitors (LDHIs) and subgroup kinetic hydrate inhibitors (KHIs).[5]

In a KHI formulation, the main active compound is one or more water-soluble polymers, which typically make up 10−30 wt %, with the remainder being one or more carrier solvents.[13] Regarding the polymers, previous studies indicate that the main KHI polymer must incorporate both hydrophilic and hydrophobic moieties. The hydrophilic functional groups of the polymer is usually provided by strong hydrogen-bonding groups such as amide, imide, or amine oxide groups.[5,14,15] The hydrophobic functional groups should preferably be present and directly bonded to or adjacent to each of the hydrophilic functional groups.[16] Polymers and copolymers based on the monomers *N*-vinylcaprolactam (VCap), *N*-vinylpyrrolidone (VP), and *N*-isopropylmethacrylamide as well as hyperbranched poly(ester amide)s based on diisopropanolamine reacted with various cyclic anhydrides make up the bulk of commercially available KHIs.[5]

The most widespread deployed KHI polymers are probably those based on *N*-vinylcaprolactam (VCap), such as the homopolymer PVCap or copolymers with VP or other monomers (Figure 1).[14,17] The mechanism behind the inhibition properties of these KHI polymers is not fully understood, but KHIs interfere with the hydrate nucleation and/or crystal growth processes.[5,14,16,18−21]

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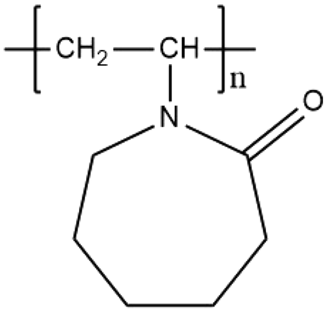

Figure 1. Structure of poly(*N*-vinylcaprolactam) (PVCap).

The other part of the KHI formulation, the carrier solvent, is often a low-molecular weight alcohol or glycol, which often has a high flash point for safety purposes.[12] The KHI polymer is diluted sufficiently to a low enough viscosity solution to enable it to be injected and pumped over long distances in umbilical flow lines. The KHI carrier solvent can also act as a synergist with the KHI polymer, enhancing the hydrate-inhibiting properties of the polymer. The solvent synergism can increase the application performance window of the pure KHI polymer or reduce the polymer dosage.[13] The solvent can also contribute to thermodynamic inhibition, especially if the KHI polymer formulation is very dilute.

Laboratory studies have shown that glycol ethers, particularly with three to four carbon atoms in the alkyl chain and phenylpropylene glycol, have good synergy with PVCap.[18,22,23] *n*-Butyl glycol ether (2-butoxyethanol or BGE) has found use as a high-flash point mutual solvent in some KHI formulations.[23] In the first part of our study, we showed that glycol ethers with five to six carbon atoms also show good KHI synergy with PVCap.[24]

Alcohols containing three to five carbon atoms have been reported to have a synergetic effect on PVCap, although it is not as powerful as monoglycol ethers such as BGE.[22,25] Smaller alcohols have even been reported to have an antagonistic effect on the performance of PVCap. Further, branching, not just the molecular weight of the alcohol, affects synergetic performance.[26]

The mechanism behind the synergism of alcohols and glycol ethers with KHI polymers is not known, but some hypotheses have been reported.[18,22,26−31] These range from mechanisms of cooperative (with the KHI polymer) adsorption on hydrate particles and/or water perturbation as well as lowering the gas/liquid interfacial tension, giving stronger adsorption of the KHI polymers on the surface of the aqueous phase where nucleation is expected to first occur.

From our earlier study of solvent synergists for PVCap, we observed that the synergetic effect appears to relate to the hydrophobicity/water solubility limit and on the size and shape of the hydrocarbyl (alkyl or aryl) tail.[24] Even other oxygenated solvents such as ketones gave reasonable synergy if they were close to their solubility limit in water at the dosage applied (e.g., 5000−10,000 ppm). The test system in this earlier study used deionized water, a synthetic natural gas blend giving structure II hydrate as the preferred thermodynamic product, and no liquid hydrocarbon phase. We also found that synergy was not confined to alkyl groups of three to five carbon atoms, but tail sizes of up to seven carbon atoms also gave good synergy with PVCap. Outstanding synergism was achieved by 4-methyl-1-pentanol (iHexOl) (Figure 2), but cycloalkanols (five to seven carbon atoms) and their glycol ethers were also powerful synergists. In addition, solvents with one or two glycol functional groups generally gave a better synergetic effect than the corresponding alcohols. Phenoxyethanol, with an aromatic tail of six carbon atoms, and butyl diglycol ether were recently shown to be synergists for PVP.[32]

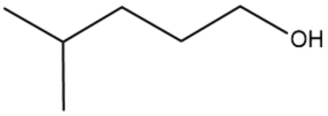

Figure 2. Structure of 4-methyl-1-pentanol (iHexOl).

In this follow-up study, we have investigated the best synergist from the first study, iHexOl, in more detail. We have also investigated some new solvent synergists, some of which were not available in the first study. Our choice of solvents was based on our knowledge of the importance of size and shape of the solvent as well as its water solubility. The choice includes glycol ethers of some of the best alcohols, which we predicted might be better than the alcohols themselves. Variations of the KHI polymer concentration, solvent concentration, and mixed solvent systems were also investigated. In addition, two different test procedures were used, the slow constant cooling (SCC) method and the isothermal method.

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** PVCap was obtained from BASF as Luvicap EG HM ($M_w$ = 10,000 g/mol). The ethylene glycol solvent was removed, leaving a dry powder of pure PVCap polymer. This PVCap powder was used throughout this study. PVCap (50 wt %) in BGE ($M_w$ = 2000 g/mol) was obtained from Ashland (IPS) as Inhibex 101, denoted as PVCapBGE from now on. PVCapSCH(COOH)-$CH_2COOH$ ($M_n$ = 4006 g/mol) was synthesized previously in our laboratory,[33] denoted as PVCapEND from now on. All solvent synergists were sourced either from VWR, Merck, Nouryon, or TCI Europe with a minimum 99% purity.

**2.2. Synthesis of 2-((4-Methylpentyl)oxy)ethane-1-ol (iHex(EO)OH).** The synthesis was based on a previously described method.[34] In two separate glass vessels, 4-methyl-1-pentanol (3 g, 29.40 mmol) was mixed with toluene (20 mL), and NaOH (1.29 g, 32.25 mmol) was dissolved in methanol (10 mL). The two solutions were then introduced into a two-necked round-bottom flask with a distilling column connected. Here, the solution was vigorously stirred at 110 °C overnight. The solvent was then removed from the reaction mixture in vacuo on a rotary evaporator. This solution was then dissolved in THF (30 mL), 2-bromoethanol (2.83 mL, 38.14 mmol) was added dropwise, and then the solution was left at room temperature to react overnight. Solids were filtered off and solvent was removed from the reaction mixture in vacuo on a rotary evaporator. The resulting brown liquid, with a yield of 86%, was confirmed pure by $^1$H NMR, and it was thus used without further purification steps.

**2.3. Polymerization of VCap in 4-methyl-1-pentanol (iHexOl).** VCap (2 g, 14.36 mmol) was dissolved in 4-methyl-1-pentanol (4 g, 39.15 mmol) in a Schlenk flask with a magnet. AIBN (1 wt %, 0.06 g) was added, and the solution was flushed with nitrogen using the standard pump−fill technique. While the solution was stirring, it was heated to 80 °C and left to react under the protection of nitrogen for 18 h. Then, the formed PVCap solution was cooled to room temperature, and the product was left in the solution.

**2.4. Experimental Procedure.** The Rocking Cell 5 (RC5) apparatus supplied by PSL Systemtechnik, Germany was used to conduct KHI performance testing. This apparatus can rock five high-pressure stainless-steel rocking cells in a cooling bath equipped with both temperature and pressure sensors. In addition, there is a stainless steel ball inside each cell for agitating the test solution.

The cells have an internal volume of 40 mL and were supplied by Svafas, Norway. Standard synthetic natural gas (SNG) was used in these performance tests (Table 1). This gas mixture preferentially forms structure II gas hydrate as the most thermodynamically stable phase.

Table 1. Composition of the Synthetic Natural Gas Mixture (SNG) Used in the Performance Testing

| component | mol % |
|---|---|
| methane | 80.67 |
| ethane | 10.20 |
| propane | 4.90 |
| *iso*-butane | 1.53 |
| *n*-butane | 0.76 |

The procedure for high-pressure kinetic hydrate inhibition testing by slow constant cooling (SCC) experiment have been described previously[35,36] and is summarized in the following:

(1) The polymer and the synergist, if applicable, were dissolved to the desired concentration in deionized water prior to initializing the test at least one day in advance.
(2) Twenty milliliters of test solution consisting of various additives dissolved in deionized water was added to each of the five cells.
(3) A sequence of vacuum and pressurizing with SNG was applied in order to replace the air in the cells with SNG. Vacuum was first applied, and then the cells were pressurized to 3−5 bar with SNG before depressurizing followed by another round of vacuum.
(4) After this procedure, the system was pressurized to the experimental pressure of 76 bar with SNG.
(5) The cells were rocked at a rate of 20 rocks per minute at an angle of 40° and cooled with a cooling rate of 1.0 °C/h from 20.5 to 2.0 °C.

By standard laboratory dissociation experiments, the hydrate equilibrium temperature ($T_{eq}$) at 76 bar have previously been determined to be 20.2 ± 0.05 °C, warming at 0.025 °C/h for the last 3−4 °C, which correlates well with calculations done by Calsep PVTSim software.[37,38]

During a constant cooling experiment, the initial pressure was 76 bar and the temperature was decreased from 20.5 to 2.0 °C during the experimental run (Figure 3). There will be a linear pressure decrease from which both the onset temperature for hydrate formation ($T_o$) and the rapid hydrate formation temperature ($T_a$) can be observed. This is caused by each cell being a closed system.

From this linear pressure decrease, the temperature at the first observable deviation is defined as $T_o$. This is the first macroscopic observation of hydrate formation done by an observation on a linear pressure decrease, and therefore, it is quite possible that the hydrate nucleation initiated at a molecular level prior to this. These experiments however, are not capable of detecting nucleation, which possibly happens earlier than $T_o$. $T_a$ is the temperature taken when the pressure decrease is at its steepest, i.e., when the hydrate formation is at its fastest (Figure 4).

The isothermal experimental procedure follows the same steps as the SCC experimental method except that in step 5, the cells were quickly cooled without rocking from 20.5 °C to 4 °C over 1 h. When the experimental test temperature of 4 °C was reached, the rocking commenced with a rate of 20 rocks per minute at an angle of 40°. During this experimental run, the temperature is kept at 4 °C, making the pressure graph horizontal (Figure 5).

The time in which the first sign of any pressure drop or first deviation from the horizontal pressure graph occurs, is defined as $t_o$. With varying intervals after $t_o$ has occurred, a rapid pressure decrease can be observed. This is where the pressure decrease is at its steepest, or in other words, the hydrate formation is at its fastest. The time at which this occurs is defined as $t_a$ (Figure 6).

## 3. RESULTS AND DISCUSSION

### 3.1. Slow Constant Cooling Experiments.

Given the good synergetic effect that 4-methyl-1-pentanol (iHexOl) achieved with PVCap polymer from the first study, this compound was now further investigated at varying concentrations in addition to PVCap being polymerized in it (Table 2).

Since the concentration of PVCap was held constant in these SSC tests, they highlight the impact that iHexOl makes on the overall KHI performance. For the most part, the behavior was as predicted, but there were some clear deviations (Figure 7).

From Table 2 and Figure 7, it can be observed that 5000 ppm iHexOl alone had almost no inhibition effect with

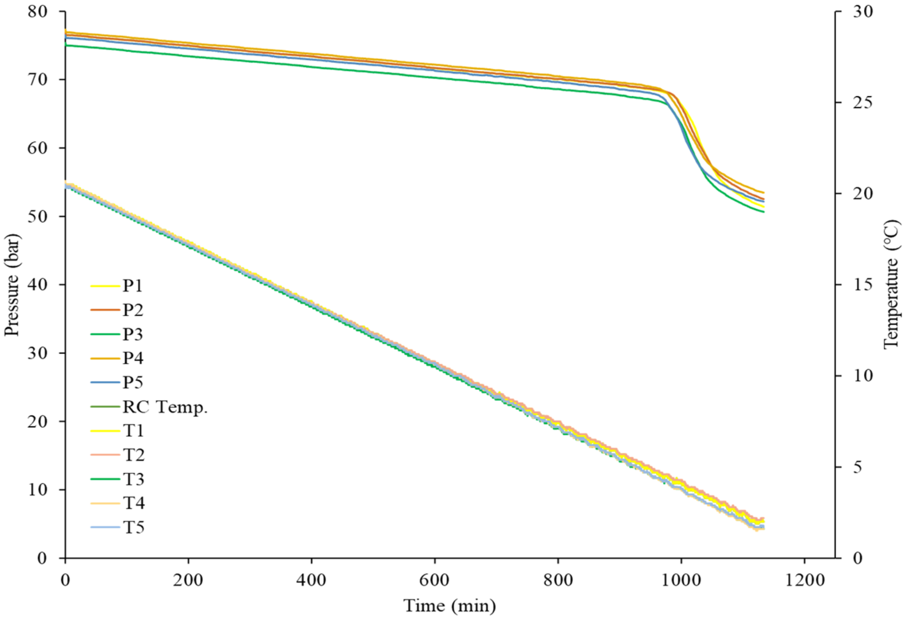

**Figure 3.** SCC tests results from all five cells, each containing in this example 2500 ppm PVCap and 5000 ppm 2-methyl-1-pentanol. "RC Temp." is the temperature recorded in the cooling bath.

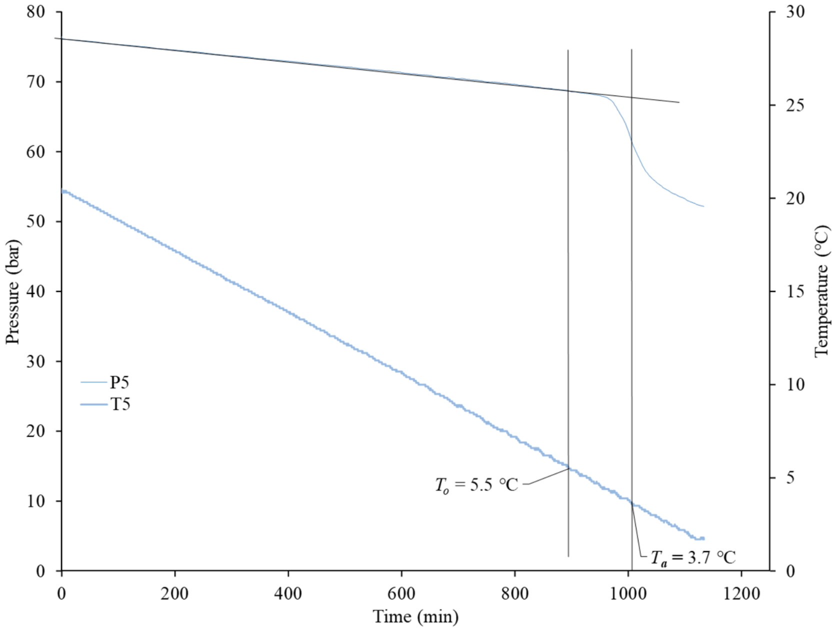

**Figure 4.** Graph from cell 1 with both $T_o$ and $T_a$ determined during an SCC experiment. In this example, the cell contained 2500 ppm PVCap and 5000 ppm 2-methyl-1-pentanol.

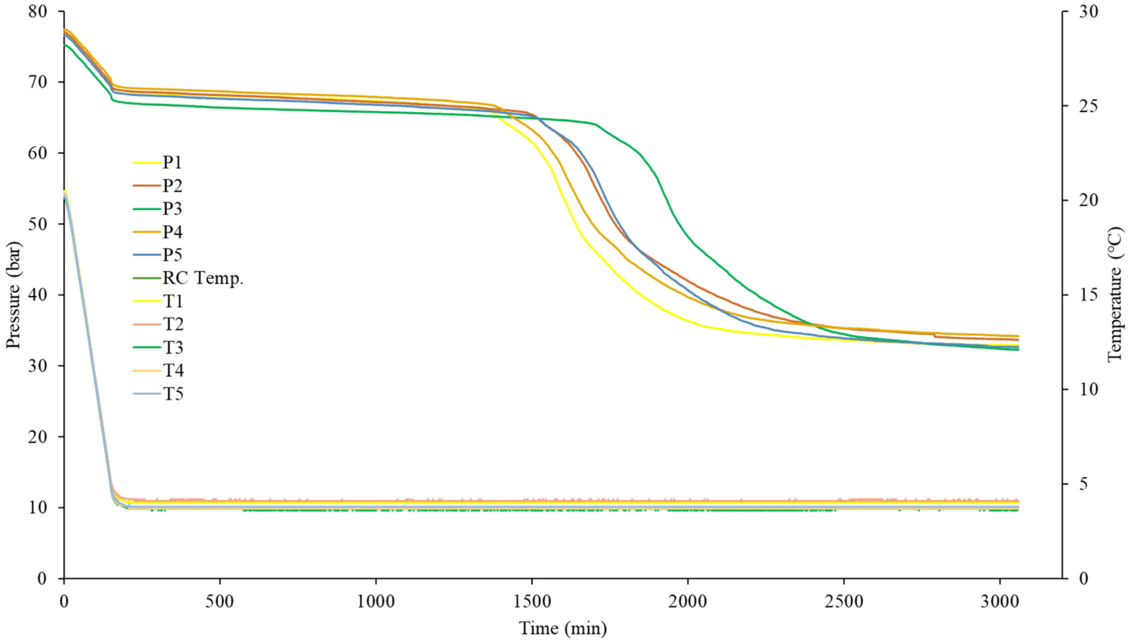

**Figure 5.** Graph containing results from an isothermal test for all five cells; in this example, the cells contained 2500 ppm PVCap and 2500 ppm iHexOl. "RC Temp." is the temperature recorded in the cooling bath.

recorded $T_o$ and $T_a$ values of 15.3 and 14.2 °C, respectively, compared to just deionized water. Therefore, this solvent is only effective when used in blends with KHI polymers. The 2500 ppm PVCap polymer alone gave $T_o$ and $T_a$ values of 10.4 and 8.9 °C, respectively. By polymerizing PVCap in iHexOl, the result was somewhat poorer than pure PVCap, resulting in $T_o$ and $T_a$ values of 11.8 and 8.9 °C, respectively. The $T_a$ values between PVCap polymerized in iHexOl and pure PVCap were not found to be significantly different ($P > 0.05$ in a statistical $t$ test). This indicates that PVCap polymerized in iHexOl and pure PVCap are equal in delaying catastrophic hydrate growth but pure PVCap can hold the system hydrate-free for longer. The result seems surprising at first sight given the powerful synergy from iHexOl added to PVCap. One possible reason for this could be linked to the low water solubility of the PVCap polymerized in iHexOl.

This product was a clear liquid, but the polymer was not totally dissolved when the product was added in water to give 2500 ppm active polymer in the test solution. This made it difficult to determine a cloud point. The low solubility could be because of the initiator causing some isohexyl groups in the solvent to be incorporated into the polymer as a good chain transfer agent and/or the solvent affecting internal hydrogen bonding in the polymer.[39]

Keeping the concentration of PVCap constant at 2500 ppm and raising the concentration of iHexOl improved performance

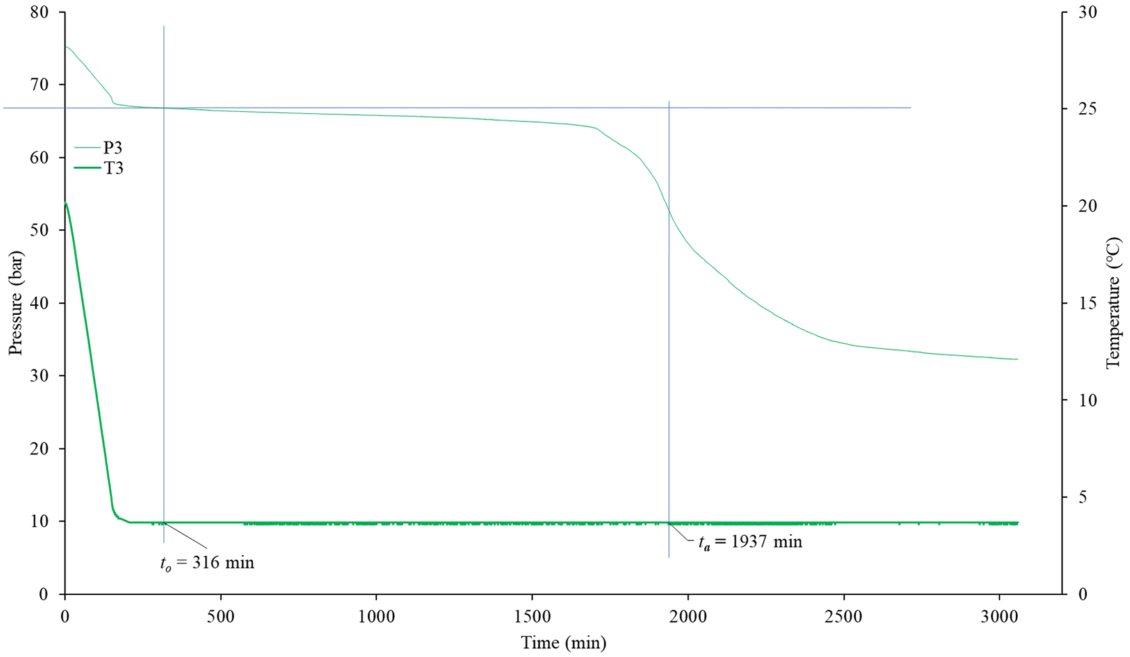

**Figure 6.** Graph from one cell with both $t_o$ and $t_a$ determined during an isothermal experiment. In this example, the cell contained 2500 ppm PVCap and 2500 ppm iHexOl.

**Table 2. Summarized Results for SCC Tests with Altering Concentrations for PVCap and iHexOl with Results for Deionized Water (DIW), iHexOl, and PVCap Alone Included**[a]

| substance | | concentration (ppm) | | | |
|---|---|---|---|---|---|
| KHI polymer | synergist | KHI polymer | synergist | $T_o$ (°C) | $T_a$ (°C) |
| DIW | | | | 17.2 | 16.6 |
| | iHexOl | | 5000 | 15.3 | 14.2 |
| PVCap | | 2500 | | 10.4 | 8.9 |
| PVCap made in iHexOl | iHexOl | 2500 | 5000 | 11.8 | 8.9 |
| PVCap | iHexOl | 2500 | 1000 | 7.1 | 4.6 |
| PVCap | iHexOl | 2500 | 2500 | 4.1 | 1.7 |
| PVCap | iHexOl | 2500 | 5000 | <3 | <3 |
| PVCap | iHexOl | 2500 | 10,000 | 7.2 | 6.0 |

[a] Volume of solution in the cells was 20 mL.

but only in the range of 1000−5000 ppm solvent. When the concentration of iHexOl was 5000 ppm, there was no observable hydrate formation when the temperature dropped down to 2 °C in all cells, which is the minimum set temperature for the cooling cycle. Increasing the concentration of iHexOl to 10,000 ppm had a negative effect on the performance compared to 5000 ppm solvent, but it was still better than PVCap polymer alone, and it is in the range of the result for 1000 ppm iHexOl. Their $T_o$ values were not found to be significantly different ($P > 0.05$ in a statistical $t$ test). iHexOl at 10,000 ppm could be better at delaying the catastrophic hydrate formation, given that it had a lower $T_a$ value than 1000 ppm iHexOl. This is a rare result where too much solvent gives a worse KHI performance. A possible reason is due to the solubility of the solvent. iHexOl has a water solubility of 7.6 g/L (i.e., 7600 ppm) at 20 °C. Therefore, at 10,000 ppm, not all the solvent will be dissolved in the aqueous phase and could cause a separate liquid phase. The PVCap polymer might partition to this phase and be less active in the water phase where hydrate formation first occurs, thus giving poorer

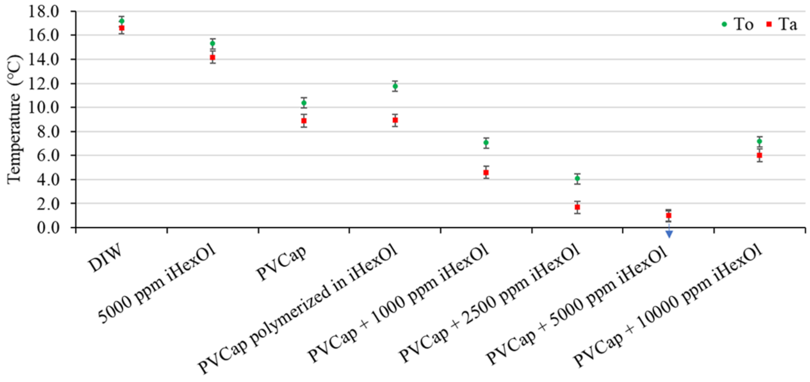

**Figure 7.** Summary of SCC test results for 2500 ppm PVCap with different concentrations of iHexOl, plus some comparative tests. Both $T_o$ and $T_a$ values are given.

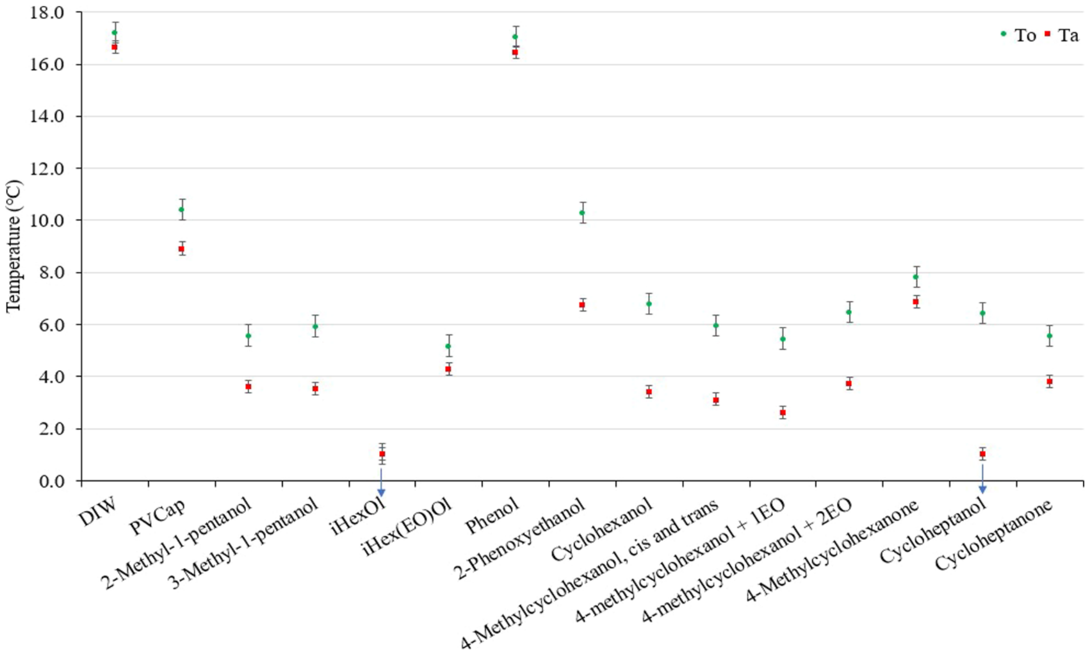

**Figure 8.** Graphical display of the $T_o$ and $T_a$ values for PVCap (2500 ppm) with different solvents added (5000 ppm).

performance. The effect can be considered similar to the addition of medium-size organic carboxylic acids such as pentanoic and hexanoic acid or 1-octanol, which have been found to be effective at displacing KHI polymers such as PVCap from produced water.[40,41] This indicates the importance of finding the right concentration in order to not under- or overinhibit the system.

In the next part of this study, we carried out SSC tests using PVCap as the KHI polymer but varying the solvent. The results are summarized in Figure 8 and Table 3. The concentrations of polymer and solvent were held constant throughout these tests at 2500 and 5000 ppm, respectively. Solvents were chosen based on our earlier work with KHI polymer and synergetic compounds.[24,42] A few results from the earlier study with PVCap solvent synergists are added to Table 3 for comparison.

**Table 3. Summarized Results for 2500 Ppm PVCap with 5000 Ppm of Different Solvents**[a]

| additive | $T_o$ (°C) | $T_a$ (°C) |
|---|---|---|
| DIW | 17.2 | 16.6 |
| PVCap | 10.4 | 8.9 |
| synergist | $T_o$ (°C) | $T_a$ (°C) |
| 2-methyl-1-pentanol | 5.6 | 3.6 |
| 3-methyl-1-pentanol | 5.9 | 3.5 |
| 4-methyl-1-pentanol (iHexOl) | <3 | <3 |
| 2-((4-methylpentyl)oxy)ethane-1-ol (iHex(EO)Ol) | 5.2 | 4.3 |
| phenol | 17.0 | 16.4 |
| 2-phenoxyethanol | 10.3 | 6.7 |
| cyclohexanol | 6.8 | 3.4 |
| 4-methylcyclohexanol (*cis* and *trans* mixture) | 5.9 | 3.1 |
| 4-methylcyclohexanol (*cis* and *trans* mixture) + 1EO | 5.4 | 2.6 |
| 4-methylcyclohexanol (*cis* and *trans* mixture) + 2EO | 6.4 | 3.7 |
| 4-methylcyclohexanone | 7.8 | 6.9 |
| cycloheptanol | 6.4 | <3 |
| cycloheptanone | 5.5 | 3.8 |
| *n*-butyl glycol ether (BGE) | 7.3 | 3.8 |
| butyl diglycol ether (DBGE) | 5.5 | 2.9 |
| di(propylene glycol)butyl ether (DPGBE) isomer mix | 5.5 | <3 |
| 2-*n*-butoxyethyl acetate | 5.5 | <3 |

[a] Volume of solution in the cells was 20 mL.

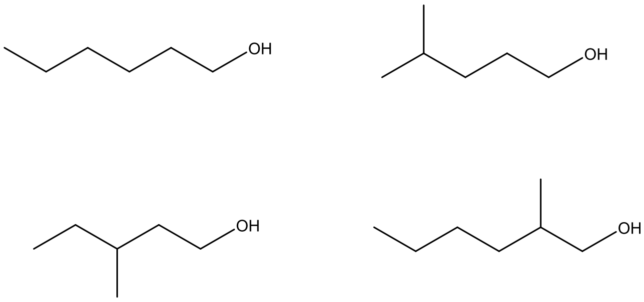

**Figure 9.** Clockwise from top left: 1-hexanol, 4-methyl-1-pentanol (iHexOl), 2-methyl-1-pentanol, and 3-methyl-1-pentanol.

From Table 3, it can be observed that most of these compounds had a synergetic effect with the PVCap polymer except phenol and 2-phenoxyethanol. We will now discuss the results in detail and the reasons for the choice of these solvents. First, we chose to investigate isomers of iHexOl as they would be expected to have roughly the same solubility in water but different alkyl shapes (Figure 9). 1-Hexanol had already been investigated in our earlier study and gave reasonable synergy with PVCap, giving average $T_o$ and $T_a$ values of 5.8 and 3.3 °C, respectively.[24] In comparison, 2-methyl-1-pentanol and 3-methyl-1-pentanol gave very similar performance to 1-hexanol but significantly lower than that of iHexOl. Neither the $T_o$ nor $T_a$ values of 2-methyl-1-pentanol and 3-methyl-1-pentanol were found to be significantly different ($P > 0.05$). For both 2-methyl-1-pentanol and 3-methyl-1-pentanol, the branching can potentially cause a steric hindering for the hydroxyl group, making them less effective at perturbing the water structure (nucleation inhibition) or interacting with hydrate surfaces (crystal growth inhibition). These results illustrate that within a set of isomeric alcohols, the shape of the alkyl group in the alcohol solvent is very important for KHI performance. Branching of the alkyl tail seems to be especially useful.

We were interested in testing small diglycol ethers of iHexOl that might have better synergetic performance with the PVCap polymer than the parent alcohol, as this had been seen for other alcohols.[24] An example is the improved performance of *n*-butyl diglycol ether and *n*-butyl triglycol ether compared to 1-butanol and *n*-butyl glycol ether (BGE). Since these substances are not commercially available, we attempted the synthesis of the monoglycol ether 2-((4-methylpentyl)oxy)-ethane-1-ol (iHex(EO)Ol) in our laboratories. However, although the NMR indicates a pure product, this glycol ether did not dissolve fully when 5000 ppm was added to a 2500 ppm solution of PVCap. This cloudy mixture gave a $T_o$ value of 5.2 °C and $T_a$ value of 4.3 °C. Clearly, this result is not as good as the alcohol but is undoubtedly due to the partial solubility in water. Nonetheless, this glycol ether still gives good synergy with PVCap and is one of the better solvents containing a glycol ether functional group.

The cyclic alcohols 4-methylcyclohexanol (*cis* and *trans* mixture), cyclohexanol, and cycloheptanol gave good synergy with PVCap in our earlier work.[24] Knowing that adding one to three glycol ether groups to an alcohol could improve the performance, we were interested in adding glycol ether groups to some of the alcohols in the first study, including these cyclic alcohols. None of the glycol ethers of these cyclic alcohols are commercially available, but Nouryon kindly synthesized and supplied us with the mono- and diglycol ethers of 4-methylcyclohexanol (Figure 10).

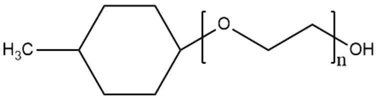

**Figure 10.** 4-Methylcyclohexanol and mono- and diglycol ethers ($n$ = 0−2).

4-Methylcyclohexanol (*cis* and *trans* mixture) gave fairly good synergetic performance with PVCap polymer, with $T_o$ and a $T_a$ values of 5.9 and 3.1 °C, respectively. By adding one oxyethylene (glycol ether) group to give 4-methylcyclohexanol + 1EO, we obtained a $T_o$ value of 5.4 °C and a $T_a$ value of 2.6 °C. When two oxyethylene (glycol ether) groups were added to the molecule making 4-methylcyclohexanol + 2EO, $T_o$ and $T_a$ values became 6.4 and 3.7 °C, respectively. However, there is no statistically significant difference at the 95% confidence level among the three solvents.

Branching of the alkyl "tail" in the alcohol solvent was shown to be beneficial for synergetic performance,[24] but branching of the ether groups in glycol ethers had not been investigated. Therefore, the branched analog of butyl diglycol ether (DBGE), di(propylene glycol)butyl ether (DPGBE), was investigated (Figure 11). It gave a good but similar synergetic effect with PVCap polymer as the linear ethylene glycol DBGE, with an average $T_o$ value of 5.5 °C and a $T_a$ value of <3 °C. It should be noted that both solvents are added at the same weight concentration, which means that DPBGE has a lower molar concentration.

Despite the findings from the previous publication that a cyclic alkyl "tail" results in better synergetic performance compared to a straight alkyl "tail," if the ring is aromatic, the results are quite different. The aromatic compounds were the only substances investigated that had an antagonistic performance with the PVCap polymer. Starting with the simplest aromatic alcohol, which is phenol, it ruined the PVCap performance completely, giving a $T_o$ value of 17.0 °C and $T_a$ value of 16.4 °C, which is very similar to adding no additive (Figure 12). There is clearly some incompatibility between the two chemicals as the solution was strongly opaque at room temperature with some white precipitate.

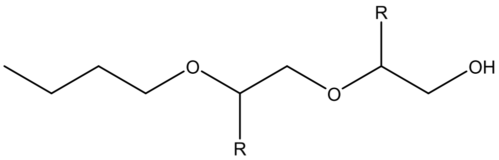

**Figure 11.** Butyl diglycol ether (DBGE) (R=H) and di(propylene glycol)butyl ether (DPGBE) (R=$CH_3$).

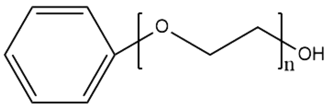

**Figure 12.** Schematic of phenol and 2-phenoxyethanol ($n$ = 0−1).

To investigate if an ether group would increase synergetic performance by making the molecule more hydrophilic, we tried 2-phenoxyethanol, which has a much less acidic proton than phenol (Figure 12). It gave $T_o$ and $T_a$ values of 10.3 and 6.7 °C, respectively (Table 3). The addition of the 2-hydroxyethyl group did not ruin the performance as phenol did, but now, the $T_o$ value is similar to PVCap polymer alone. The growth rate is slowed compared to PVCap as seen with a lower $T_a$ value. The results suggest that solvents with aromatic rings, especially phenols, are predicted to be bad choices as synergists for PVCap.

One possible reason for the poor synergetic effect for both phenol and 2-phenoxyethanol lies in the properties of the aromatic ring. Both compounds have a conjugated aromatic ring system. This ring system is accompanied by delocalized $\pi$ electron clouds in place of individual double and single bonds. These six $\pi$ electrons in the cloud circulate in regions both above and below the plane of the ring, making $p$ orbitals. It is these $p$ orbitals that could interact with the PVCap polymer. This plausible explanation is supported by the synergetic test results for cyclohexanol and other nonaromatic ring structures (Table 3), which in contrast show good synergy with PVCap. In addition, it has previously been reported that the addition of aromatic groups to the polymer ends of PVCap also lowered PVCap performance.[33]

It was also shown in earlier work that compounds containing ketone as the functional group possess reasonable synergetic performance with PVCap and that the best ketone, 5-methyl-2-hexanone, had the largest end-branched alkyl group as long as sufficient water solubility is maintained.[24] It was also found that if the branching of the alkyl "tail" is too close to the hydrophilic carbonyl group (ketone group), steric hindrance will diminish the synergetic effect of the ketone. Good results with cyclic alcohols made us consider that ketones with cyclic alkyl "tails" might also be good synergists, provided that they were water-soluble. Two cyclic ketones, 4-methylcyclohexanone and cycloheptanone, were investigated for their

Table 4. Isothermal Tests Conducted on PVCap and Synergist Solvents with 68 Bar SNG at 4 °C[a]

| substance | | concentration (ppm) | | | | |
|---|---|---|---|---|---|---|
| polymer | synergist | polymer | synergist | $t_o$ (min) | standard deviation for $t_o$ | $t_a$ (min) |
| PVCap | | 2500 | | 0 | 0 | 0 |
| PVCap | iHexOl | 2500 | 1000 | 166 | 3 | 176 |
| PVCap | iHexOl | 2500 | 2500 | 270 | 29 | 1711 |
| PVCap | iHexOl | 2500 | 5000 | 352 | 74 | 2807 |
| PVCap | iHexOl | 2500 | 10,000 | 293 | 56 | 1059 |
| PVCap | iHexOl | 5000 | 5000 | 604 | 105 | n/r |
| PVCap | iHexOl | 5000 | 10,000 | 1145 | 206 | n/r |
| PVCap | iHexOl | 7500 | 5000 | 1531 | 113 | n/r |
| PVCap | iHexOl + BGE | 5000 | 10,000 + 5000 | 869 | 265 | 3060 |
| PVCap | cycloheptanol | 2500 | 5000 | 149 | 3 | 210 |
| PVCap | TBGE | 7500 | 5000 | 262 | 88 | 336 |

[a] n/r = not reached.

potential synergetic effect with PVCap polymer. They were compared to their alcohol analogs 4-methylcyclohexanol (*cis* and *trans* mixture) and cycloheptanol, respectively (Table 3).[24] Further, 4-methylcyclohexanone had reasonable synergetic performance with PVCap polymer, giving $T_o$ and $T_a$ values of 7.8 and 6.9 °C respectively. Its alcohol analog, 4-methylcyclohexanol (*cis* and *trans* mixture), gave significantly lower values for the same conditions, with $T_o$ being 5.9 °C and $T_a$ being 3.1 °C. Cycloheptanone had a better synergetic performance with a $T_o$ value of 5.5 °C and $T_a$ value of 3.8 °C, with its alcohol analog cycloheptanol giving $T_o$ and $T_a$ values of 6.4 and <3 °C respectively. In general, although some ketones are quite good synergists for PVCap, there appears to be no great benefit in using ketones over alcohols. The ketones giving the best (and similar) synergetic performance results are the acyclic 5-methyl-2-hexanone (previous study) and the cyclic cycloheptanone, both containing seven carbon atoms but are sufficiently water-soluble for KHI testing. The larger ring and more hydrophobic nature of cycloheptanone could help these molecules in perturbing the water phase, preventing nucleation as well as possible direct inhibition of growing hydrate particles.

Butyl lactate has previously been shown to be a good synergist for PVCap and other polymers and contains both an ester and hydroxyl functional group.[42] We were also interested in investigating the potential synergetic performance of 2-*n*-butoxyethyl acetate, which is *n*-butyl glycol ether (BGE) with an acetate ester functional group. BGE and monoglycol ethers in general are well known for their proven synergetic effect on different KHI polymers, including poly(*N*-vinyl lactam)s and poly(*N*-alkyl(meth)acrylamide)s.[5,14,22,43−45] In the previous publication, BGE had a reasonable synergetic effect with PVCap polymer, resulting in a $T_o$ value of 7.3 °C and $T_a$ value of 3.8 °C. 2-*n*-Butoxyethyl acetate had a significantly better synergetic effect, giving $T_o$ and $T_a$ values of 5.5 and < 3 °C, respectively. These results parallel those of the alcohols, glycol ethers, and ketones, such that making the molecule more hydrophobic (compared to BGE) without losing water solubility was beneficial for synergetic performance with PVCap.

**3.2. Isothermal Experiments.** To further investigate the synergetic properties of the compounds that gave good results with SCC experiments, isothermal tests were conducted (Table 4). In these tests, different PVCap-based KHI products were investigated, including the PVCaps used in the SCC studies: a PVCap as 50% solution in BGE (PVCapBGE) and a PVCap end-capped with mercaptosuccinic acid (PVCapEND). We also used a saline aqueous phase (0.5 wt % NaCl) in some tests, a liquid hydrocarbon phase (decane), and varied liquid volumes in the cells.

We carried out a range of tests on three PVCap-based products to try to determine issues such as:

- Is the ranking in the SCC maintained in the isothermal tests?
- Does the performance always improve by adding more polymer or solvent synergist?
- Can two solvent synergists both boost the performance of a polymer?
- Does salinity or a liquid hydrocarbon phase affect the performance?

We tested only two of the three PVCap-based products by themselves. As Table 4 shows, PVCap gave zero delay in all tests at 2500 ppm and 4 °C. This is why we never tested PVCapEND, as we assumed that it would be just as poor by itself with no synergist solvent. A solution of 2500 ppm PVCapBGE also contains 2500 ppm BGE and gave an average $t_o$ value of about 166 min.

As can be observed in Table 4, the synergetic performance of the various concentrations of iHexOl on 2500 ppm PVCap polymer gave the same trend as with the SCC tests for the same substances and concentrations (Figure 13). Increasing the concentration of iHexOl from 1000 to 5000 ppm improved the synergetic performance. At a concentration of 5000 ppm iHexOl the synergetic performance had the best result on 2500 ppm PVCap, with $t_o$ and $t_a$ values of 352 and 2807 min,

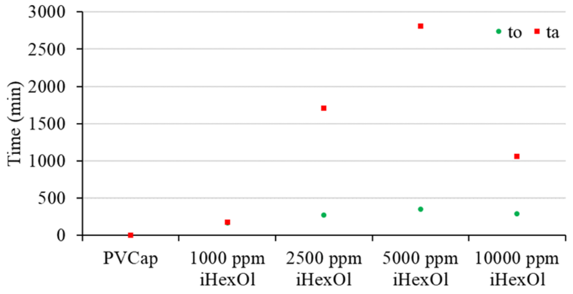

**Figure 13.** A graphical representation of the isothermal test results (68 bar, 4 °C) for 2500 ppm PVCap together with different concentrations of iHexOl, all with 20 mL of test solution ($t_o$ and $t_a$ overlap for PVCap and PVCap + 1000 ppm iHexOl).

respectively. At these combinations of concentrations, the $t_a$ value was also the best, indicating that not only will it keep the system hydrate-free the longest but it will also be capable of delaying the catastrophic hydrate growth for very long periods when hydrates first start to form. This will benefit operative personnel so that there will be time for taking action when hydrate formation begins.

The concentration of iHexOl was further increased to 10,000 ppm. At this concentration, the synergetic performance with PVCap polymer diminished. These results emphasize the importance of finding the right concentrations for optimizing synergetic performance between the KHI polymer and the solvent synergist. We speculate that there may be solvent—polymer interactions that render either the surface of the polymer and/or the solvent less available to function as a KHI.

Increasing the concentration of PVCap to 5000 ppm and combining it with the concentration of iHexOl that gave the best result for 2500 ppm PVCap, namely, 5000 ppm, improved performance (Table 4). The hold time increased with more polymer, and this was the first concentration combination of these substances that did not give a $t_a$ value within the timeframe of the experiment, which was about 2.5 days (3600 mins). The hold time increased even further by keeping the concentration of PVCap at 5000 ppm and doubling the concentration of iHexOl to 10,000 ppm. At these concentrations, the components were not totally dissolved. The results suggested that increasing the concentration of PVCap was beneficial but increasing the PVCap concentration further would not be beneficial without lowering the concentration of iHexOl. Therefore, we wanted to test the synergetic performance of 7500 ppm PVCap and only 5000 ppm iHexOl. This combination of concentrations was fully soluble and gave the best synergetic performance of all the combinations of concentrations tested, with a $t_o$ value of 1531 min and the $t_a$ not reached. This combination of concentrations became the general benchmark for isothermal testing in the rest of this research study, as will be discussed below.

From our previous research publication, we found that cycloheptanol had the best synergetic effect with PVCap of all the cyclic alcohols investigated in that study and that triethylene glycol monobutyl ether (TBGE) was one of the better glycol ethers investigated.[24] It was of interest to see how this cyclic alcohol and this glycol ether would perform in the isothermal tests. We tested cycloheptanol together with PVCap at concentrations of 5000 and 2500 ppm. The synergetic effect was not nearly as good as the same conditions for PVCap with iHexOl at the same concentrations. TBGE was tested at 5000 ppm together with 7500 ppm PVCap, resulting in a synergetic performance inferior to the results at the same conditions for PVCap with iHexOl. These results demonstrated that superior performance of iHexOl was maintained in the isothermal tests.

In this next part, we wanted to investigate the synergetic effect of iHexOl on other PVCap-based polymer blends (Figure 14 and Table 5). We chose PVCapBGE, which is PVCap 50 wt % in BGE, and PVCapEND, which is PVCap polymer with mercaptosuccinic acid used as a chain transfer agent.

Tests with 2500 ppm PVCapBGE (i.e., 2500 ppm of PVCap (2000 g/mol) + 2500 ppm BGE) gave an average $t_o$ value of 146 min and a $t_a$ value of 200 min. BGE is a well-known synergist for PVCap, but at these conditions, the hold time was low. Adding 2500 ppm iHexOl to the 2500 ppm PVCapBGE solution gave similar average $t_o$ and $t_a$ values. However, these values were well below the $t_o$ and $t_a$ values when the same concentrations were used for PVCap (10,000 g/mol) with iHexOl (Table 4). With increased concentrations of either PVCapBGE or iHexOl, the $t_o$ values significantly increased, but in all the tests in Table 5, we always reached the rapid hydrate formation stage within 2.5 days. This included a comparison of the benchmark from Table 4, i.e., 7500 ppm polymer (now PVCapBGE) and 5000 ppm iHexOl.

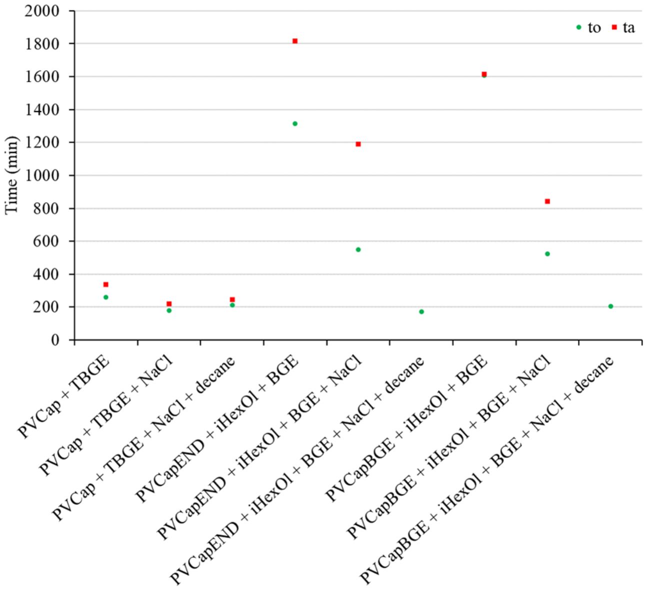

**Figure 14.** Isothermal test results at 68 bar, 4 °C. Concentrations were 7500 ppm polymer and 5000 ppm of all solvents as 15 mL aqueous solutions. Decane (1 mL) and/or 0.5 wt % NaCl was added where denoted.

Comparing the polymers PVCap and PVCapBGE, it is difficult to affirm whether the similarity in results was caused by the synergetic effect of BGE or the difference in molecular weights. Both factors have been shown to affect performance.[42,43] Therefore, we conducted some tests with PVCapBGE where the BGE was removed and some tests where BGE was added to both PVCap and PVCapEND. At a concentration of 7500 ppm, PVCapBGE with the BGE removed together with 5000 ppm iHexOl, the $t_o$ value was 1354 min and the $t_a$ value was 1741 min. Interestingly, when BGE was removed, only about 90% of the polymer dissolved, so it was tested as a cloudy solution. Comparing these values to the same ones when BGE was present, the average $t_o$ value decreased and the average $t_a$ value increased, but there is no statistical significantly different behavior as seen by the standard deviations (Table 5). The same similar performance was observed for 7500 ppm PVCapEND with 5000 ppm iHexOl and 5000 ppm BGE. In this case, addition of BGE aided the dissolution of the polymer and iHexOl.

The last round of isothermal tests was done with added hydrocarbon phase and/or saline conditions. Here, we tested a combination of the best-performing polymers with iHexOl in addition to the more water-soluble synergist TBGE (Figure 14 and Table 6). Some salinity is often present even in gas lines, so we wanted to explore the effect of added 0.5 wt % NaCl. Earlier work had suggested that sparingly soluble solvent synergists might lose their activity if they partition to the liquid hydrocarbon phase.[46] Therefore, we were interested in confirming this claim using iHexOl, which has limited water

Table 5. Isothermal Tests Conducted on PVCapEND and PVCapBGE with Synergists[a]

| substance | | concentration (ppm) | | | | |
|---|---|---|---|---|---|---|
| polymer | synergist | polymer | synergist | $t_o$ (min) | standard deviation for $t_o$ | $t_a$ (min) |
| PVCapEND | iHexOl | 5000 | 5000 | 463 | 111 | n/r |
| PVCapEND | iHexOl + BGE | 5000 | 5000 + 5000 | 1239 | 418 | n/r |
| PVCapEND | iHexOl + BGE | 7500 | 5000 + 5000 | 1315 | 247 | 1818 |
| PVCapBGE | BGE | 2500 | 2500 | 146 | 0 | 200 |
| PVCapBGE | iHexOl + BGE | 2500 | 2500 + 2500 | 163 | 2 | 172 |
| PVCapBGE | iHexOl + BGE | 2500 | 5000 + 2500 | 789 | 230 | 3360 |
| PVCapBGE | iHexOl + BGE | 5000 | 5000 + 5000 | 1352 | 290 | 1638 |
| PVCapBGE | iHexOl + BGE | 5000 | 10,000 + 5000 | 2194 | 1639 | 2949 |
| PVCapBGE | iHexOl + BGE | 7500 | 5000 + 7500 | 1606 | 530 | 1613 |
| PVCapBGE w/o BGE | iHexOl | 7500 | 5000 | 1354 | 378 | 1741 |

[a]Test conditions of 68 bar SNG, temperature of 4 °C and aqueous volume of 20 mL in each cell. n/r = not reached.

Table 6. Isothermal Tests on PVCapEND and PVCapBGE with iHexOl and TBGE as Synergists and NaCl and/or Decane[a]

| substance | | concentration (ppm) | | | | | |
|---|---|---|---|---|---|---|---|
| polymer | synergist | polymer | synergist | additive | $t_o$ (min) | standard deviation for $t_o$ | $t_a$ (min) |
| PVCap | TBGE | 7500 | 5000 | NaCl | 178 | 15 | 220 |
| PVCap | TBGE | 7500 | 5000 | NaCl + decane | 213 | 11 | 246 |
| PVCapEND | iHexOl + BGE | 7500 | 5000 + 5000 | | 1315 | 247 | 1818 |
| PVCapEND | iHexOl + BGE | 7500 | 5000 + 5000 | NaCl | 548 | 162 | 1190 |
| PVCapEND | iHexOl + BGE | 7500 | 5000 + 5000 | NaCl + decane | 172 | 17 | n/r |
| PVCapBGE | iHexOl + BGE | 5000 | 5000 + 5000 | | 1352 | 290 | 1638 |
| PVCapBGE | iHexOl + BGE | 5000 | 5000 + 5000 | NaCl | 1706 | 238 | n/r |
| PVCapBGE | iHexOl + BGE | 5000 | 5000 + 5000 | NaCl + decane | 274 | 67 | n/r |
| PVCapBGE | iHexOl + BGE | 7500 | 5000 + 7500 | NaCl | 523 | 186 | 843 |
| PVCapBGE | iHexOl + BGE | 7500 | 5000 + 7500 | NaCl + decane | 204 | 6 | n/r |

[a]68 bar SNG, 4 °C with 15 mL of aqueous solution. n/r = not reached.

Table 7. Summarized Results for SCC Experiments for 2500 ppm PVCap with 5000 ppm of iHexOl or TBGE under Harsher Conditions

| substance | | concentration (ppm) | | | | | |
|---|---|---|---|---|---|---|---|
| KHI polymer | synergist | KHI polymer | synergist | volume (ml) | additive | $T_o$ (°C) | $T_a$ (°C) |
| DIW | | | | 20 | | 17.2 | 16.6 |
| PVCap | | 2500 | | 20 | | 10.4 | 8.9 |
| PVCap | | 2500 | | 20 | 3.5 wt % NaCl + 0.2 wt % $CaCl_2$ | 8.2 | 6.2 |
| PVCap | | 2500 | | 15 | 1 mL decane | 9.5 | 8.8 |
| PVCap | iHexOl | 2500 | 5000 | 20 | | <3 | <3 |
| PVCap | iHexOl | 2500 | 5000 | 20 | 3.5 wt % NaCl + 0.2 wt % $CaCl_2$ | <3 | <3 |
| PVCap | iHexOl | 2500 | 5000 | 15 | | 4.1 | <3 |
| PVCap | iHexOl | 2500 | 5000 | 15 | 1 mL decane | 5.4 | 2.2 |
| PVCap | TBGE | 2500 | 5000 | 20 | | 5.3 | 3.2 |
| PVCap | TBGE | 2500 | 5000 | 15 | | 6.9 | 4.5 |
| PVCap | TBGE | 2500 | 5000 | 15 | 1 mL decane | 5.8 | 4.8 |

solubility, and TBGE, which is very water-soluble and not expected to partition to the hydrocarbon phase.

For a concentration of 5000 ppm of both PVCapBGE and iHexOl with 0.5 wt % NaCl, despite the lower liquid volume (which reduces the hydrate induction time), the synergetic effect improved compared to the test without NaCl. Under these test conditions, $t_a$ was not reached in the test period (3600 mins or 2.5 days), which is the first time for this polymer-and-solvent combination. The addition of NaCl can lower $T_{eq}$ for hydrate formation but the effect is weak at this salinity. For PVCapEND, the hold time $t_o$ decreased with the addition of NaCl. We are not sure of the reason behind the difference between the two polymers. The relative solubility of iHexOl with and without NaCl could be a factor, as well as the solvent's interaction with the polymer.

For both PVCapEND and PVCapBGE, we observed that further addition of 1 mL of decane reduced the hold time $t_o$, but still, there were no observable $t_a$ values at 2.5 days. The decane has two main effects. First, it lowers the equilibrium temperature, in this case by about 0.3 °C.[46] Second, it can become a solvent for the KHI formulation, in particular, iHexOl, in this study. Removal of the iHexOl from the water phase to the decane phase appears to have a significant effect on the $t_o$ value but not on the $t_a$ value.

As iHexOl has limited solubility, we wanted to use the same test conditions on a more water-soluble synergetic compound, TBGE, together with PVCap. With the lower liquid volume and NaCl added, the synergetic performance was less compared to when the liquid volume was higher and without NaCl present. Interestingly, when 1 mL of decane was added, both the $t_o$ and $t_a$ values increased, although based on the number of experiments (10), the difference is not significant. A small improvement might be expected based on the lower subcooling of the system with added decane. Importantly, the performance was certainly not lowered, indicating that the TBGE did not partition to the decane phase.

**3.3. Slow constant cooling experiment with brine and/or liquid hydrocarbon phase.** In the last round of tests, we went back to conducting SCC tests to investigate some of the conditions used in the isothermal tests that had not been tried, such as the use of 3.5 wt % NaCl or a liquid hydrocarbon phase (decane) or varying the aqueous solution volume. NaCl (3.5 wt %) was used to see the effect on iHexOl solubility at a higher salinity. The new SCC results are summarized in Table 7. These measures were implemented to the concentration of PVCap polymer and iHexOl that gave the best performance at SCC tests, namely 2500 ppm PVCap polymer and 5000 ppm iHexOl. The same concentrations were also used for PVCap with TBGE in order to shed some light on the potential role the solubility of the solvent synergist plays in the presence of a liquid hydrocarbon phase.

From Table 7, it can be observed that adding salts to PVCap improved inhibition performance. The PVCap polymer with salts gave $T_o$ and $T_a$ values of 8.2 and 6.2 °C, respectively, compared to a $T_o$ value of 10.4 °C and a $T_a$ value of 8.9 °C for PVCap alone. Salts are well known for their thermodynamic hydrate inhibition properties.[47,48] PVCap polymer and iHexOl gave no hydrates below 3 °C with or without salts. This is despite the solution being cloudy, which we believe is due to the lower solubility of iHexOl.

Reducing the aqueous volume to 15 mL gave a worse result as observed previously in the same equipment.[49] This is clearly seen for PVCap with iHexOl and with TBGE. Lowering the liquid volume will make the system more favorable for gas hydrate formation because there would be more shear forces, resulting in more turbulence and mixing of the different phases. Thus, the gas−liquid interface would be increased. Addition of 1 mL of decane to the 15 mL aqueous solution of PVCap and iHexOl gave a worse result with the $T_o$ now at 5.4 °C.

For the system only consisting of PVCap polymer, it is possible that the liquid hydrocarbon phase could interact with the hydrophobic part of the polymer and reshape the structure so that the surface/volume ratio of the polymer structure increased. To investigate these hypotheses, we tried the same conditions but used a more water-soluble solvent in TBGE together with PVCap. Compared to the system without added decane, there was a clear improvement in the synergetic performance for the $T_o$ value while the $T_a$ value had a minor decrease. The same trend was also observed under the isothermal experiments. Since TBGE is very water-soluble and probably does not partition to the decane phase, we presume that the performance improvement comes from lowering the equilibrium temperature of the system by adding decane. This could indicate that the less water-soluble solvent in iHexOl is likely partly partitioning in the liquid hydrocarbon phase, thus partly losing the synergetic activity in the water phase. Although the equilibrium temperature of the system is lowered by introducing decane, the partitioning effect would counteract this. We recently demonstrated this partitioning effect for the acetylenic diol gemini surfactant 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD).[46] Since some liquid hydrocarbon phase is often present even in gas flow lines, these results provide further confirmation that the solubility of the solvent must be optimized so that it is not lost to the hydrocarbon phase.

Both the SCC and isothermal tests with and without the harsher conditions of added salt and decane, together with our findings in a previous study, show that iHexOl still has an outstanding synergetic performance with PVCap polymers.[24] We speculated that the branched tail and maximum hydrophobicity without losing water solubility were key features. One possible reason for the solvent synergetic performance could lay in the fact that iHexOl may form structure II hydrates by stabilizing $5^{12}6^4$ cages. This has been reported to be the case for 1-pentanol with a $NH_4^+$ and $F^-$ ion-doped hydrate.[50] Alcohols possess both a hydrophilic part and a hydrophobic part. The hydrophilic part can destabilize the hydrogen-bonded water cages while the hydrophobic part can stabilize the host framework. For potential guest molecules of alcohols in the range of two to five carbon atoms that have complex hydrophilic and hydrophobic features, the balance can be shifted toward hydrate formation by using hydrophobic helper gases like methane or xenon.[51−58] Although the molecular size may be too big to be able to stabilize $5^{12}6^4$ cages based on van der Waals radii, these relatively large molecules can still fit into the large cages of structure II hydrate. This is possible because of the guest-to-host hydrogen bonding between the hydroxyl group of the alcohols and host water molecules.[1,54] iHexOl fits into this latter category, with its molecular size being on the limit to be able to stabilize $5^{12}6^4$ cages of structure II hydrate in addition to the limit in water solubility (maximum hydrophobicity).

## 4. CONCLUSIONS

We have expanded our initial study on solvent synergists for PVCap with focus on 4-methyl-1-pentanol (iHexOl) using both SCC as well as isothermal tests.[24] All tests were conducted by utilizing high-pressure KHI experiments with a SNG that preferentially forms structure II gas hydrates as the most thermodynamically stable phase. We included altering the iHexOl concentration when added to different PVCap polymers, polymerizing PVCap in iHexOl and using added decane as a liquid hydrocarbon phase as well as brines. In addition, we investigated a few more solvents, some of which were recommended from the earlier study but were not available.

Both SCC and isothermal experiments highlighted that it is important to find the right concentrations for both PVCap and iHexOl when used together. For example, increasing the solvent concentration from 5000 to 10,000 ppm led to worse KHI performance. This may be due to changes in polymer−solvent interactions as well as iHexOl being above its solubility limit. The undissolved droplets of iHexOl could possibly act as nucleation sites for hydrate or even a solvent for partitioning of the PVCap. PVCap polymerized in iHexOl gave a surprisingly poor KHI test result on SCC tests, which is possibly caused by the initiator incorporating isohexyl groups from the solvent into the polymer, thus changing the polymer conformation.

In conjunction with the results from the SCC tests, isothermal tests also indicate that through the optimal combination of KHI polymer and synergist, the gas hydrate growth rate is maintained at a low formation rate for a considerable amount of time. This means that although there is gas hydrate growth in the system, its rate is maintained at a low growth rate, giving the operative personnel adequate time to take action.

A glycol ether version of iHexOl, iHex(EO)Ol, did not give better synergetic performance with PVCap. However, a monoglycol ether analog of 4-methylcyclohexanol gave better synergetic performance with PVCap polymer, but the diglycol ether did not.

The branching and placement of the alkyl "tail" were found to be important structural features to optimize in alcohols and glycol ether synergists. Two isomers of iHexOl (2-methyl-1-pentanol and 3-methyl-1-pentanol) showed good but poorer synergetic performance with PVCap polymer than iHexOl. For the glycol ethers, we showed that di(propylene glycol)butyl ether (DPGBE) (methyl branches) gave a better synergetic performance than butyl diglycol ether (DBGE) (no branching) with PVCap.

Besides tail-branching in the synergist, a cyclic alkyl "tail" can also be beneficial for the synergetic performance but not if the ring is aromatic. Phenol was detrimental and 2-phenoxyethanol gave no synergetic performance with PVCap. In contrast, cyclohexanol gave a good synergetic performance with PVCap polymer. Two cyclic ketones, 4-methylcyclohexanone and cycloheptanone, gave a good synergetic effect with the PVCap polymer. Given that butylated oxygenated solvents are well-known synergists for PVCap, we investigated a new ester solvent, 2-*n*-butoxyethyl acetate, and showed that it gave good synergetic performance.

Isothermal tests showed that iHexOl had good synergetic performance with different PVCap polymers. The further addition of BGE also improved performance and could act as a cosolvent to improve the solubility of sparingly soluble iHexOl. However, when decane was added to the cells (SCC or isothermal tests), the KHI performance decreased significantly when using iHexOl but improved a little when TBGE was added. We speculate that this is caused by the difference in the hydrophilicity between the solvents. The less water-soluble iHexOl partitions far more to the decane phase (rendering it unavailable for hydrate inhibition) than for TBGE. Since some liquid hydrocarbon phase is often present even in gas flow lines, it is important to check the partitioning of the solvent in this phase.

The optimal molecular weight distribution for the KHI polymer when used with a solvent synergist is not the same as the optimum distribution when using the polymer alone. In this study, PVCap ($M_w$ = 10,000 g/mol) gave better synergy than PVCap ($M_w$ = 2000 g/mol) with solvent synergists such as iHexOl. This may be because the low $M_w$ polymer fraction (closer to the synergist size) prevents smaller gas hydrate particle growth (e.g., nucleation), whereas the higher $M_w$ fraction prevents growth more of larger particles. This fits with the Japanese modeling work of Yagasaki et al. using the Gibbs–Thompson effect.[59−61]

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### Notes

The authors declare no competing financial interest.

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# Paper V

Powerful Synergy of Acetylenic Diol Surfactants with Kinetic Hydrate Inhibitor Polymers—Choosing the Correct Synergist Aqueous Solubility

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Article

# Powerful Synergy of Acetylenic Diol Surfactants with Kinetic Hydrate Inhibitor Polymers—Choosing the Correct Synergist Aqueous Solubility

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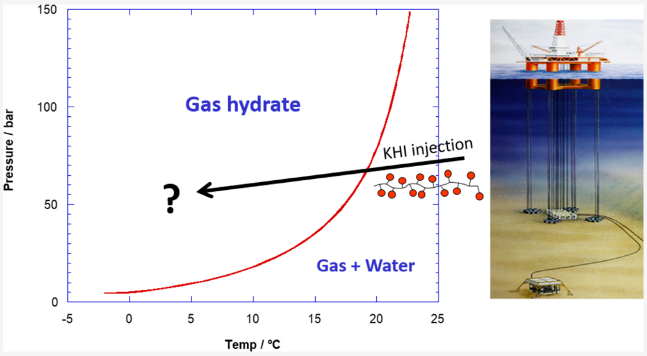
**ABSTRACT:** The performance of injected kinetic hydrate inhibitor (KHI) polymer solutions can be boosted considerably by judicious choice of the polymer solvent system. We report the excellent KHI synergism of the low-foaming acetylenic diol gemini surfactant 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD) with poly(*N*-vinyl caprolactam), *N*-vinyl caprolactam:*N*-vinyl pyrrolidone copolymer, and poly(*N*-isopropylmethacrylamide). High-pressure rocking cell tests, using the slow constant cooling method or the isothermal method, were carried out with a natural gas mixture giving structure II hydrates as the preferred thermodynamically stable phase. Poly(oxyethylene) derivatives of TMDD, which are far more water-soluble than TMDD, gave significantly lower synergetic KHI performance with the same polymers. It is conjectured that the low aqueous solubility of TMDD (1700 ppm at 20 °C) and its two isobutyl groups are key features contributing to the synergism. However, when decane was added to the system as a model liquid hydrocarbon phase, the synergetic performance decreases, probably due to partitioning of TMDD to the hydrocarbon phase. This highlights the need to choose synergist systems which are retained in the aqueous phase for optimal performance when condensate or oil is present in the produced fluids. Optimizing the structure and aqueous solubility of the synergist (solvent or otherwise) can be seen as complementary to the known principle of optimizing the structure and solubility of the KHI polymer.



## 1. INTRODUCTION

Gas hydrates are ice-like solids that are formed under conditions of elevated pressure and low temperatures, which are common conditions in gas and oil transportation flow lines.[1−3] These flow lines may be subsea or on land in cold-climate regions. Gas hydrate blockages in flow lines are a major challenge for flow assurance in the upstream gas and oil industry.[4−10] The most common chemical method to prevent gas hydrate blockages is the use of thermodynamic inhibitors (antifreezes), such as methanol, monoethylene glycol, and electrolytes.[11,12] However, high concentrations (often 20−60 wt % of the water present) are required, necessitating high capital and operational costs.[13]

An alternative method that has been in use since the mid-1990s is deployment of kinetic hydrate inhibitors (KHIs).[13−17] The main component of a liquid and pumpable KHI formulation is one or more water-soluble polymers in one or more solvents. The solvent and various classes of non-polymeric synergists can be added to improve the performance. Typical effective polymers include poly(*N*-vinyl caprolactam) (PVCap) and poly(*N*-*iso*-propyl methacrylamide) (PNIPMAM) and copolymers thereof (Figure 1). Both PVCap and PNIPMAM have quite low cloud points in water at typical KHI polymer dosages of 0.1−1.0 wt % based on the water phase. We proposed that a low polymer cloud point (i.e., near-hydrate-forming temperatures) is a useful property for high KHI performance as long as certain other criteria are met.[18] These included sufficient pendant amphiphilic groups with good hydrogen-bonding (e.g., amide or amine oxide) and correct-size hydrophobic groups. Placing these groups in a low-molecular-weight polymer or oligomer can be beneficial for KHI performance because it gives a high polymer surface area/hydrodynamic volume (or surface area/weight) ratio and often a lower cloud point than higher-molecular-weight polymers.

Following on from this study, we determined that alcohols and glycols, which also were close to their solubility limit at

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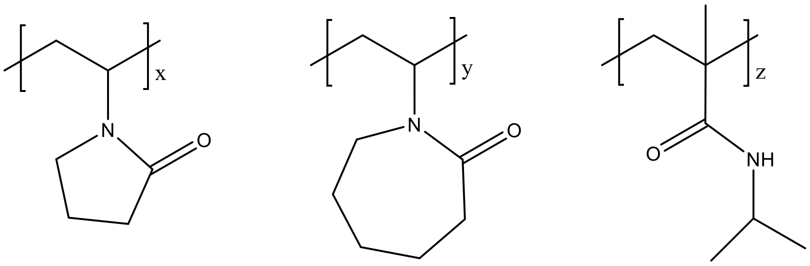

**Figure 1.** Structures of typical KHIs. From right to left: PVP, PVCap, and PNIPMAM.

typical KHI dosages and had the correct-size hydrophobic groups, performed well as KHI synergists for PVCap.[19] In particular, 4-methylpentan-1-ol (iHexOl) showed remarkable synergy, greater than classic KHI solvents such as butyl glycol ether (BGE). 4-Methyl-1-pentanol has a flash point of 57 °C and a water solubility of 7.6 g/L (i.e., 7600 ppm) at 20 °C, which is in the range of the KHI polymer solvent at typical field dosages. Another alcohol with a similar solubility is cycloheptanol. This also showed better synergy with PVCap than smaller cycloalkanols.

Recently, another class of synergists, those of ethoxylated acetylenic diols, was shown to give good synergy with a 1:1 commercial VP/VCap copolymer.[20] These synergists are nonionic surfactants, also sold under the trade names Surfynol 465 and Surfynol 485, with the chemical names being 2,4,7,9-tetramethyl-5-decyne-4,7-diol decaethoxylate (TMDD-EO10) and TMDD tricontaethoxylate (TMDD-EO30). In high-pressure tests using methane gas, a 1:2 mixture of VP/VCap copolymer and TMDD-EO10 gave the best performance. TMDD-EO10 is characterized by high solubility in water, low foaming, and lower cost than the vinyl lactam-based KHI.

Based on our earlier work regarding the powerful synergy of the sparingly soluble iHexOl with PVCap, it occurred to us that it might be possible to increase the synergy of TMDD-EO10 by reducing or even removing the ethoxylate groups to give a surfactant that is more sparingly soluble in water, just a few thousand ppm. The unethoxylated surfactant is TMDD. It is used on a large scale as a wetting and antifoaming agent in the paper, ink, pesticide, and adhesive industries.[21] The physicochemical properties indicate only slow biodegradation, but due to its HLB of about 8, it has low bioaccumulation potential.

The solubility of TMDD in water is about 0.2 g/L (2000 ppm) at 20 °C which we thought was about the right level for a sparingly soluble KHI polymer synergist.[22] TMDD is made by the reaction of methyl isobutyl ketone with a base and two equivalents of sodium carbide or ethyne.[23] In the process of making TMDD, the intermediate 5-methyl-1-hexyn-3-ol (5-MH) is formed. This is also commercially available. TMDD is a gemini surfactant with two isobutyl groups, whereas 5-MH has only one. This study investigates the synergistic properties of 5-MH, TMDD, and TMDD-EO10 with PVCap and PNIPMAM in high-pressure slow constant cooling (SCC) experiments with a synthetic natural gas mixture. Experiments to study the effect of the addition of a liquid hydrocarbon to the KHI test solution were also carried out.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials.

1-Bromo-2-methyl-propane, tetrahydrofuran, TMDD (mixture of ± and meso), TMDD decaethoxylate, and 5-methyl-1-hexyne-3-ol were purchased from VWR (Avantor). PVCap ($M_w$ = 8−10 kg/mol) was supplied from BASF as a 41.1 wt % ethylene glycol solution but with the solvent being removed. A lower-molecular-weight PVCap (Inhibex 101, abbreviated here as PVCap/BGE) was supplied by Ashland chemical company as a 50 wt % solution in BGE.

### 2.2. KHI Performance Tests.

Similar to many of our previous studies, the KHI performance tests were carried out in a high-pressure rock rig with five cells (RC5), supplied by PSL Systemtechnik, Germany.[24−26] Each cell contains a stainless-steel ball (ca. 15 mm diameter) for agitation of the fluids. A synthetic natural gas (SNG) mixture (Table 1) was used to provide the high-pressure gas hydrate formation atmosphere. The SNG was prepared by Praxair, Norway, and the composition was analyzed before sale to be within ±0.1% of all the required concentrations. For the sensors, the maximum pressure error is ±0.2 bar and the maximum temperature error is ±0.1 °C, as previously reported.[27] Pressure and temperature sensors are calibrated using the "calibration dialogue" box in the rocking cell software.

**Table 1. Composition of the SNG Mixture**

| component | mol % |
|---|---|
| nitrogen | 0.11 |
| *n*-butane | 0.72 |
| isobutane | 1.65 |
| propane | 5.00 |
| $CO_2$ | 1.82 |
| Ethane | 10.3 |
| methane | 80.4 |

### 2.3. SCC Tests.

These were carried out to evaluate the KHI performance of the polymers and synergists. The procedure for SCC tests was as follows:

1. Around 105 mL of KHI solution with dissolved maleamide polymers in it was prepared at least 1 day before the KHI performance tests to ensure complete dissolution. Around 20 mL of the KHI solution was added to each cell.
2. The procedure of purging with SNG and then vacuum was applied twice to remove the air in the system.
3. Approximately 76 bars of SNG was loaded to each cell at a temperature of 20.5 °C. The gas inlet/outlet valve of each cell was then turned off, so each cell was a separately closed system. The equilibrium temperature ($T_{eq}$) for sII gas hydrate at 76 bar was predicted to be 20.5 °C using the PVTSim software, Calsep.[28]
4. The cells were slowly cooled down at a cooling rate of 1 °C/h and rocked at a rocking rate of 20 full swings/min with maximum 40°. The pressure and temperature data during the cooling period were recorded using sensors.

An example of the pressure−time and temperature−time curves obtained from one experiment is shown in Figure 3.

The determination of hydrate onset temperature ($T_o$) and rapid hydrate formation temperature ($T_a$) from the temperature and pressure curves obtained from one cell can be seen in Figure 4. In the closed system, the pressure decreased linearly due to the constant

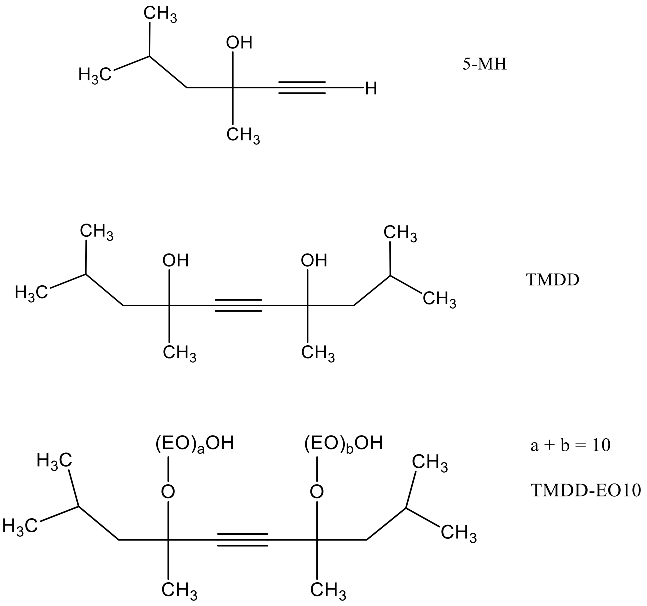

**Figure 2.** 5-Methyl-1-hexyn-3-ol (5-MH); TMDD; and TMDD decaethoxylate (TMDD-EO10).

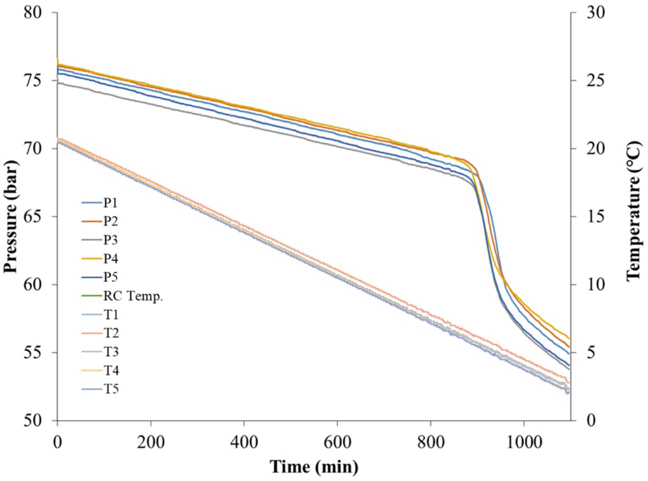

**Figure 3.** Example of a set of SCC pressure−time and temperature−time graphs obtained from all five cells. (RC temp. is the cooling bath temperature).

cooling of the temperature. Once gas hydrates started to form, the pressure deviated from the original linear track, and this first pressure drop point was marked as $P_o$. The corresponding temperature at $P_o$ was determined as $T_o$. The fastest pressure drop point was marked as $P_a$ and its corresponding temperature was determined as $T_a$.

**2.4. Isothermal Test Procedure.**[29] The flushing of the rocking cells was carried out as the same as for the SCC tests. Then, the cells were charged with 75 bar SNG at 20.5 °C. The fluids were cooled with rocking (the same rate as for SCC tests) to the experimental temperature (6.0 or 4.0 °C) and held at this temperature for at least 48 h. When the cells are cooled to 4 °C, the pressure drops to ca. 68 bar. The equilibrium temperature ($T_{eq}$) is ca. 19.8 °C at this pressure predicted using PVTSim software. This means that the subcooling ($\Delta T$) is ca. 15.8 °C. The starting time at the set temperature is taken as time zero. From the pressure drop or gas consumption curves, as shown in Figure 5, it is possible to determine the hold time, $t_i$, as the start of detectable hydrate formation, and the fast hydrate growth time, $t_a$, as the time when the growth rate is first at its fastest. It should be noted that nucleation may have started before the hold time.

## 3. RESULTS AND DISCUSSION

The results obtained from SCC tests are summarized in Table 2. Deionized water (DIW) and PVCap ($M_w$ = 8−10 kg/mol) by itself were also tested for comparison. Results of synergetic tests with mono-*n*-BGE, butyl diglycol ether (BDGE), and 4-methyl-1-pentanol (iHexOl) are included from previous studies carried out by the same person, under identical test conditions and in the same equipment.[19]

We begin a discussion of the results by looking at the motivation for this study, that is, whether TMDD is a better synergist for KHI polymers than the more water-soluble TMDD-EO10. The SCC test results in Table 3 clearly show that TMDD or TMDD-EO10 used alone is very poor KHIs with average $T_o$ values only a little better than water. For PVCap, the synergy of TMDD-EO10 is a little weaker than that for BGE. TMDD-EO10 shows negligible synergy with the VP/VCap copolymer and only weak synergy with PNIPMAM. However, when used in combination with all three polymers, TMDD (5000 ppm) is a far better synergist than TMDD-EO10. The synergy of TMDD appears to be the most powerful (greatest drop in onset temperature) for PVCap with the average $T_o$ dropping from 10.4 °C for PVCap alone to no hydrates at a minimum test temperature of 2 °C. Using a lower concentration of TMDD (2500 pm) gives a smaller decrease in the onset temperature, now with a measurable average $T_o$ value of 4.3 °C. The only alcohol previously found to have comparable synergy in blends with PVCap is iHexOl, which also gave no hydrates down to the minimum test temperature, in this case, 3 °C.

TMDD and the ethoxylated derivatives are unusual small di amphiphiles that have a triple bond in the middle. We speculate that the strong synergy of TMDD is related to several factors, including solubility, dual hydrophobic head groups, and the optimum shape and size of these isobutyl groups. These factors are discussed below. The alkyne triple bond may also be important for the KHI synergy by having no rotation and fixing the two isobutyl end groups to be kept away from each other. We would have liked to investigate the hydrogenated version of TMDD, which would have a C−C single bond in the middle that does rotate, but this was not commercially available.

TMDD at 5000 ppm gives a cloudy solution either alone or when mixed with 2500 ppm of the polymers. According to various nonpeer-reviewed online sources, the solubility of TMDD (or Surfynol 104 as one of its trade names) at 20 °C is 1.7 g/L (1700 ppm). We checked the limit of solubility in our hands and we found that solutions up to 900 ppm gave clear solutions but 1000 ppm and higher concentrations gave some insoluble materials as small flakes. This may change during SCC tests as the temperature decreases to 2 °C. The solubility of TMDD is thus fairly low. In comparison, the synergist solvent iHexOl has a solubility of 7.6 g/L in water (7600 ppm) at 20 °C, somewhat higher than that of TMDD.[19] As discussed previously, it seems that alcohols or glycols, with the correct-size and -shape hydrophobic alkyl groups, when applied close to their solubility limits are good synergists particularly for PVCap (We will be exploring the synergy of iHexOl with polymers other than PVCap in a subsequent publication). When close to the solubility limit, a solvent will give maximum hydrophobic interactions with bulk water or growing hydrate particles. This solubility factor is akin to the improved performance of KHI polymers when they have low cloud

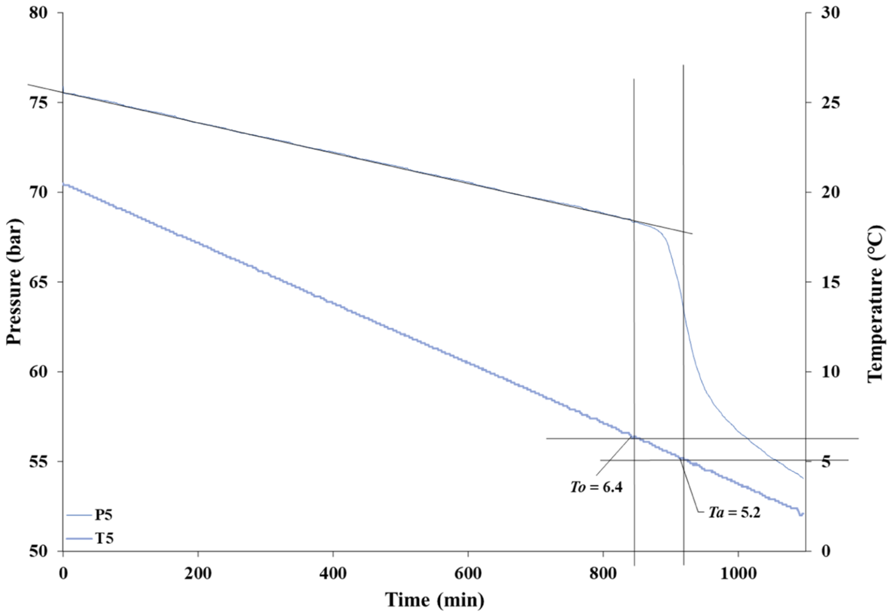

**Figure 4.** Determination of $T_o$ and $T_a$ values for one rocking cell.

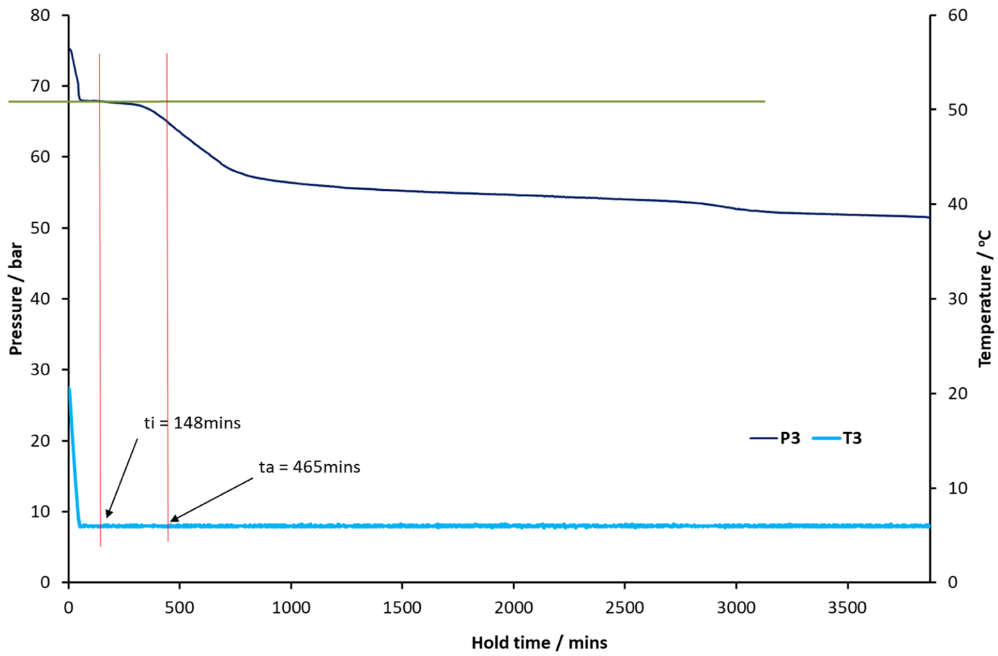

**Figure 5.** Determination of hold time ($t_i$) and fast growth time ($t_a$) in an isothermal test in cell 3 at 6.0 °C and 68 bar ($\Delta T$ ca. 13.8 °C).

points (less than about 40 °C), for example, PVCap or PNIPMAM.[18]

TMDD can be thought of as having two terminal isobutyl groups (Figure 2). The usefulness of isobutyl groups in solvent synergists has also been seen previously. We suggested that tail-branched alkyl groups, such as isobutyl, give better synergy with PVCap than the straight chain. See, for example, results in Table 3 for the glycols BGE and isobutyl glycol ether (iBGE) in combination with PVCap or PNIPMAM.[30]

The final factor we considered as important for the powerful synergy of TMDD is that it contains two hydrophobic groups. To determine the significance of the twin hydrophobic end groups, we also investigated 5-MH, which is as close to half the molecule as is commercially available, with only one isobutyl end group. The addition of 5000 ppm 5-MH to PVCap gave good synergy, on a par with iBGE or BDGE, but clearly not as good as either TMDD or iHexOl. There are probably two reasons for this observation. Solutions of 5000 ppm 5-MH alone or with 2500 ppm polymer are clear at 20 °C indicating that 5-MH is more soluble in water than TMDD or iHexOl. As discussed earlier, sparingly soluble solvents, with the correct-size and -shape hydrophobic groups, appear to give better synergy than more soluble solvents as this maximizes the hydrophobic interactions with water or hydrate particles.

**3.1. Effect of the Gas–Water Ratio and Liquid Hydrocarbon Phase.** Gas fields with associated produced water are currently the main application for KHIs. Gas fields usually have some liquid hydrocarbon production. Therefore, as we knew that TMDD was sparingly soluble in water, we wanted to investigate the effect of adding some liquid

Table 2. Summary Information of KHI SCC Tests[a]

| polymer | synergist | [synergist] ppm | $T_o$ (av.) ± deviation [°C] | $T_a$ (av.) ± deviation [°C] | $T_o$ (av.) − $T_a$ (av.) [°C] |
|---|---|---|---|---|---|
| DIW | | | 17.2 ± 0.6 | 16.7 ± 0.5 | 0.5 |
| | 5-MH | 5000 | 16.7 ± 0.4 | 16.1 ± 0.5 | 0.6 |
| | TMDD[d] | 5000 | 15.6 ± 0.4 | 15.2 ± 0.4 | 0.4 |
| | TMDD-EO10 | 5000 | 15.7 ± 0.3 | 15.5 ± 0.3 | 0.2 |
| PVCap | | | 10.2 ± 0.3 | 8.8 ± 0.5 | 1.4 |
| PVCap | -[b] | | 10.6 ± 0.5 | 9.3 ± 0.1 | 1.3 |
| PVCap | -[c] | | 9.5 ± 0.2 | 8.8 ± 0.2 | 0.7 |
| PVCap | BGE | 5000 | 7.3 ± 0.4 | 3.8 ± 0.4 | 3.5 |
| PVCap | BDGE | 5000 | 5.5 ± 0.4 | 2.9 ± 0.4 | 2.6 |
| PVCap | iBGE | 5000 | 5.7 ± 0.4 | 2.5 ± 0.3 | 3.2 |
| PVCap | iHexOl | 5000 | <3.0 | <3.0 | |
| PVCap | 5-MH | 5000 | 5.4 ± 0.4 | 3.9 ± 0.3 | 1.5 |
| PVCap | TMDD[d] | 2500 | 4.3 ± 0.5 | 3.0 ± 0.3 | 1.3 |
| PVCap | TMDD[d] | 5000 | <2.0 | <2.0 | |
| PVCap | TMDD[bd] | 5000 | 2.8 ± 0.2 | 2.2 ± 0.2 | 0.6 |
| PVCap | TMDD[d] | 5000 | 5.9 ± 0.5 | 4.8 ± 0.5 | 1.1 |
| PVCap | TMDD-EO10 | 2500 | 8.8 ± 0.3 | 7.8 ± 0.2 | 1.0 |
| PVCap | TMDD-EO10 | 5000 | 8.3 ± 0.4 | 8.0 ± 0.3 | 0.3 |
| VP/VCap | | | 8.1 ± 0.9 | 5.7 ± 0.4 | 2.4 |
| VP/VCap | BDGE | 5000 | 6.8 ± 0.4 | 4.2 ± 0.3 | 2.6 |
| VP/VCap | 5-MH | 5000 | 7.0 ± 0.6 | 4.5 ± 0.4 | 2.5 |
| VP/VCap | TMDD[d] | 5000 | 5.5 ± 0.4 | 3.7 ± 0.3 | 1.8 |
| VP/VCap | TMDD-EO10 | 5000 | 8.2 ± 0.6 | 5.9 ± 0.2 | 2.3 |
| PNIPMAM | | | 10.5 ± 0.8 | 10.2 ± 0.6 | 0.3 |
| PNIPMAM | BGE | 5000 | 6.2 ± 0.8 | 5.0 ± 0.3 | 1.2 |
| PNIPMAM | iBGE | 5000 | 5.5 ± 0.5 | 4.2 ± 0.2 | 1.3 |
| PNIPMAM | iHexOl | 5000 | 4.6 ± 0.8 | 2.9 ± 0.3 | 1.7 |
| PNIPMAM | 5-MH | 5000 | 7.2 ± 0.2 | 5.5 ± 0.2 | 1.7 |
| PNIPMAM | TMDD[d] | 5000 | 5.8 ± 0.4 | 3.2 ± 0.4 | 2.6 |
| PNIPMAM | TMDD-EO10 | 5000 | 8.8 ± 0.4 | 8.2 ± 0.2 | 0.6 |

[a]Average of five tests using 20 mL of aqueous solution unless otherwise stated. [b]15 mL. [c]15 mL + 1 mL decane. [d]Cloudy solution.

Table 3. Isothermal Test Results Using 2500 ppm PVCap and Synergist

| polymer | concn. Ppm | synergist | concn. ppm | temp. °C | ΔT °C | hold time ($t_o$) min | fast growth time ($t_a$) min |
|---|---|---|---|---|---|---|---|
| PVCap | 2500 | | | 6 | 13.8 | 80−90[a] | 80−100[a] |
| PVCap | 2500 | iBGE | 5000 | 6 | 13.8 | 117, 119, 148, 128, 123 (Av. 127) | 421, 398, 465, 476, 487 |
| PVCap | 2500 | TMDD | 5000 | 4 | 15.8 | 523, 826, 716, 679, 572 (Av. 663) | 763, 1180, 1063, 968, 899 (Av. 974) |
| PVCap | 2500 | TMDD[b] | 5000 | 4 | 15.5[c] | 95−100[d] | 95−100 |
| PVCap | 7500 | | | 4 | 15.8[e] | 100−150 | 100−155 |
| PVCap | 7500 | TMDD | 5000 | 4 | 15.8[e] | 624, 366, 348, 371, 286 (Av. 398) | <1 bar pressure drop due to hydrates in 3600 min |
| PVCap | 7500 | TMDD | 5000 | 4 | 15.5[bce] | 324, 279, 282, 263, 272 (Av. 284) | <1 bar pressure drop in 3600 min |

[a]Hydrates formed before reaching 4 °C. [b]1 mL of decane was also added. [c]Calculated.[28] [d]Hydrate formation started in all cells on reaching approximately 4 °C. [e]15 mL of aqueous solution.

hydrocarbon to the test cells as some of the TMDD might partition to this phase lowering its activity in the aqueous phase. We also lowered the total liquid volume to 16 mL, made up of 15 mL of aqueous phase and 1 mL of decane as a model hydrocarbon phase.

Reducing the liquid volume to 16 mL made sure the steel balls are not fully covered in liquid, which could affect the efficacy in rocking cell tests. An earlier study with *N*-vinyl lactam-based polymers has shown that reducing the volume of the aqueous KHI solution from 20 to both 15 to 10 mL gave a small but significant reduction in the performance (SCC or isothermal tests).[31]

Reduction of the aqueous PVCap solution (2500 ppm) from 20 to 15 mL gave slightly higher average $T_o$ (10.2 °C for 15 mL instead of 10.6 °C) and $T_a$ values but statistically insignificant at the 95% level given the variation in test results. However, 15 mL of a solution containing 2500 ppm PVCap and 5000 ppm TMDD gave a significantly higher $T_o$ value of 2.8 °C compared to using 20 mL of solution which gave no macroscopic hydrates down to a minimum temperature of 2 °C. Furthermore, when 1 mL of decane as a model liquid hydrocarbon was added to 15 mL of the same synergistic mixture, the average $T_o$ value increased to 5.9 °C. We believe that the poorer KHI performance is related to the partitioning of the sparingly water-soluble TMDD to the decane phase. We have attempted to determine the partitioning percentage in using the mixture of water and decane and TMDD shaken in a separation funnel, but the formation of emulsion layers has so far precluded reaching a quantitative conclusion. However, the water that does separate is no longer cloudy, suggesting loss of dispersed TMDD from the initially cloudy aqueous phase.

We wondered if the good synergetic effect of the sparingly soluble TMDD may be due to coating the surfaces of the cell or walls with the chemical, reducing the access of gas or water to the metal surfaces which in turn could inhibit hydrate heteronucleation. However, other sparingly soluble chemicals such as 1-hexanol or 1-octanol showed poor synergy with PVCap, as do a number of film-forming corrosion inhibitor surfactants, so we believe that the powerful synergetic effect of TMSS is related to its structure and not just the low solubility.[19,32,33] In addition, TMDD when tested by itself had a very little effect on the KHI performance giving $T_o$ values only 1.5−2.0 °C lower than using no additive (Table 2).

Although the $T_o$ value is the most important parameter in SCC tests, the $T_a$ value and especially the $T_o - T_a$ value can give a measure of the ability to slow the growth of the nucleated gas hydrates. As seen in Table 2, many solvent synergists not only lower the $T_o$ value but also lower the $T_a$ value even more compared to using the KHI polymer alone. For example, for PVCap, the average $T_o - T_a$ value is significantly greater when good solvent synergists such as iBGE or TMDD are added. The $T_o$ value for the blend of TMDD with iHexOl gave such low $T_o$ values (ca. 3 °C) that rapid hydrate growth giving $T_a$ values was not obtained even at a minimum test temperature of 2 °C. For the blend with added decane, the $T_o - T_a$ value is only 0.6 °C. This is not very high compared to some other synergist blends. However, the subcooling increases as $T_o$ decreases such that it becomes increasingly more difficult to prevent rapid hydrate growth as the thermodynamic driving force (chemical potential) for hydrate formation increases.

**3.2. Isothermal KHI Test Results.** For further conformation of the powerful synergism of TMDD with PVCap, we carried out a series of isothermal tests (Table 3). We used just 20 mL aqueous solutions and the same SNG for these tests as used in the SCC tests. With no liquid hydrocarbon phase at approx. 68 bar and a test temperature of 6.0 °C, 2500 ppm PVCap formed hydrates before reaching this temperature. Cooling to 6 °C takes about 120 min so that the hold time ($t_i$) measured from the start of cooling was in the range 80−90 min. iBGE has previously been shown to be a good synergist for PVCap, somewhat better than *n*-BGE.[19] In the isothermal tests at 6 °C, the addition of 5000 ppm iBGE to 2500 ppm PVCap did not have much effect on the hold time (117−148 min), but the time to fast growth ($t_a$) was considerably longer, 398−509 min.

Tests with 2500 ppm PVCap plus 5000 ppm TMDD were conducted at 4 °C, as we expected the hold times were much higher than those for iBGE based on the SCC test results. When the cells are cooled to 4 °C, the pressure drops to ca. 67 bar. Cooling to 4 °C takes about 155 min. The equilibrium temperature ($T_{eq}$) is ca. 19.8 °C at this pressure predicted using PVTSim software giving a subcooling ($\Delta T$) of about 15.8 °C. The addition of TMDD to the PVCap increased the hold time to the range 523−826 min, significantly higher than adding iBGE and at 2 °C lower temperature. This indicates the powerful synergism of TMDD. The pressure drop during rapid hydrate growth varied greatly between tests, sometimes dropping to as low as 30 bar.

To confirm the trends from the SCC tests with added decane, we conducted further isothermal tests with added 1 mL of decane as an artificial liquid hydrocarbon phase. The subcooling was reduced by this addition to approximately 15.5 °C calculated using PVTSim software.[29] The same blend of 2500 ppm PVCap with 5000 ppm TMDD now gave much worse performance with hydrates forming in all cells at about the time when a minimum temperature of 4 °C was reached. As with the SCC tests, we believe that the poorer result is due to TMDD partitioning to the decane phase.

The SCC tests with added decane showed that the addition of TMDD still gave a synergetic improvement in performance. Therefore, in order to see the synergy in an isothermal test, we conducted tests with a higher concentration of KHI polymer, 7500 ppm PVCap, with 5000 ppm TMDD. As shown in Table 2, without the TMDD synergist, hydrates form before reaching a minimum temperature of 4 °C. With the synergist and no decane, the average hold time was 398 min. More interestingly, there was no major pressure drop even after 3500 min (nearly 2.5 days). After this time, the total pressure drop was less than 1 bar. This was a major improvement on crystal growth inhibition compared to the synergistic blend with only 2500 ppm PVCap. Vinyl caprolactam-based polymers such as PVCap are known to be good hydrate crystal growth inhibitors. Therefore, at such a small amount of water-to-hydrate conversion, it is possible that the hydrates are still dispersed in the aqueous phase and not agglomerated or deposited.[34,35]

When 1 mL of decane was added to the same system of 7500 ppm PVCap and 2500 ppm TMDD, the hold times decreased relative to the system without decane. This agrees with the SCC tests. The average hold time dropped from 398 to 284 min. This is still significantly better than 7500 ppm PVCap by itself, suggesting that some TMDD was still active in the aqueous phase for a synergetic effect.

## 4. CONCLUSIONS

The KHI performance of several well-known KHI polymers, PVCap, *N*-vinyl caprolactam/*N*-vinyl pyrrolidone copolymer, and poly(*N*-isopropylmethacrylamide), was significantly boosted by blending with the low-foaming acetylenic diol gemini surfactant TMDD. This was borne out in both SCC and isothermal high-pressure rocking cell experiments. More water-soluble ethoxylated versions of TMDD or the use of 5-MH with a single isobutyl group did not give good synergy. We believe that the low aqueous solubility of TMDD (1700 ppm at 20 °C) and the presence of two isobutyl groups are key features contributing to the synergism.

The addition of decane as a model liquid hydrocarbon phase lowered the synergetic performance of polymer blends with TMDD in both the SCC and isothermal tests. This is probably due to partitioning of TMDD to the hydrocarbon phase. This study highlights the need to choose solvent synergist systems carefully. In future studies, we will be exploring the effect of the added liquid hydrocarbon phase on both KHI polymers and solvent synergists in more detail. We will also explore the effect of a structure I hydrate-forming gas (methane) and salinity with a range of synergist solvents, including other sparingly soluble solvents with structural features similar to TMDD. We predict that solvent synergists that do not significantly partition to the liquid hydrocarbon phase (condensate or oil) should not lose their synergetic effect with KHI polymers as much as more sparingly water-soluble solvent synergists. Thus, just as one can tailor the solubility of a KHI polymer as one of the factors involved in obtaining optimal performance in a given system, this principle also holds for the solvent synergist.

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### Notes

The authors declare no competing financial interest.

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# Paper VI

Boronic and Organic Acids as Synergists for a Poly(*N*-vinylcaprolactam) Kinetic Hydrate Inhibitor

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Article

# Boronic and Organic Acids as Synergists for a Poly(*N*-vinylcaprolactam) Kinetic Hydrate Inhibitor

Malcolm A. Kelland* and Erik G. Dirdal

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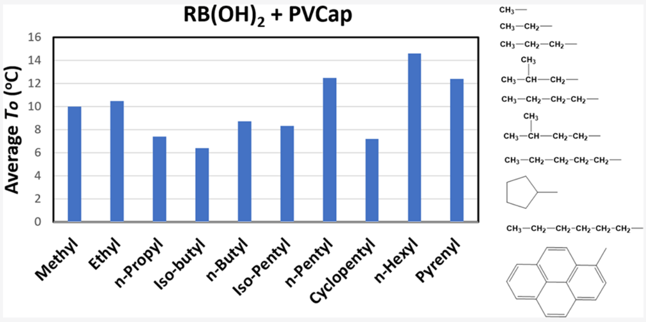
**ABSTRACT:** A range of boronic acids have been investigated as synergists for the kinetic hydrate inhibitor (KHI) polymer, poly(*N*-vinylcaprolactam) (PVCap, $M_w \approx 10{,}000$ g/mol) using high pressure rocking cells, a natural gas mixture, and a slow constant cooling (1 °C/h) test method from 76 bar. Surprisingly, unlike other classes of synergists such as alcohols and quaternary ammonium salts, the boronic acids that gave the best synergy had an alkyl or cycloalkyl tail with a maximum of a 3 carbon atom distance from the boron atom. The tail-branched iso-butylboronic acid was the best of these, yet it showed a negligible KHI effect when tested alone. However, consistent with the other classes of synergists, tail branching or use of a cyclic alkyl group was beneficial. Interestingly, boronic acids with chains of 5 to 6 carbon atoms, i.e., *n*-pentyl- and *n*-hexylboronic acids, were antagonistic to the PVCap KHI performance. For comparison, several organic acids were also investigated as synergists with PVCap. The same trend as for the boronic acids regarding the size and branching of the acid was seen. 3-Methylbutanoic acid gave the best synergy although worse than that of iso-butylboronic acid. The synergistic performance of sodium salts of some organic acids differed markedly to that of the free organic acids. Sodium 3,3-dimethylbutanoate gave the best synergy with PVCap.



## 1. INTRODUCTION

Kinetic hydrate inhibitors (KHIs) have been used since the mid 1990s to prevent plugging of flow lines with gas hydrates.[1−6] KHIs are a class of low-dosage hydrate inhibitors (LDHIs) and as the name suggests are added to well streams at low concentrations, usually between 0.3 and 3.0 wt % as the finished formulation at a pumpable viscosity. A KHI formulation contains one or more specifically designed water-soluble polymers as the main active components (often 10−20 wt %), plus synergists and enhancers, some of which make up the solvent carrier system. KHIs are able to delay gas hydrate crystal nucleation and crystal growth depending on the subcooling, residence time, the absolute pressure, and a range of other factors including salinity and compatibility with other production chemicals. Recent evidence suggests that KHIs can totally inhibit hydrate crystal growth up to a certain subcooling level (driving force).[7−9]

Most current commercial KHI polymers are water-soluble (or water-dispersible) polymers with multiple amide functional groups. They include homopolymers and copolymers of *N*-vinyllactams, *N*-isopropylmethacrylamide (NIPMAM), and hyperbranched poly(esteramide)s[3−6,10,11] (Figure 1). Many other classes of polymers, both amides and non-amide-based functional groups, have been investigated.[2,4,6−12] In addition, a wide range of synergists or performance enhancers have been studied.[2−4,13−16] Synergism occurs when the interaction or cooperation of two or more substances produces a combined effect greater than the sum of their separate effects. Based on this definition, many chemicals currently called synergists are actually only performance enhancers as these chemicals by themselves have poor ability to prevent gas hydrate formation. However, the word "synergist" is being used to cover both terms as this is the general industry practice.

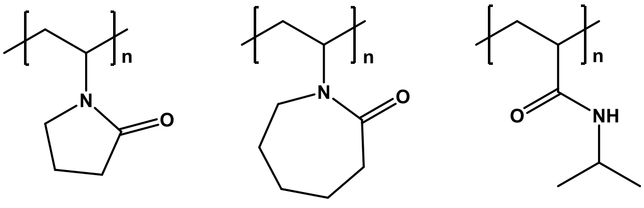


**Figure 1.** Monomer units in the structures of well-known classes of KHI polymers. From left to right: PVP, PVCap, and PNIPMAM.

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Some of the first synergists to be discovered were the quaternary ammonium salts (Figure 2). They were found by Shell and BP to enhance the performance of *N*-vinylcaprolactam polymers. In particular, tetrabutylammonium bromide (TBAB) was deployed in some of the early KHI formulations with these polymers.[17−19] The ideal chain length for quaternary ammonium salt synergists appears to be 5 carbon atoms (*n*-pentyl), but the performance is improved if the tail is split once (iso-hexyl) or twice (*t*-heptyl).[20,21] However, these branched tail salts are more expensive to make. Quaternary phosphonium salts have also been investigated, with the tetrabutylphosphonium bromide salt giving better synergy than the equivalent butylated ammonium version, TBAB (Figure 2).[22,23] The size of the central quaternized atom would therefore appear to be important. Variations of the quaternary onium salts with multiple alkyl groups have also been investigated, some of which were shown to be excellent synergists with VP, VCap, and other polymers, including hexaalkylguanidinium salts and trialkylamine oxides (Figure 2).[24,25]

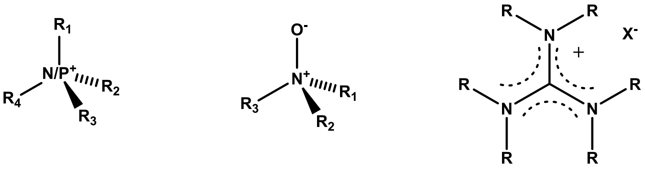

**Figure 2.** Tetraalkylammonium salts, trialkylamine oxides, and hexaalkylguanidinium salts.

Although many classes of synergists have been found for the common KHI polymers, few studies have been carried out in which the size and shape of the alkyl group have been varied systematically. Until recently, the performance of single-alkyl tailed molecules, non-ionic, cationic, and anionic, appeared to give worse synergy than the multitailed synergists described above. A range of small organic acids or alkyl carboxylate salts showed some synergy with PVCap as well as non-ionic alcohols, diols, and glycols such as butyl glycol ether (BGE) (Figure 3).[14−16,26−28] BGE as the polymerization solvent has been used in several KHI formulations because it has a high flash point and is a good synergist to many KHI polymer classes.[29]

**Figure 3.** Butyl glycol ether (BGE, left) and 4-methyl-1-pentanol (iHexOl, right).

Recently, 4-methyl-1-pentanol (iHexOl) was shown to have excellent synergy with PVCap as well as several other KHI polymers (Figure 3).[13] The authors speculated that the branched tail and maximum hydrophobicity without losing water solubility were key features. Interestingly, 1-pentanol was clathrated to form the sII hydrate when doped with ammonium fluoride.[30] This suggests that it may also be possible to enclathrate iHexOl and the reason why it is a good synergist, i.e., it is at the limit of the structural size to be able to form sII hydrate $5^{12}6^4$ cages around it while being at the limit of water solubility (maximum hydrophobicity).

The inspiration for studying non-ionic boronic acids came from a report on the use of boronic acids as gas hydrate anti-agglomerants (AAs).[31] Two notable examples tested are pyrene-1-boronic acid and methyl butyl boronic acid (isopentyl boronic acid), both of which performed equally as well as industry standard AAs. A range of other polyaromatic boronic acids are also claimed as AAs. This work appears to be partly based on the use of aromatic carboxylic acids such as pyrene acetic acid to reduce hydrate interparticle cohesion forces.[32] This study in turn was based on studies of natural surfactants such as naphthenic acids, which are able to prevent hydrate deposition and plugging with some oils (i.e., non-plugging oils).[33,34] Isopentylboronic acid was found to be extremely hydrate-philic (attracted to hydrate surfaces) and able to strongly reduce the surface oil-hydrate interfacial tension, lower than a threshold observed for industry standard AAs. In fact, a range of boronic acids lowered this interfacial tension, far better than lactam-based surfactants such as octyl/decyl pyrrolidones. Octylboronic was shown to have emulsifying tendencies (strong interaction at oil−water interfaces), whereas shorter tails such as isopentyl gave demulsifier tendencies. Isopentylboronic acid also showed low ecotoxicity to crustaceans and algae.

Boronic acids are based on boric acid [$B(OH)_3$] in which one of the three hydroxyl groups is replaced by an alkyl or aryl group.[35] The pKa of a boronic acid is about 9. They are known to be good Lewis acids. The unique feature of boronic acids is the ability to form reversible covalent complexes with sugars, amino acids, hydroxamic acids, and other functional organic classes.

Due to their hydrate-philic nature, it occurred to us that boronic acids might act as synergists toward KHI polymers. Here, we report the first study on the synergistic behavior of a range of alkyl and aromatic boronic acids with PVCap.

## 2. EXPERIMENTAL METHODS

**2.1. Chemicals.** The PVCap homopolymer used in this study was kindly supplied by BASF as Luvicap EG HM ($M_w \approx 10{,}000$ g/mol). The ethylene glycol solvent in this product was removed by heating an aqueous solution to about 50−60 °C and precipitating out the polymer. This was repeated three times, and the polymer was placed under vacuum to give a dry powder. The glycol-free PVCap, as shown by Fourier transform infrared (FTIR), was used in all synergistic experiments in this work. Boronic acids and organic acids were used as supplied by TCI Europe or VWR (Avantor) with a minimum 98% purity (Figure 4). Solutions of salts of organic acids were prepared by addition of an equimolar amount of sodium hydroxide to concentrated aqueous solutions of the acid.

**2.2. KHI Performance Experiments.** Evaluation of the polymers' performance as KHIs was carried out by the slow constant cooling (SCC) method in a so-called "rocker rig" as previously described.[13,14,20] The rocker rig consists of a water bath containing five 40 mL high pressure steel cells each containing a steel ball for agitation. The original equipment was supplied by PSL Systemtechnik, Germany, but the cells were supplied by Svafas, Norway. Table 1 shows the composition of the synthetic natural gas (SNG) used in the experiments, which preferentially forms structure II gas hydrates as the thermodynamically stable phase.

The slow constant cooling experiments were carried out according to a procedure we have previously described.[20] The test chemicals were dissolved in deionized water at the desired concentration at least 1 day in advance of the KHI test. This test solution (20 mL) was added to each cell. Air in the cells was removed using alternatively vacuum and replaced by SNG at up to 3−5 bar (repeated twice more) with subsequent rocking for 2−3 mins. Finally, 76 bar of SNG was added to the cells and rocking started at a rate of 20 rocks per minute

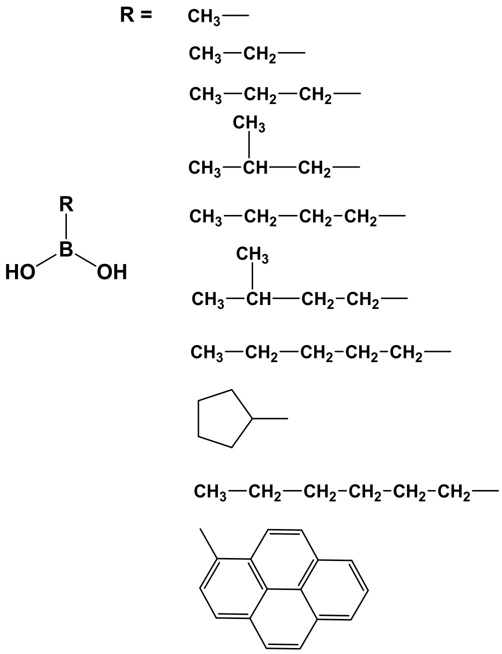

**Figure 4.** Boronic acids used in this study.

**Table 1. Composition of the Synthetic Natural Gas (SNG) Mixture Used in the KHI Experiments**

| component | mol % |
|---|---|
| methane | 80.67 |
| ethane | 10.20 |
| propane | 4.90 |
| isobutane | 1.53 |
| *n*-butane | 0.76 |
| $N_2$ | 0.10 |
| $CO_2$ | 1.84 |

at an angle of 40°. Cooling of the water bath was started from room temperature (20.5 °C) to 2.0 °C at a rate of 1.0 °C/h.

Figure 5 shows an example of the results from a run with five cells of a mixture of 2500 ppm PVCap with 5000 ppm *n*-butylboronic acid, and Figure 6 shows the result and analysis for one individual cell from the same run. A linear pressure decrease is seen as the system is cooling down due to each cell being a closed system during the experiment. The onset temperature for hydrate formation, $T_o$, is the temperature at which the first deviation from the linear pressure decrease is seen. In Figure 6, $T_o$ is found after 695 min at a temperature of 9.3 °C. As this is a macroscopic observation, hydrate nucleation may have occurred prior to this but is not detectable in our experiments. The $T_o$ value remains the most important parameter determined as this is the temperature at which gas hydrates are first observed. The rapid hydrate formation temperature, $T_a$, is the temperature where the pressure decrease (i.e., hydrate growth) is at its most rapid, and its determination is also shown in Figure 6. In this example, we see that there is a long period of slow growth before $T_a$ is reached after 946 min at a temperature of 5.1 °C.

In general, the temperatures for all the cells and the water bath were found to be homogeneous. Unless otherwise stated, 8−10 individual experiments were carried out for each polymer sample. For a set of 8−10 experiments, we typically observe 10−15% scattering in $T_o$ and $T_a$ values.[38] This is due to the stochastic nature of the hydrate nucleation process. We did not observe any systematic errors causing some cells to consistently give better or worse results.

## 3. RESULTS AND DISCUSSION

The results of slow constant cooling (SCC) KHI tests in rocking cells are summarized in Table 2. The average onset temperature value ($T_o$ (av.)) is the most important of the two temperature parameters determined since complete hydrate inhibition is what is required, not a decrease in the hydrate growth rate. However, the $T_a$ value can also be useful as some KHI polymers are capable of arresting the growth rate considerably. Thus, the parameter $T_o - T_a$ of SCC tests can give information of relative growth rates of KHIs but only if the $T_o$ values (driving forces at the onset of hydrate formation) to be compared are similar. If hydrate formation is somehow detected in a flow line, then a slow growth rate can give enough time for remedial treatment before complete plugging of the line occurs.

With no additive, the $T_o$ (av.) value was 17.2 °C, about 3.3 °C below the equilibrium temperature ($T_{eq}$). The baseline polymer PVCap by itself at 2500 ppm gave a $T_o$ (av.) value of 10.4 °C, a typical value we have seen in a previous study under the same test conditions.[13]

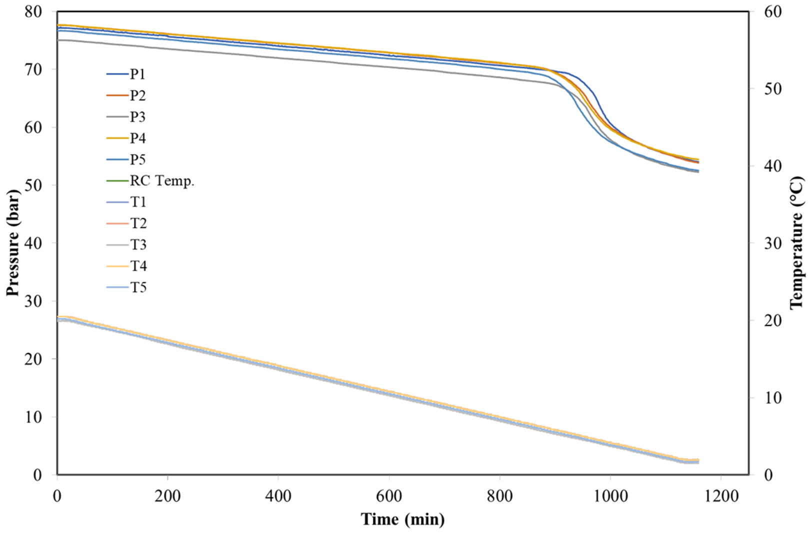

**Figure 5.** Results from five cells after a standard slow constant cooling experiment with 2500 ppm PVCap + 5000 ppm *n*-butylboronic acid.

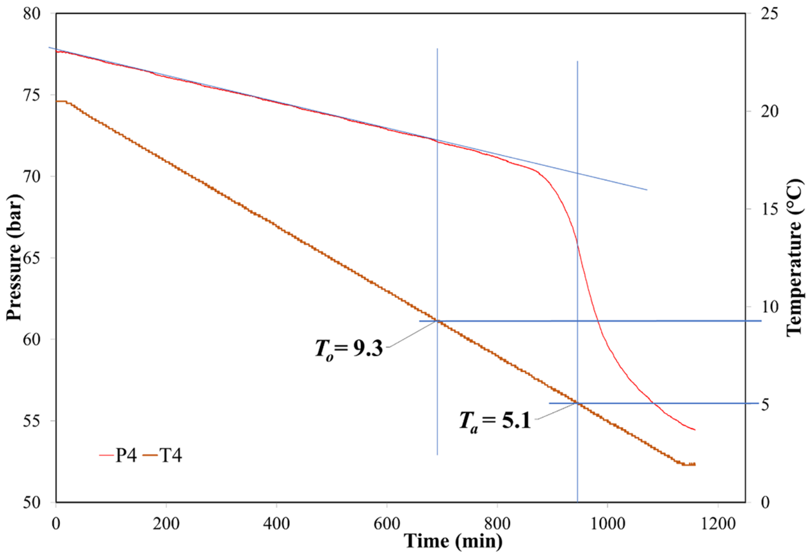

Figure 6. Determination of $T_o$ and $T_a$ for cell 3 after a slow constant cooling experiment with 2500 ppm PVCap + 5000 ppm *n*-butylboronic acid.

### Table 2. SCC KHI Test Results with PVCap and Boronic Acids

| PVCap concn ppm | synergist | concn ppm | $T_o$ (av.) °C | $T_a$ (av.) °C |
|---|---|---|---|---|
| | | | 17.2 | 16.7 |
| | | | 16.5 | 16.4 |
| 2500 | | | 10.4 | 8.9 |
| | Alkylboronic acid | | | |
| 2500 | methyl | 5000 | 10.0 | 9.1 |
| 2500 | ethyl | 5000 | 10.5 | 9.0 |
| 2500 | *n*-propyl | 5000 | 7.4 | 4.1 |
| | iso-butyl | 5000 | 16.8 | 15.8 |
| 1000 | iso-butyl | 5000 | 7.1 | 4.4 |
| 2500 | iso-butyl | 1000 | 9.2 | 8.1 |
| 2500 | iso-butyl | 2500 | 8.4 | 5.9 |
| 2500 | iso-butyl | 5000 | 6.4 | 3.3 |
| 2500 | iso-butyl | 5000[a] | 5.3 | 3.0 |
| 2500 | *n*-butyl | 5000 | 8.7 | 5.2 |
| 2500 | iso-pentyl | 5000 | 8.3 | 2.9 |
| 2500 | *n*-pentyl | 5000 | 12.5 | 12.1 |
| 2500 | cyclopentyl | 5000 | 7.2 | 4.1 |
| 2500 | cyclopentyl | 5000[a] | 7.2 | 2.3 |
| 2500 | *n*-hexyl | 5000 | 14.6 | 14.3 |
| 2500 | pyrenyl | 5000 | 12.4 | 11.9 |
| | Organic acids and salts | | | |
| 2500 | 2-methylpropanoic acid | 5000 | 10.7 | 9.9 |
| 2500 | 3-methylbutanoic acid | 5000 | 8.2 | 5.8 |
| 2500 | 4-methylpentanoic acid | 5000 | 14.2 | 14.0 |
| 2500 | sodium 4-methylpentanoate | 5000 | 7.8 | 7.7 |
| 2500 | 3,3-dimethylbutanoic acid | 5000 | 11.5 | 11.2 |
| 2500 | sodium 3,3-dimethylbutanoate | 5000 | 5.1 | 5.0 |

[a] 1 mL of decane added.

From the results with 2500 ppm PVCap + 5000 ppm alkylboronic acid, we see that there is no significant performance enhancement with the methyl or ethyl derivatives (Table 2 and Figure 7). For the larger alkyl groups, we observed that some alkylboronic acids enhanced the KHI performance, while others even decreased the performance. Iso-butylboronic acid gave the greatest performance enhancement decreasing the average $T_o$ for PVCap from 10.4 to 6.4 °C. We carried out extra KHI tests (15 in all) to give a better statistical assurance. This performed better than *n*-propylboronic, indicating that the end branching of the alkyl group is beneficial. (It should be noted that iso-propylboronic acid was not available at the time of this study). This will give better van der Waals interactions with hydrate cage structures as discussed previously.[36] Interestingly, the optimal alkyl group for PVCap synergy was not the same that gave the best anti-agglomerant effect. This was the four-carbon chain 3-methylbutylboronic acid (iso-pentylboronic acid).[31] This indicates that one does not need a good anti-agglomerant effect (the ability to disperse hydrate particles) to get good KHI synergy. This can be further explained by considering hexadecyltributylammonium bromide (HDTBAB), which is known to have good AA properties and tetrabutylammonium bromide (TBAB). Both HDTBAB and TBAB are so-called hydrate-philic molecules, slowing hydrate crystal growth, but only the former is a good AA.[17] However, both molecules were shown to be synergists with VCap-based polymers and lowered the hydrate onset temperature in ramping tests compared to the polymer alone. Thus, TBAB is a KHI synergist but has no AA effect.

We also tested iso-butylboronic acid at 5000 ppm by itself for KHI performance, but it gave no significant effect (Table 2). The pH of a solution of 5000 ppm iso-butylboronic acid, with or without added PVCap, was found to be about 5, which is a typical flow line-produced water pH.

Adventitious alkyl branching has been seen in other synergists such as alcohols, where 4-methyl-1-pentanol (iso-hexanol) was the best, and with tetraalkylammonium salts, where iso-hexyl or *t*-heptyl groups are the best.[24,37] Thus, the ideal chain length for the alcohols and quaternary ammonium salts is five carbon atoms. However, it is interesting to note that, for the alkylboronic acids, the ideal alkyl chain length (away from the boron atom) is not five carbon atoms, or even four, but three carbon atoms, preferably branched or cyclic. (The cyclopentyl group has 2 carbon atoms at a distance of 3 carbons from the boron atom). Surprisingly, *n*-pentylboronic was antagonistic to PVCap performance, increasing the average

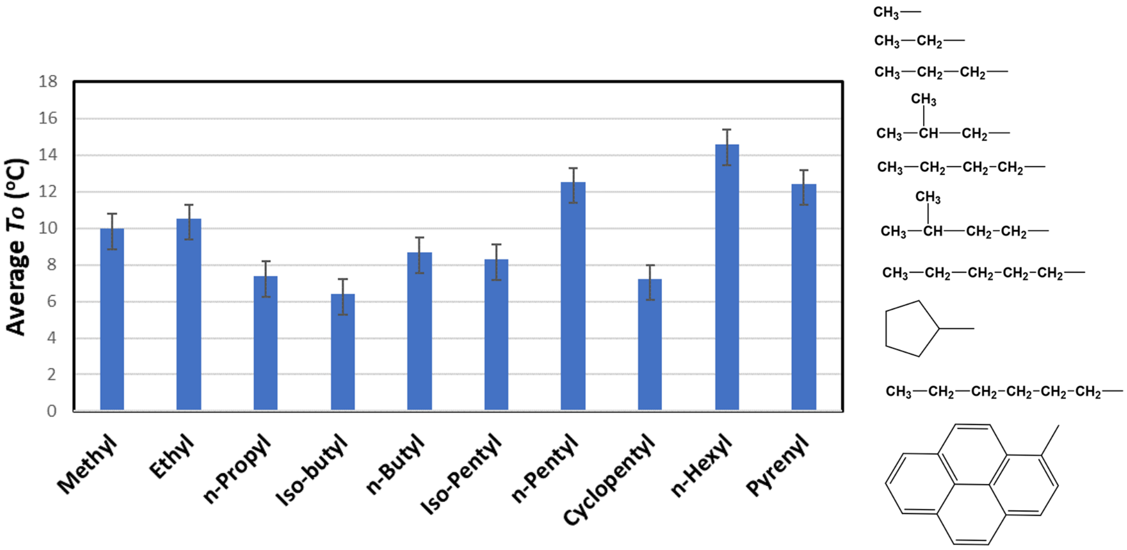

**Figure 7.** Average onset temperatures (average $T_o$) with error bars for 2500 ppm PVCap and 5000 ppm alkylboronic acids.

$T_o$ from 10.4 to 12.5 °C (Table 2). The longer *n*-hexylboronic was even worse giving a $T_o$ of 14.6 °C. Boronic acids with a length of 3 carbon atoms include straight chain propylboronic acid, branched iso-butylboronic acid, and cyclic cyclopentylboronic acid. We can consider the cyclopentyl group as having its outer two carbon atoms as the third carbon in a chain from the boron atom.

Another point to consider is that both alcohols and the quaternary salts gave the best performance close to the limits of water solubility for the test concentration used.[13,24,37] Thus, increasing to heptanol or isomers thereof or using tetrahexylammoniumbromide did not give a good performance enhancement with PVCap. In contrast, iso-butylboronic acid is not at the limit of solubility since *n*-pentyl-, isopentyl-, and *n*-hexylboronic acids are all fully soluble in water at 5000 ppm. We presume therefore that the optimal synergistic performance with iso-butylboronic acid is more due to the size and shape of the molecule and less to do with its solubility.

We carried out a few other synergy tests with varying ratios of PVCap and iso-butylboronic acid (Figure 8). Using 2500 ppm PVCap but only 2500 ppm iso-butylboronic acid, the average $T_o$ dropped to 8.4 °C. With an even less synergist, 1000 ppm, the $T_o$ value dropped to 9.2 °C. With 1000 ppm PVCap and 5000 ppm iso-butylboronic acid, the average $T_o$ dropped only a little to 7.1 °C. Thus, within these concentration ranges, we observe that increasing either the KHI polymer or synergist concentration gives improved performance.

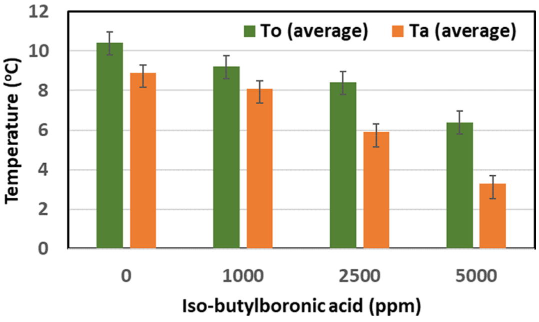

**Figure 8.** Effect on average $T_o$ and $T_a$ values with error bars of varying concentrations of iso-butylboronic acid with 2500 ppm PVCap.

We also added 1 mL of decane as a liquid hydrocarbon phase to the KHI experiments with 2500 ppm PVCap and 5000 ppm iso-butylboronic acid. Most current field applications on gas fields have some associated liquid hydrocarbon. It is possible that the KHI polymer or synergists could partition into this phase and lose their KHI activity in the water phase. We recently demonstrated this for the acetylenic diol gemini surfactant, 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD).[38] Addition of 1 mL of decane to 20 mL of 2500 ppm PVCap and 5000 ppm iso-butylboronic acid lowered the average $T_o$ from 6.4 to 5.3 °C. Fifteen experiments were carried out on both the decane-free and decane systems. The results show a statistically significant improvement by the addition of decane. Since iso-butylboronic acid is very water-soluble and probably does not partition to the decane phase, we presume that the performance improvement comes from lowering the hydrate equilibrium temperature (HET) of the system by adding decane. We carried out an SCC test with deionized water with added 1 mL of decane (Table 2). The result was that decane lowered the average $T_o$ from 17.2 to 16.5 °C in agreement with a lower HET.

We also investigated the effect on the cloud point of PVCap with addition of the best synergist, iso-butylboronic acid.[37] In general, the boronic acid caused a small decrease in the cloud point of PVCap. A solution of 2500 ppm PVCap in deionized water gave a cloud point ($T_{cl}$) of 39 °C. Addition of 5000 ppm iso-butylboronic acid lowered the $T_{cl}$ value to 34 °C. For 5000 ppm PVCap plus 5000 ppm iso-butylboronic acid, the $T_{cl}$ value was 33 °C.

We also added decane to the cyclopentylboronic acid synergy tests. Ten experiments were conducted on both the decane and decane-free systems. This time, no improvement in performance from the addition of decane was observed. Both gave the same average $T_o$ value of 7.2 °C, although the average $T_a$ value was 1.8 °C lower for the decane system. Cyclopentylboronic acid is more hydrophobic than iso-butylboronic acid, which would explain the difference in results with these two synergists. Since the equilibrium temperature is reduced in this system, we presumed that a little cyclopentylboronic acid may have partitioned to the decane phase, lowering its activity in the water. This effect would counteract the lower equilibrium temperature. To check this experimentally, we stirred 0.1 g of cyclopentylboronic acid in 10 mL of hexane in a sealed vessel for 18 h. Careful decantation of the solvent and drying of the remaining solid showed that approximately 4−5% of the acid had partitioned into the hexane. Hexane has similar polarity to decane. Therefore, we assume that a small portion of this boronic acid also partitioned to decane in the high pressure KHI tests.

We now consider the obtained average $T_a$ values, i.e., the maximum growth rates of gas hydrate in these synergistic systems with PVCap and alkylboronic acids. The $T_o - T_a$ value can be used to give some indication of the ability of the KHI blend to inhibit crystal growth, but caution must be used. When comparing results, the $T_a$ values ought to be similar or else the different driving forces at nucleation will also affect the relative crystal growth rates. Looking at the average $T_a$ values for systems without decane, iso-pentylboronic acid gave the lowest value, 2.9 °C, but the $T_o$ value for this system was 1.9 °C higher than for the iso-butylboronic system. Since the $T_o$ value for the iso-butylboronic acid system was lower and the $T_a$ value was still quite low (3.3 °C), it indicates that this boronic acid is a good hydrate crystal growth inhibitor. Iso-pentylboronic acid is also a good hydrate crystal growth inhibitor. This may relate to the good anti-agglomerant performance seen for this molecule.[17,18] Cyclopentylboronic acid also shows good hydrate crystal growth inhibition due to the low $T_o$ value (7.2 °C) and fairly low $T_a$ value (4.3 °C). Interestingly, addition of decane lowers the $T_a$ value to 2.3 °C. We speculate that cyclopentylboronic acid might be an even better anti-agglomerant than iso-pentylboronic acid.

It is interesting to compare the synergistic effects of boronic acids with organic acids as synergists for PVCap. There appear to be no studies reported of small organic acids as synergists with any KHI polymer. The closest study was with several sodium alkyl carboxylate salts.[26] As organic acids are weak, a minor percentage of these organic carboxylates will be in the acid form in water. Alkylboronic acids are weak acids, but organic acids are a little more dissociated in water. The pKa of small boronic acids is ∼9. As mentioned earlier, we measured the pH of 5000 ppm iso-butylboronic acid to be ∼5. However, they can form tetrahedral boronate complexes with pKa ∼7.[35] The pKa value of small organic acids is about 4.8, meaning that they are more deprotonated, making aqueous solutions more acidic than for boronic acids.

In this study, we investigated a few organic acids and their sodium salts (Table 2). We used only tail-branched organic acids as we were confident from studies with several other classes of synergists that this was beneficial over acids with a straight chain of carbon atoms. The equivalent organic acid of iso-butylboronic acid can be thought of as 3-methylbutanoic acid with the same chain length between the OH group and the end of the alkyl group. 3-Methylbutanoic acid has a carbon chain length of 4 carbon atoms, with tail-end branching. In Table 2, we see that it gave reasonable synergy with PVCap, lowering the $T_o$ value for PVCap alone from 10.4 to 8.2 °C. This is better synergy than observed for the shorter acid, 2-methylpropanoic acid. When we increased the alkyl chain length to 5 carbon atoms, for 4-methylpentanoic acid, this molecule was observed to be antagonistic to the performance of PVCap, giving an average $T_o$ value of 14.2 °C. (The solubility of 4-methylpentanoic acid in water at room temperature is 5.3 g/L or 5300 ppm). This trend is very similar to that of the alkylboronic acids if we equate the B−OH moiety to the C−OH moiety (Figure 9). We tested one more organic acid with a double-branched tail, 3,3-dimethylbutanoic acid. This acid has the same carbon chain length of 4 carbon atoms as 2-methylbutanoic acid. Surprisingly, this acid did not improve the performance of PVCap but was weakly antagonistic.

**Figure 9.** 2-Methylbutanoic acid (left) and iso-butylboronic acid (2-methylpropyl boronic acid) (right).

The final part of this study was to enlarge the study of alkyl carboxylates first investigated about a decade ago.[26] We knew from this earlier work that the sodium salt of 3-methylbutanoic acid (iso-valeric acid or iso-pentanoic acid) showed negligible synergy with PVCap. So, we increased the carbon chain length to 5 carbon atoms (Table 2). Sodium 4-methylpentanoate (iPeCOONa) showed reasonable synergy lowering the average $T_o$ value to 7.8 °C, in agreement with the earlier study. This contrasts strongly with the antagonistic effect of 4-methylpentanoic acid. For sodium 3,3-dimethylbutyrate, we observed good synergy with PVCap, with the average $T_o$ lowered to 5.1 °C. Hydrates formed rapidly at 5.0 °C, indicating the poor ability to stop hydrate crystal growth at this subcooling.

We also wanted to test the double tail-branched 4,4-dimethylpentanoic acid and its sodium salt, but it was too costly to get a hold of in the quantities required for our studies. However, based on the results discussed here, we predict that the acid form would be an antagonist and the sodium salt would be a strong synergist for enhancing the performance of PVCap.

## 4. CONCLUSIONS

Boronic acids have been investigated as synergists for a KHI polymer for the first time, in this case for PVCap. A natural gas mixture was used, giving the structure II hydrate as the thermodynamically preferred phase. The ideal chain length from the boron atom appears to be 3 carbon atoms, but particularly, branching of the tail (iso-butyl) or use of a cycloalkyl group of a similar shape at the tail gives an even better performance. In contrast to the optimum alkyl group for AA performance (iso-pentyl), the optimum alkyl group for synergy with PVCap was found to be iso-butyl. For example, addition of 5000 ppm isobutylboronic acid to 2500 ppm PVCap lowered the average $T_o$ value in SCC tests from 10.4 to 6.4 °C. This is different from the optimum chain length of 5 and 4 carbon atoms for the best synergy from alcohols and tetraalkyl quaternary ammonium salts. Longer alkyl tails could make the alkylboronic acids antagonistic to the PVCap performance. Overall, the ranking of the alkyl groups in terms of synergy is iso-butyl > cyclopentyl/*n*-propyl > iso-pentyl/butyl. Methyl and ethyl had no significant effect on the PVCap performance, while *n*-pentyl, *n*-hexyl, and pyrenyl showed antagonistic behavior. The best synergist, iso-butylboronic acid, lowered the cloud point of PVCap. For example, 2500 ppm PVCap ($T_{cl}$ = 39 °C) plus 5000 ppm iso-butylboronic acid in deionized water had $T_{cl}$ = 34 °C.

A similar synergy trend (with PVCap) in the size and branching of the alkyl tail was seen for organic acids, although

3-methylboronic acid was found to be a better synergist than 3-methylbutanoic acid. The salts of these organics were also investigated as synergists. The performance deviated considerably from that of the free acid. Sodium 3,3-dimethylbutanoic acid was found to give the best synergy with PVCap, but sodium 4,4-dimethylpentanoate was predicted to also be a strong synergist.

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### Notes

The authors declare no competing financial interest.

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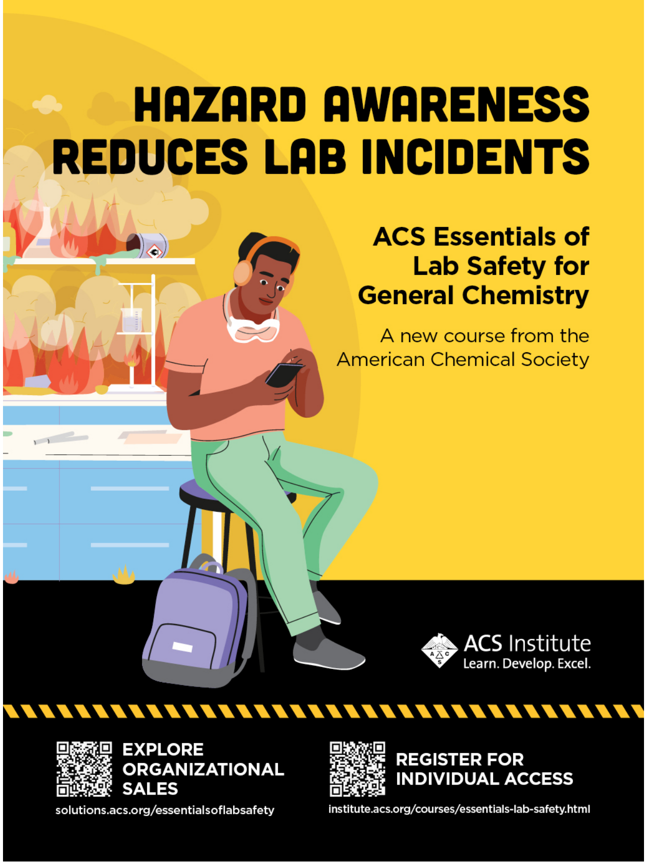

# Paper VII

Synthesis and Investigation of Polymers of 2-Methacrylamido-caprolactam as Kinetic Hydrate Inhibitors

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Article

# Synthesis and Investigation of Polymers of 2-Methacrylamido-caprolactam as Kinetic Hydrate Inhibitors

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**ABSTRACT:** Poly(*N*-vinylcaprolactam) (PVCap) and related copolymers have been used as kinetic hydrate inhibitors (KHIs) for over 25 years to combat gas hydrate formation in oil and gas field production flow lines. The caprolactam groups in this polymer class have been shown previously to have a particularly strong interaction with hydrate surfaces, inhibiting crystal growth but probably also gas hydrate nucleation. We report here a study on an alternate class of copolymers with pendant caprolactam groups from the 2-methacrylamido-caprolactam (2-MACap) monomer. KHI experiments were carried out in high pressure steel rocking cells using a structure-II-forming natural gas mixture. The KHI performance of some of these copolymers exceeded that of PVCap of similar molecular weight, with further performance enhancement provided by solvent synergists.

## 1. INTRODUCTION

Gas hydrates are nonstoichiometric crystalline solids where gases of certain molecular weights stabilize the hydrogen-bonded molecular water cages. Thus, if suitable low-molecular-weight hydrocarbon gases combine with water under specific conditions of temperature and pressure, typical favoring conditions will be temperature and pressure in the ranges of <25 °C and >30 bar, respectively, and gas hydrates will form.[1−4]

It is not uncommon to encounter such conditions when producing or transporting oil and gas, and if it is left untreated formation of gas hydrate plugs can occur, potentially jeopardizing the operation.[4−12] There exist multiple measures to handle and treat gas hydrate: one of them is the utilization of low dosage hydrate inhibitors (LDHIs) and the subgroup kinetic hydrate inhibitors (KHIs).[5]

The main active compound of a KHI formulation is the water-soluble polymer, which typically makes up 10−30 wt %, with the remainder being carrier solvent.[13] Regarding the polymers, it appears that they need two structural features in order to perform well as hydrate inhibitors, namely, to be able to have both hydrophilic and hydrophobic capabilities. It is usually amide, imide, or amine oxide groups that make up the hydrophilic functional groups of the polymer.[5,14,15] The hydrophobic functional group must be present directly or adjacent to each of the hydrophilic functional groups.[16] Polymers and copolymers based on the monomers *N*-vinylcaprolactam (VCap), *N*-vinylpyrrolidone (VP), and *N*-isopropylmethacrylamide, as well as hyperbranched poly(ester amide)s based on diisopropanolamine and various cyclic anhydrides, make up the bulk of commercially available KHIs.[5] The other part of the KHI formulation, the carrier solvent, is often a low-molecular-weight alcohol, glycol, or glycol ether, such as methanol, ethanol, monoethylene glycol (MEG), and 2-*n*-butoxyethanol (nBGE).[12] In addition to easing the pumping of the KHI formula, the carrier solvent also can act as a synergist with the KHI polymer, thus enhancing the hydrate inhibiting properties of the polymer.[13]

The mechanism behind the inhibition properties of these KHI polymers is not fully understood, but the KHIs kinetically interact with the hydrate formation process. They are assumed to interfere with the hydrate nucleation and crystal growth processes.[17,18]

Poly(*N*-vinylcaprolactam) (PVCap) is one of the best KHIs currently available (Figure 1). Several copolymers of VCap have also been applied in the field.[19] Therefore, we were interested in investigating other polymers containing the caprolactam ring.

VCap-based KHI polymers are known to be particularly good at inhibiting hydrate crystal growth compared to other KHI polymer classes such as polyalkyl(meth)acrylamides.[1,5,20] This means that with the use of a VCap-based polymer the

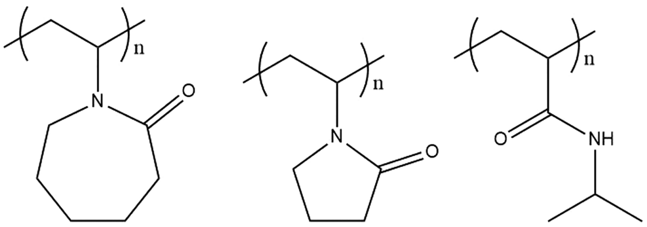

**Figure 1.** Structures of common polyvinylic KHIs. From left to right: poly(*N*-vinylcaprolactam) (PVCap), poly(*N*-vinylpyrrolidone) (PVP), and poly(*N*-isopropyl methacrylamide) (PNIPMAM).

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time before enough hydrate crystals have formed to cause catastrophic hydrate growth is prolonged. Therefore, this can give the field operator a better opportunity to avoid plugging of the flow line completely once hydrates are first suspected to be formed. This also gave us incentive to explore alternate caprolactam-based polymers.

Very few studies on polymers (other than VCap-based polymers) containing caprolactam rings as KHIs have been reported. In an earlier attempt in our research group, 2-aminocaprolactam was reacted with poly(dichlorophosphazene) (PDCP) in order to make poly(caprolactam-2-amino)phosphazene, which was water-soluble as a homopolymer[21] (Figure 2). This polymer showed some KHI effect, but it had two major drawbacks: First, the water solubility for even ethyl derivative was low; increasing the hydrophobicity (thereby probably increasing the KHI performance) by using pendant propyl groups would have been futile as the polymer became insoluble in water. Second, especially at the pH of produced oilfield water, the polymer has limited stability in water. The water-soluble polyphosphazenes are proven to be biodegradable, which is of interest when they are considered as KHIs.[22] The making of these polymers was challenging, and in general the trend was that the longer the pendant alkyl group the more hydrolytically stable was the polymer, with the result of being less water soluble.[21] In one patent a research group reported that caprolactam groups can be attached to amines and polyamines via a Mannich reaction with formaldehyde.[23] In our hands, this reaction does not work and was unofficially confirmed by contact with the patent owners.

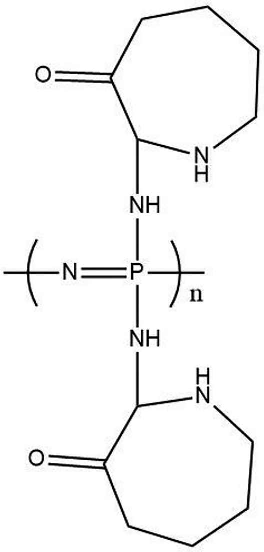

**Figure 2.** Structure of poly(caprolactam-2-amino)phosphazene.

We previously synthesized acryloyloxyethylcaprolactam and acryloyloxymethylcaprolactam, but it proved surprisingly difficult to make poly(*N*-acryloyloxyalkylcaprolactams), probably due to steric problems during the polymerization procedure (Figure 3). We presume the methacryloyl polymers, with extra methyl groups in the backbone, would also be difficult to make by radical polymerization.[21]

In this study, we have synthesized a new class of caprolactam-containing polymers. They are based on 2-methacrylamido-caprolactam (Figure 4). In these polymers the caprolactam ring will be two atoms further from the backbone than is the case for PVCap. We chose to use the methacrylamido monomer unit as previous work has shown that an extra methyl group in the polyvinyl backbone is favorable for KHI performance of *N*-alkyl acrylamide polymers.[24] The beneficial extra methyl group in the polyvinyl backbone has also been recently demonstrated for poly(*N*,*N*-dimethylhydrazido methacrylamide) compared to poly(*N*,*N*-dimethylhydrazido acrylamide).[25,26] The improved KHI effect given by this extra methyl group in the polyvinyl backbone is presumed to be due to the steric effect of the methyl group, opening the polymer structure and increasing its surface-to-volume ratio. One other important aspect of having the methyl group in the polyvinyl backbone is the potential to keep the molecular weight of the polymer or copolymer low. This is particularly useful for the efficacy of a KHI. In radical polymerization or copolymerization, an acrylamide forms secondary radicals as the propagating end group, while methacrylamide forms tertiary radicals.[27] Tertiary radicals are more stable than secondary radicals, and they are thus thought to decrease the reactivity of the propagating end for further polymerization. In addition, with methacryl, there is always a greater steric effect of approach than with acryl monomer to monomer radical. This effect is more pronounced for methacrylamides, and therefore they polymerize more slowly.

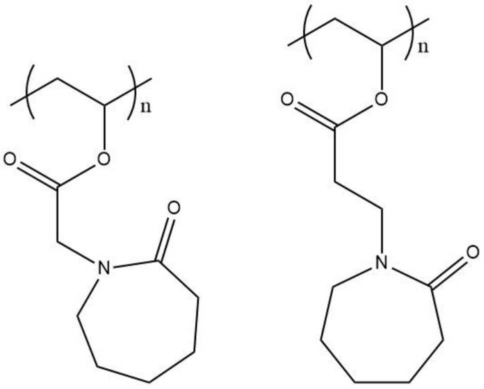

**Figure 3.** Structures of polyacryloalkylenecaprolactams with one (left) and two (right) carbon atoms in the chain connecting the caprolactam ring, respectively.

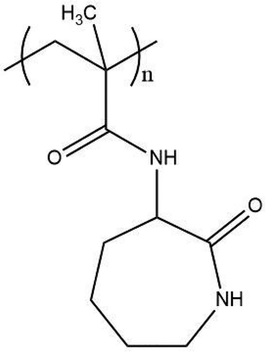

**Figure 4.** Structure of poly(2-methacrylamido-caprolactam) (poly(2-MACap)).

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** $\alpha$-Amino-$\varepsilon$-caprolactam was obtained from ABCR, Germany. Triethylamine and solvents used in this study

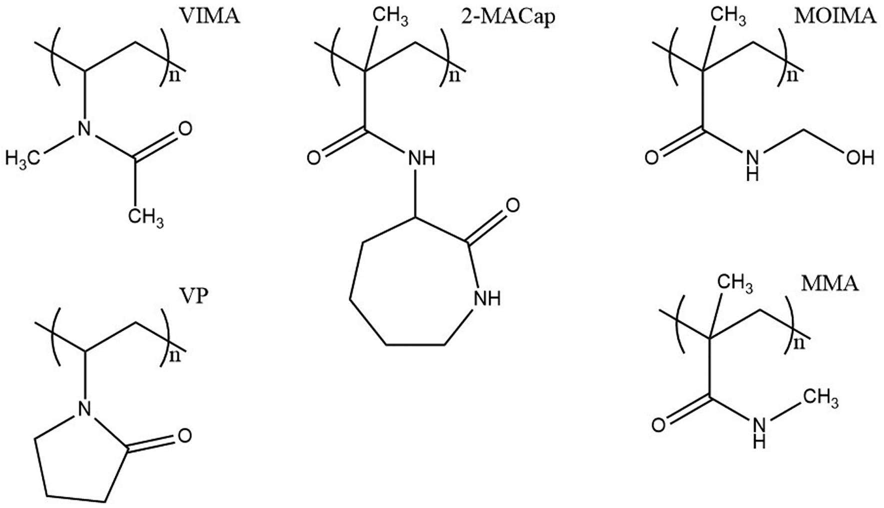

**Figure 5.** Structure of comonomer units used with 2-MACap copolymers: *N*-vinyl-*N*-methylacetamide (VIMA), *N*-vinylpyrrolidone (VP), *N*-methylol methacrylamide (MOlMA), and *N*-methylmethacrylamide (MMA). Poly(2-MACap) is shown in the center.

were obtained from Merck. *N*-Methylol methacrylamide was obtained from Evonik, Germany. *N*-Methylmethacrylamide was obtained from Tokyo Chemical Industry (TCL). Methacryloyl chloride, *N*-vinyl-2-pyrrolidone, and *N*-vinyl-*N*-methylacetamide were obtained from Sigma-Aldrich. All chemicals were commercially available and used without further purification. NMR spectra were recorded on a Bruker Ascend NMR 400 MHz spectrometer at ambient temperature unless otherwise stated.

**2.2. Synthesis of 2-Methacrylamido-caprolactam (2-MACap).** The synthesis was based on the described method,[28] by dissolving $\alpha$-amino-$\varepsilon$-caprolactam (1 g, 7.8 mmol) in dichloromethane (20 mL) in a 100 mL round-bottom flask. Then triethylamine (0.789 g, 7.8 mmol) was added and the mixture was cooled to 0 °C in an ice bath. Methacryloyl chloride (0.816 g, 7.8 mmol) dissolved in dichloromethane (10 mL) was added dropwise to the solution in the round-bottom flask with vigorous stirring. The mixture was slowly heated to room temperature and stirred overnight. The reaction mixture was washed with NaCl brine. Then the organic phase was extracted, washed with DI water, and dried with $Na_2SO_4$. The precipitated $NEt_3HCl(s)$ was filtered off and solvent was removed *in vacuo* on a rotary evaporator to yield 2-methacrylamido-caprolactam (2-MACap). $^1H$ NMR confirmed that the resulting product was pure, and it was thus used without further purification steps.

**2.3. Poly(2-methacrylamido-caprolactam) (Poly(2-MACap)) Synthesis.** The polymerization synthesis was done in the same general manner for all homopolymers and copolymers. 2-MACap did not polymerize in 2-propanol, so the solvent used in the following polymer synthesis was DMSO. 2-MACap (0.5 g, 2.5 mmol) was dissolved in DMSO (2 g) in a Schlenk flask with a magnet. AIBN (1 wt %, 0.005 g) was added, and the solution was flushed with nitrogen using the standard pump-fill technique. While the solution was stirring, it was heated to 70 °C and left to react under the protection of nitrogen overnight. Then the poly(2-MACap) solution was cooled to room temperature and the product was left in solution. $^1H$ NMR showed that all monomer was consumed.

The comonomers used to make copolymers of 2-MACap were *N*-vinylpyrrolidone (VP), *N*-vinyl-*N*-methylacetamide (VIMA), *N*-methylol methacrylamide (MOIMA), and *N*-methylmethacrylamide (MMA) (Figure 5). The copolymerizations followed the same steps as for the 2-MACap homopolymer, except that the comonomer was added in the first step.

**2.4. GPC Analysis.** In order to determine the molecular weight as well as the polydispersity index (DPI) of the polymers made, a GPC analysis was conducted. The apparatus used was a JASCO Chem NAV size exclusion chromatography (SEC) system. This system was equipped with PU-2080, AS-2055, CO-2065 RI-2031, and two commercial columns (TSKgel SuperH4000 and TSKgel GMHXL). The testing was done at 40 °C with dimethylformamide (DMF) as eluent. Polystyrene standards were used for calibrating the molecular weights of the polymers.

**2.5. Cloud Point (Tcl) Measurements.** A sample of the polymer was dissolved in deionized water, making a concentration of 1.0 wt %. This solution was then heated at approximately 2 °C/min, during heating visual observation was continuously done, and the Tcl was determined at the temperature where the first sign of haze was observed. This was repeated at a minimum one more time for each polymer for verification of the Tcl temperature. Deposition points (Tdp's), which are usually a maximum of 5−10 °C above the Tcl, were not measured.

**2.6. Gas Hydrate Performance Testing in High-Pressure Apparatus.** The apparatus used for conducting the performance testing was The Rocking Cell 5 (RC5) apparatus supplied by PSL Systemtechnik, Germany. With this apparatus, five high-pressure stainless steel rocking cells, supplied by Svafas, Norway, are rocked in a cooling bath. The cells have an internal volume of 40 mL and are equipped with a stainless steel ball for agitating the test solution. The gas used in these tests was a standard natural gas mixture (SNG), which preferentially forms a structure II gas hydrate. The composition of the gas mixture is provided in Table 1.

**Table 1. Composition of the Synthetic Natural Gas Mixture Used in the Performance Testing**

| component | mol % |
|---|---|
| methane | 80.67 |
| ethane | 10.20 |
| propane | 4.90 |
| isobutane | 1.53 |
| *n*-butane | 0.76 |
| $N_2$ | 0.10 |
| $CO_2$ | 1.84 |

In the following, the procedure for high-pressure kinetic hydrate inhibition testing by the use of constant cooling is summarized and it has been described previously:[29,30]

1. The polymer, and if applicable the synergist, was dissolved to the desired concentration in deionized water at least 1 day in advance before initialization of the test.

2. The test solution consisted of various additives dissolved in distilled water, and 20 mL was added to each of five cells.

3. A sequence of vacuum and pressurizing with SNG was applied: first vacuum and then pressurizing with SNG to 3−5 bar; then

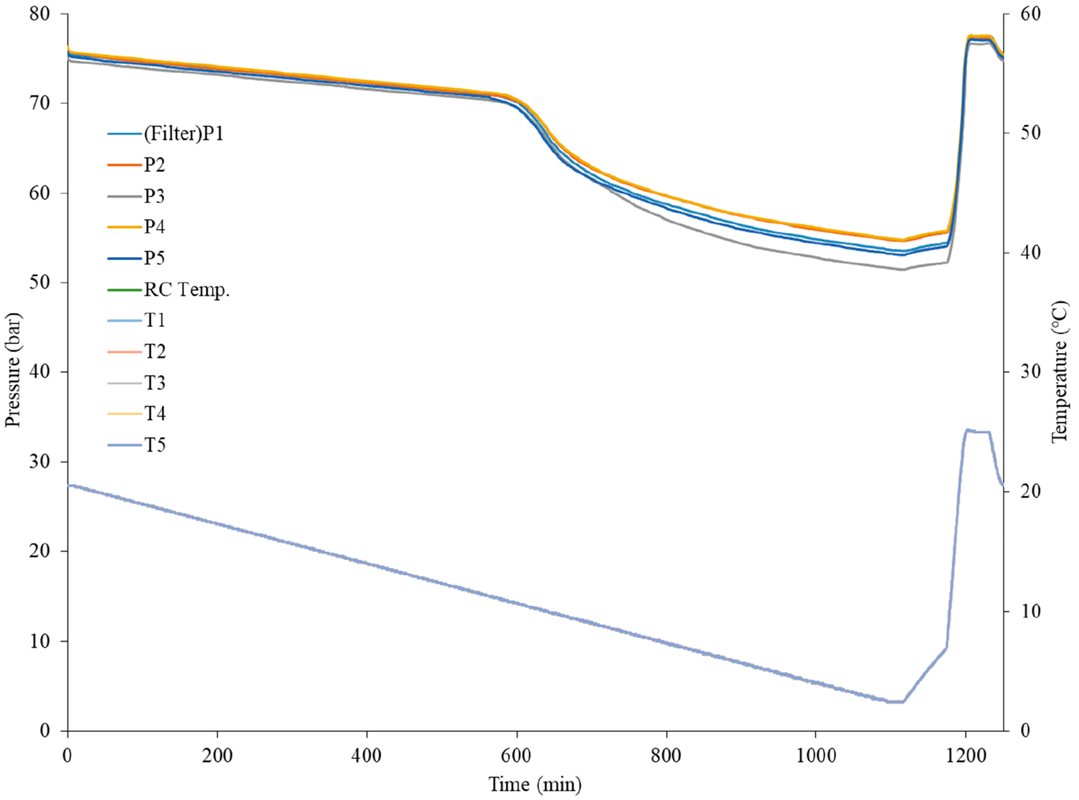

**Figure 6.** Graph containig the results from all five cells during a standard constant cooling experiment. In this example, each cell contained 2-MACap:VP (1:1) copolymer in DMSO.

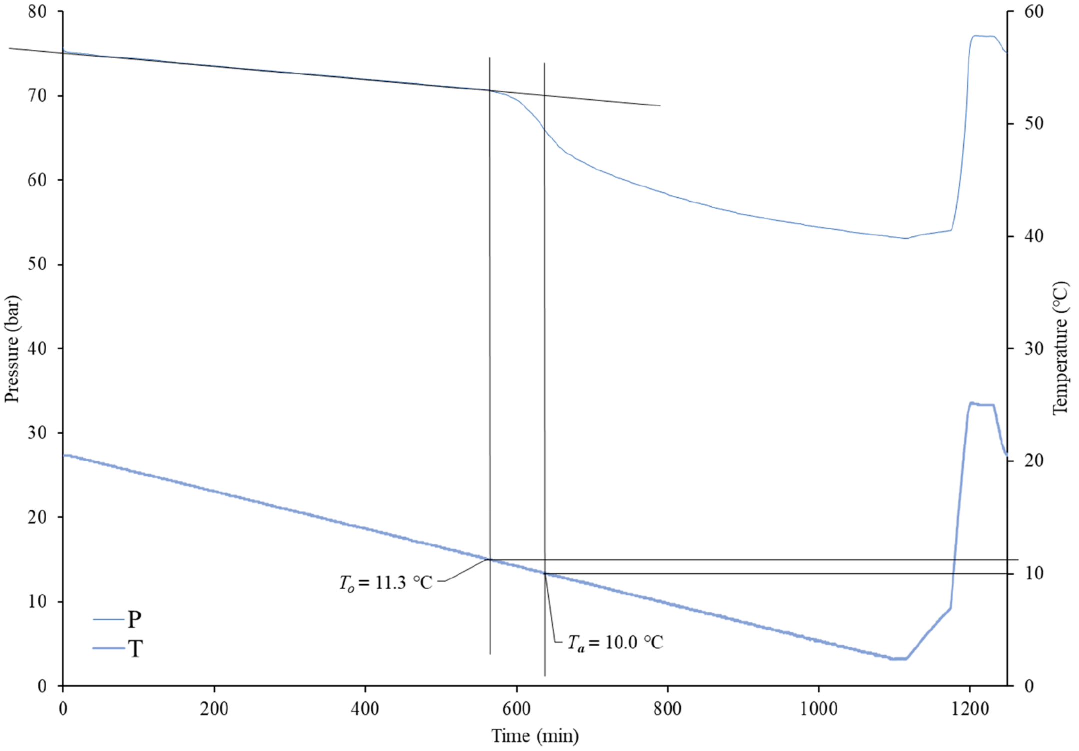

**Figure 7.** Graph from cell 5 containing 2-MACap:VP (1:1) in DMSO during a standard constant cooling experiment. Both $T_o$ and $T_a$ are determined in the graph.

depressurizing before another round with vacuum. This was done in order to replace the air with SNG in the cells.

4. The system was then pressurized with SNG to the experimental pressure of 76 bar.

Table 2. Polymers Synthesized in This Study

| polymer | Tcl (°C) | mol wt (g/mol) | PDI |
|---|---|---|---|
| poly(2-MACap) | <0 | 12 600 | 5.42 |
| 2-MACap:VP 1:1 copolymer | 27 | 99 400 | 2.67 |
| 2-MACap:VIMA 1:1 copolymer | 28 | 61 500 | 2.93 |
| 2-MACap:VIMA 1:2 copolymer | 35 | aggregated | |
| 2-MACap:VIMA 2:1 copolymer | 43 | aggregated | |
| 2-MACap:MOlMA 1:1 copolymer | >95 | not soluble in DMF | |
| 2-MACap:MMA 1:1 copolymer | 58 | 2 100 (major), 120 800 (broad minor) | 1.16, 12.21 |

5. While the cells were rocking at a rate of 20 rocks/min at an angle of 40°, the cells were cooled at a cooling rate of 1.0 °C/h from 20.5 to 2.0 °C.

In standard laboratory dissociation experiments warming at 0.025 °C/h for the last 3−4 °C, the hydrate equilibrium temperature ($T_{eq}$) at 76 bar has previously been determined to be 20.2 ± 0.05 °C. This correlated well with calculations done by the Calsep PVTSim software.[31,32]

Figure 6 shows an example of a constant cooling experiment with results from all five cells. In this particular experiment all five cells contain 2-MACap copolymerized 1:1 with VP. The initial pressure is 76 bar and the temperature is decreased from 20.5 to 2.0 °C during testing. There will be a linear pressure decrease since each cell is a closed system. From this linear pressure decrease both the onset temperature for hydrate formation ($T_o$) and the rapid hydrate formation temperature ($T_a$) can be observed. $T_o$ is defined as the temperature at which the first observable deviation from the linear pressure decrease is observed. It is however possible that the hydrate nucleation initiated at a molecular level is not detected by the test equipment. Instead, the deviation from the pressure trend corresponding to the first macroscopic observation of hydrate formation is measured. A rapid pressure decrease can be observed with varying interval after the $T_o$ has occurred. $T_a$ is defined as the temperature at which the pressure decrease is at its steepest, in other words, where the hydrate formation is at its fastest. An example of how these values are determined from one of the cells can be found in Figure 7.

## 3. RESULTS AND DISCUSSION

In our first attempts at polymerizing 2-MACap the solvent used was 2-propanol, with the result that the monomer did not polymerize. When we switched to DMSO as solvent, we managed to polymerize 2-MACap to form poly(2-MACap). However, this homopolymer was not soluble in water. Considering that the side groups are more hydrophilic than caprolactam in PVCap, we were initially surprised by this result. We suspect that considerable internal hydrogen bonding might be present in the homopolymer.[33]

Therefore, in order to obtain water-soluble polymers containing the 2-MACap monomer, we had to make copolymers. The majority of KHI polymers are based upon free radical polymerization of vinylic monomers, thus making the backbone polyvinyl. Formation of statistical copolymers with no particular order of the comonomers is the result of free radical polymerization of two or more vinylic comonomers.[34,35] Polymers and copolymers based on *N*-vinylcaprolactam (VCap) are the most commonly used. Comonomers such as *N*-vinylpyrrolidone (VP), *N*-vinylpyridine, *N*-methyl-*N*-vinylacetamide, vinyl acetate, (acrylamide)-propanesulfonic acid (AMPS), and (dimethylamino)-ethyl methacrylate (DMAEMA) have been investigated as KHIs.[18,36−39]

The monomers used to copolymerize with 2-MACap were *N*-vinyl-2-pyrrolidone (VP), *N*-vinyl-*N*-methylacetamide (VIMA), *N*-methylol methacrylamide (MOlMA), and *N*-methylmethacrylamide (MMA). The reason for choosing these is that they are hydrophilic and it was hoped they would not diminish the performance of poly-2-MACap assuming it had been water-soluble. It is also possible that the KHI performance could be increased by copolymerization, e.g., for VIMA as reported for its VCap copolymers.[19,20] Table 2 summarizes all the polymers and copolymers made in this study, with Tcl, molecular weight, and PDI where available. We assume the molar ratio of the two comonomers in the copolymer end product is approximately the same as the molar ratio before the start of polymerization since there were negligible protons on a C=C double bond by $^1$H NMR spectroscopic analysis.

Table 2 indicates that we encountered aggregation problems with the GPC analysis for two of the polymer samples, 2-MACap:VIMA (2:1) and 2-MACap:VIMA (1:2). We were able to see broad peaks for the nonaggregated state for 2-MACap, 2-MACap:VP (1:1), and 2-MACap:VIMA (1:1) at $M_n$ values of 12 600, 99 400, and 61 500 respectively. The GPC trace was too broad to see the unaggregated state for polymers 2-MACap:VIMA (2:1) and 2-MACap:VIMA (1:2). The reason for the bimodal distribution of 2-MACap:MMA (1:1) is not known but may be due to very uneven polymerization rates of the monomers. Some of the polymer molecular weights were not ideal for optimal performance or comparison. However, this was our first foray into 2-MACap polymer chemistry and the results discussed below still give a good indication of the potential of this new KHI technology.

Besides Table 2, the cloud points for the 2-MACap polymers are graphically represented in Figure 8. It can be observed that, of the water-soluble copolymers, 2-MACap:VP (1:1) had the lowest cloud point and the 2-MACap:MOlMA (1:1) had the highest. The VIMA copolymers had an increase in cloud point from 2-MACap:VIMA (1:1) to 2-MACap:VIMA (1:2) and 2-MACap:VIMA (2:1). Adding a hydrophilic comonomer to a

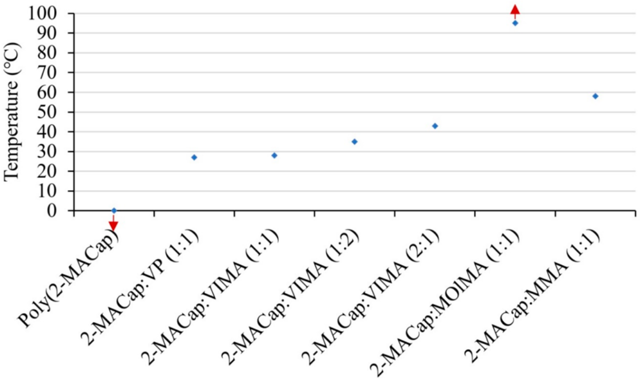

**Figure 8.** Graphical presentation of cloud points for water-soluble copolymers together with the homopolymer.

### Table 3. Summarized KHI Test Results for the Water-Soluble Polymers, Also with Synergist Solvents[a]

| copolymer | solvent synergist | concentration (ppm) polymer | concentration (ppm) synergist | $T_o$ (°C) | $T_a$ (°C) |
|---|---|---|---|---|---|
| no additive | | | | 17.2 | 16.6 |
| PVCap | | 2500 | | 10.4 | 8.9 |
| PVP K-15 | | 2500 | | 13.3 | 9.1 |
| PVIMA | | 2500 | | 14.2 | 13.2 |
| 2-MACap:VP (1:1) | | 2500 | | 11.2 | 10.0 |
| | | 5000 | | 8.9 | 7.5 |
| | iBGE | 2500 | 5000 | 8.3 | 6.7 |
| | 4-MePeOl | 2500 | 5000 | 6.7 | 5.4 |
| 2-MACap:VIMA (1:1) | | 2500 | | 8.8 | 7.7 |
| | | 5000[b] | | 9.2 | 8.2 |
| | iBGE | 2500 | 5000 | 7.4 | 6.3 |
| | 4-MePeOl | 2500 | 5000 | 5.7 | 4.6 |
| 2-MACap:VIMA (1:2) | | 2500 | | 10.9 | 10.1 |
| | | 5000 | | 7.6 | 7.2 |
| 2-MACap:VIMA (2:1) | | 2500 | | 11.0 | 10.5 |
| 2-MACap:MOlMA (1:1) | | 2500 | | 14.7 | 14.5 |
| 2-MACap:MMA (1:1) | | 2500 | | 8.8 | 8.1 |
| | | 5000 | | 6.4 | 5.7 |
| | iBGE | 2500 | 5000 | 6.2 | 5.4 |
| | 4-MePeOl | 2500 | 5000 | 4.6 | 3.8 |

[a] iBGE = isobutyl glycol ether; 4-MePeOl = 4-methyl-1-pentanol. [b] 97+% soluble.

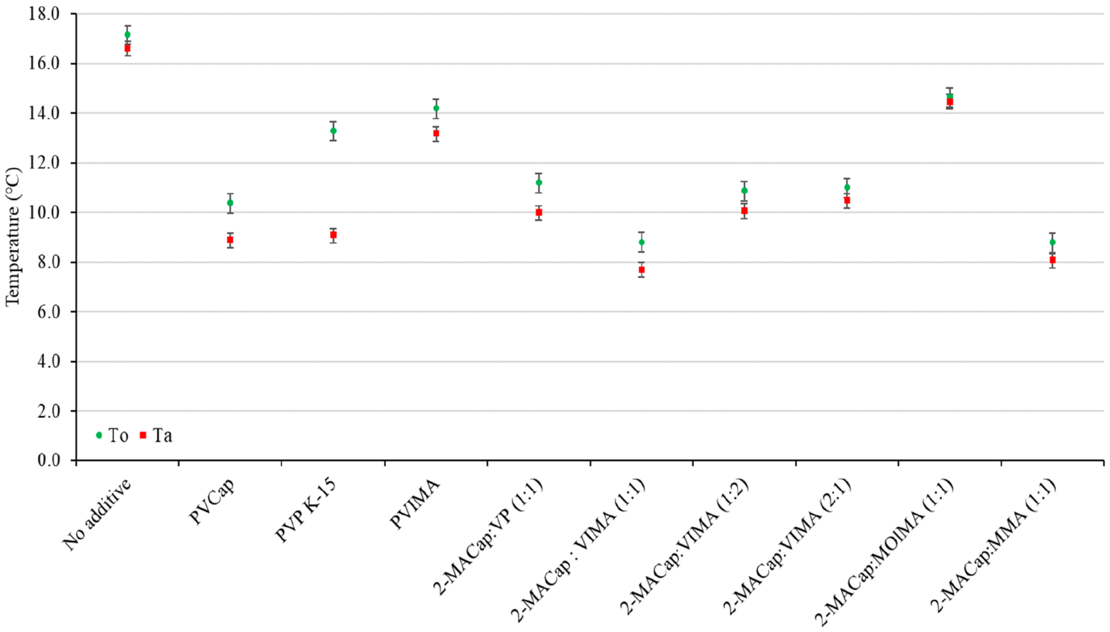

**Figure 9.** Graphical summary of polymers and copolymer KHI test results at 2500 ppm.

very active KHI monomer forming a copolymer will usually increase the cloud point.[19] This is also demonstrated by the cloud point of 2-MACap:MMA (1:1). The addition of the synergist solvents 4-methyl-1-pentanol (4-MePeOl) and isobutyl glycol ether (iBGE), used and discussed later in this study, had a negligible effect on the cloud point of this copolymer at the concentrations tested.

The benefit of low cloud point for high KHI performance, given the correct size functional groups, has been investigated previously.[40] This advantage has been suggested as being due to maximizing the KHI polymer surface area/hydrodynamic volume ratio. For example, copolymers of VIMA:VCap have better performance than PVCap homopolymer despite a higher cloud point, which is assumed to be due to a greater surface area/hydrodynamic volume (SA/HV) ratio for the copolymers. Further, copolymers of *N*-vinylazacyclooctanone (VACO) with *N*-vinyl-*N*-methylacetamide (VIMA) perform better than PVACO (due to higher SA/HV factor) or VIMA:VCap (due to SA/HV and lower cloud point).[19]

Only the polymers that were water-soluble were tested for their inhibition performance in KHI tests. The KHI test results are summarized in Table 3. For each copolymer, a minimum of five tests were done. The maximum number of tests for a copolymer was 14, where we needed more tests for a statistically significant result. Thus, both the $T_o$ and $T_a$ values reported in the following are averages. The focus will be on the

$T_o$ value, since the $T_a$ values are not easy to get meaningful comparative data from, unless the $T_o$ values are similar. When synergist was added, the concentration was always 2500 ppm for the copolymer and 5000 ppm for the synergist. Also included in Table 3 are results for PVCap ($M_w$ = 10 000 g/mol),[41] PVP K-15 ($M_w$ = 8000 g/mol),[42] and PVIMA ($M_w$ = 12 401 g/mol)[43] from previous studies using the same equipment and test method.

From Table 3 one can observe that all the copolymers gave some KHI effect compared to no additive. The solubility for the copolymers differed. Interestingly, not all of them showed complete solubility at 5000 ppm. Those that were completely soluble, plus 2-MACap:VIMA (1:1) with <3% insoluble material, were tested at 5000 ppm. We speculate that there may be considerable internal hydrogen bonding, making the pendant groups less available for hindering gas hydrate nucleation or crystal growth. In the polymer and in the copolymers there exist many options where this type of bonding can take place: between 2-MACap units, between copolymerization units, and between 2-MACap units and copolymerization units. Hydrogen bonding can also occur between polymer strands. In addition, polymerization rates of the monomers were different, and this could possibly make blocks of each monomer rather than an even distribution throughout the copolymer, causing some of the copolymer strands to exhibit low water solubility or even surfactant properties. For example, 2-MACap:VIMA (1:1) at 2500 ppm gave a foamy solution, and at a concentration of 5000 ppm a very small amount of the copolymer was not soluble (<3%). Since all the copolymers were water-soluble at 2500 ppm, we present results from their KHI performance tests graphically in Figure 9 together with PVCap, PVP-K15, and PVIMA for comparison. For those copolymers that were completely water-soluble, i.e., 2-MACap:VP (1:1), 2-MACap:VIMA (1:1), 2-MACap:VIMA (1:2), and 2-MACap:*N*-methylmethacrylamide (1:1), their performances as KHIs are compared for 2500 and 5000 ppm in Figure 10.

Beginning with the first copolymer made, 2-MACap:VP (1:1), at 2500 ppm we obtained $T_o$ and $T_a$ values of 11.2 and 10.0 °C, respectively. This copolymer was also the copolymer in this study with the lowest cloud point (27 °C). The performance was a little bit poorer than that of pure PVCap, but significantly better than that of PVP K-15 which had $T_o$ and $T_a$ values of 13.3 and 9.1 °C, respectively. This indicates that the caprolactam group in the 2-MACap monomer is a more effective monomer for KHI polymers than the VP monomer. This is further underlined by the nonoptimal high molecular weight of 2-MACap:VP (1:1) copolymer (99 400 g/mol) compared to the relatively low value for PVP-K15 (8000 g/mol). When the concentration of 2-MACap:VP (1:1) was increased to 5000 ppm, the $T_o$ value dropped to 8.9 °C, showing a clear improvement in the KHI performance of the copolymer compared to that at 2500 ppm.

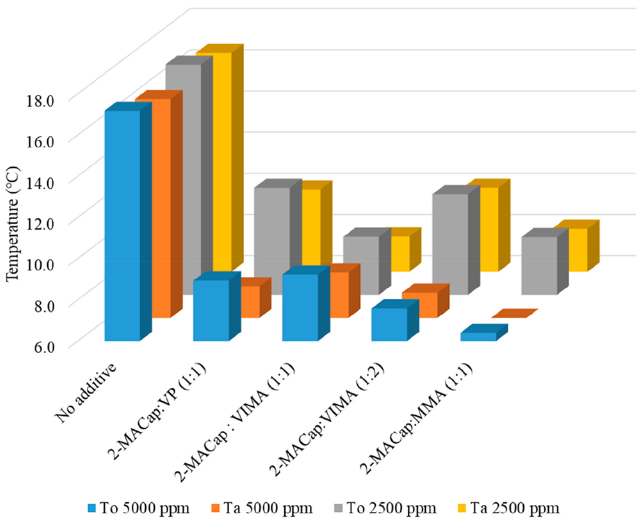

**Figure 10.** Comparison of $T_o$ and $T_a$ values at concentrations of 2500 and 5000 ppm for copolymers that were water-soluble at both concentrations.

For 2-MACap:VIMA (1:1) the $T_o$ value was 8.8 °C and the $T_a$ value was 7.7 °C when the concentration was 2500 ppm. This copolymer had a low cloud point (28 °C) similar to 2-MACap:VP (1:1). This copolymer had a better performance than pure PVCap had at the same concentration. Copolymers with other ratios of these monomers (1:2 and 2:1) had poorer performances at 2500 ppm (Figure 11). This correlates well with results for VIMA:VCap copolymers, where it was shown that a 1:1 copolymer had the best KHI performance.[19,20] One possible reason for this beneficial KHI effect of the VIMA in the copolymers of VIMA:VCap is that it causes a greater surface area/hydrodynamic volume ratio compared to PVCap homopolymer, thus allowing caprolactam groups more interaction with the water phase and hydrate particle surfaces.[20,40]

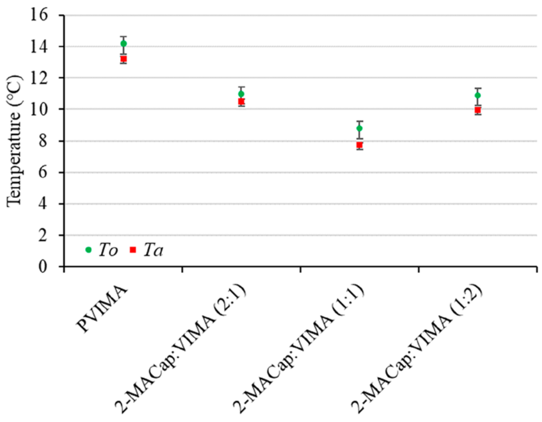

**Figure 11.** 2-MACap:VIMA in the ratios 1:1, 1:2, and 2:1 compared with PVIMA, all with 2500 ppm concentration.

When the concentration of 2-MACap:VIMA (1:1) was increased to 5000 ppm, it was expected that there would be a clear improvement in the performance as KHI, but this was not the case. The $T_o$ value between 2-MACap:VP (1:1) at 5000 ppm and at 2500 ppm was not found to be significantly different ($p > 0.05$ in a statistical $t$-test). This was most likely caused by the solubility issue at the higher concentration. This fits with the even poorer solubility of 2-MACap:VIMA (2:1) copolymer at 5000 pm and the KHI results with 2-MACap:VIMA (1:2) copolymer. This 1:2 copolymer, which is more hydrophilic and fully soluble at 5000 ppm, showed a marked improvement in KHI performance when the concentration was increased from 2500 to 5000 ppm.

Because of solubility issues and surfactant properties of some of the 2-MACap:VIMA copolymers, we therefore tried acrylamide monomers. We hoped these conjugated vinyl

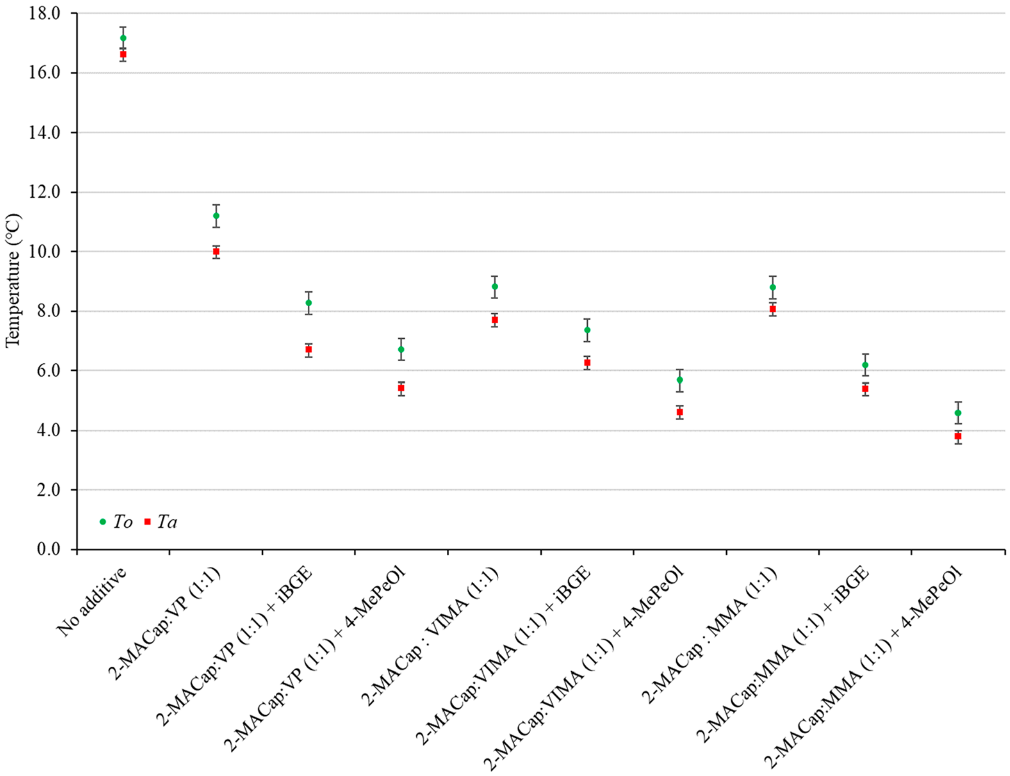

**Figure 12.** KHI synergetic effect of 5000 ppm iBGE or 4-MePeOl added to 2500 ppm 1:1 2-MACap copolymers with VP, VIMA, and MMA.

monomers would have a polymerization rate fairly similar to that of 2-MACap, which hopefully would diminish the solubility and surfactant issues. 2-MACap:MOlMA (1:1) copolymer had a $T_o$ value of 14.7 °C and a $T_a$ value of 14.5 °C at a concentration of 2500 ppm. Do to the poor result, this copolymer was not tested at a concentration of 5000 ppm. The poor result may be due to being overly hydrophilic causing a lack of cloud point up to 95 °C as discussed earlier.

2-MACap:MMA (1:1) had a much better KHI performance, with $T_o$ and $T_a$ values of 8.8 and 8.1 °C, respectively, at a concentration of 2500 ppm. This is better than PVCap and with a more useful cloud point (58 °C) for field use. The $T_o$ value of 2-MACap:MMA (1:1) at 2500 ppm was in the same range as the $T_o$ value for both 2-MACap:VP (1:1) at 5000 ppm and 2-MACap:VIMA (1:1) at 2500 ppm. The average $T_o$ and $T_a$ values between 2-MACap:MMA (1:1) at 2500 ppm and 2-MACap:VIMA (1:1) at 2500 ppm were not found to be significantly different ($p > 0.05$). This indicates that the performances of these copolymers are similar although the molecular weights are clearly different.

2-MACap:MMA (1:1) copolymer, which was fully soluble at a concentration of 5000 ppm, gave an average $T_o$ value of 6.4 °C and a $T_a$ value of 5.7 °C. This shows the same trend as for the other fully water-soluble copolymers, i.e., that higher concentration of copolymer results in better KHI performance, which is typically seen within this concentration range. In addition, 2-MACap:MMA (1:1) has a bimodal molecular weight distribution with most of the polymer being of low molecular weight. This could be an advantage compared to a monomodal distribution of only low molecular weight, as was found for PNIPMAM.[44,45]

From previous research it is well-known that certain solvents can act as synergists with the KHI polymer.[20] For example, we have shown previously that isobutyl glycol ether (iBGE) had a strong good synergetic effect on PVCap and PNIPMAM. Further, 4-methyl-1-pentanol (4-MePeOl) had a very strong synergetic effect on PVCap.[41,46] Therefore, we were interested to see the possible synergetic effect of these two solvents with 2-MACap copolymers. Results with 2500 ppm 1:1 copolymers of VP, VIMA, and MMA with 5000 ppm solvent are given in Table 3 and graphically in Figure 12.

All three of the copolymers had an improved KHI performance when synergists iBGE and 4-MePeOl were added. The effect of 4-MePeOl was larger for all copolymers. The best result was obtained for 2-MACap:MMA (1:1) copolymer with added 4-MeHexOl, resulting in a $T_o$ value of 4.6 °C and a $T_a$ value of 3.8 °C. Looking back over the past 10 years of work from our research group with the same test method, this represents one of the best results for polymers with reasonably high cloud points, useful for many field applications.

The mechanisms behind the synergetic effect of alcohols or glycol ethers on KHI polymers are not well-established. One reported hypothesis is that alcohols or glycol ethers increase the ability of the KHI polymers to adsorb on nucleation and/or growth sites.[47,48] The reason that 4-MePeOl worked so well as synergist with PVCap is thought to be because both the size and shape of the alkyl group are important for the synergy, but also the fact that the alcohol is close to the solubility limit may also be a factor.[40] We suspect that this is also the case for the good synergy between 2-MACap copolymers and 4-MePeOl.

## 4. CONCLUSION

We have synthesized and investigated the KHI properties of polymers of 2-methacrylamido-caprolactam (2-MACap) for the first time. Poly(2-MACap) homopolymer was found to be insoluble in water; therefore, a range of copolymers were made. The solubility and molecular weights of the copolymers varied and may be due to significantly different polymerization rates of 2-MACap and the other comonomers. All the copolymers showed KHI effects compared to no additive. The 2-MACap:MOlMA (1:1) copolymer, which was the most hydrophilic copolymer with no cloud point, gave the poorest result. Of the copolymers investigated, several had better KHI performances than PVCap, with 2-MACap:MMA (1:1) copolymer giving outstanding results as well as possessing a fairly high cloud point for a wide range of field applications. However, comparisons of performances are hampered by the variation in molecular weights of the copolymers. Several 2-MACap copolymers performed significantly better when blended with synergist solvents, iBGE and 4-MePeOl, with the latter giving the more powerful effect.

Although this study is the first time that polymers of 2-MACap have been synthesized and tested as KHIs, the results are very promising. Further optimizing of the polymers should be possible for improved KHI performance. Both 2-MACap:VIMA (1:1) and 2-MACap:MMA (1:1) show the potential to be further optimized, with the latter probably having the greater potential. Further synthesis work will focus on investigating other comonomers, optimizing the molecular weight of the copolymers, adjusting the polymerization procedure, and the monomer feed ratio. Other KHI test methods and test conditions will also be investigated for the best polymers.

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### Notes

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# Paper VIII

Alternative Lactam-Based Kinetic Hydrate Inhibitors─ Investigation of Polymers of 2-Methacrylamido-caprolactam

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Article

# Alternative Lactam-Based Kinetic Hydrate Inhibitors—Investigation of Polymers of 2-Methacrylamido-caprolactam

Erik G. Dirdal* and Malcolm A. Kelland

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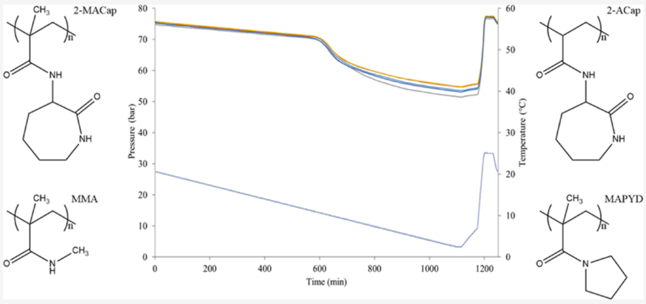

**ABSTRACT:** Kinetic hydrate inhibitors (KHIs), such as poly(*N*-vinylcaprolactam) (PVCap) and related copolymers, are a well-known method to help combat gas hydrate formation in oil and gas field production flow lines. The caprolactam groups in this polymer class have been shown previously to have a particularly strong interaction with hydrate surfaces, inhibiting crystal growth, but probably also gas hydrate nucleation. In an earlier study, we reported on the first alternate KHI polymer class with pendant caprolactam groups based on the 2-methacrylamido-caprolactam (2-MACap) monomer. This report builds on that study, by optimizing the best copolymers from that study and copolymerizing 2-MACap with other comonomers. KHI experiments were carried out in high-pressure steel rocking cells using a structure II-forming natural gas mixture. The KHI performance of some of these copolymers exceeded that of PVCap of similar molecular weight. In addition, the importance of the methyl group in 2-MACap for enhanced KHI performance was confirmed by making and testing polymers with 2-acrylamido-caprolactam, which has no methylated backbone. Further confirmation from 2-MACap copolymers with 1-acryloylpyrrolidine and *N*-methacryloylpyrrolidine, for which the latter copolymer performed best. Finally, it was shown that a series of well-known synergists for PVCap were able to give excellent KHI performance enhancement of the selected 2-MACap copolymers, although some molecules showed antagonistic effects. This could be due to unhelpful polymer−synergistic interactions or both molecules competing in the same KHI mechanistic processes.

## 1. INTRODUCTION

Gas hydrates are non-stoichiometric crystalline solids that have many similarities with ice. Gases of certain molecular-weight stabilize the hydrogen-bounded molecular water cages. These relatively low-molecular-weight gases are entrapped within the cavities of the lattice of solid water molecules. Thus, gas hydrates will form if suitable low-molecular-weight hydrocarbon gases combine with water under specific favoring conditions of temperature (<25 °C) and pressure (>30 bar).[1−4] The formation of the gas hydrate is an energetically (enthalpy) favored process because of the extraordinary amount of energy that is released as heat as additional hydrogen bonds form. Gas hydrate formation is thus an exothermal process. Because of these additional hydrogen bonds formed, a more ordered structure is formed. Therefore, the formation of the gas hydrate is not favored by entropy.[5,6]

These gas hydrate favorable conditions are not uncommon to encounter when producing or transporting oil and gas. If the situation is left unattended, then gas hydrate plugs can occur, potentially jeopardizing the operation.[4,7−14] There exist multiple measures to handle and treat gas hydrates, with one of them being the utilization of chemicals. More specifically, low-dosage hydrate inhibitors and the sub-group kinetic hydrate inhibitors (KHIs).[7] The concentration range, in which these KHIs are added is 0.1−1.0 wt %.[10,15−19]

The KHI formulation consists of two parts, the water-soluble polymer and the carrier solvent.[20]

Regarding the carrier solvent, it typically makes up 70−90 wt % of the KHI formulation. This is often a low-molecular-weight alcohol, glycol, or glycol ether, like methanol, ethanol, monoethylene glycol, and 2-*n*-butoxyethanol (BGE).[14] The viscosity of the KHI polymer solution is diluted sufficiently to enable it to be injected and pumped over long distances in umbilical flow lines. The carrier solvent can enhance the hydrate inhibiting properties of the polymer, and thus act as a synergist with the KHI polymer. The solvent synergism is therefore able to increase the application performance window of the pure KHI polymer or reduce the total polymer dosage.[20]

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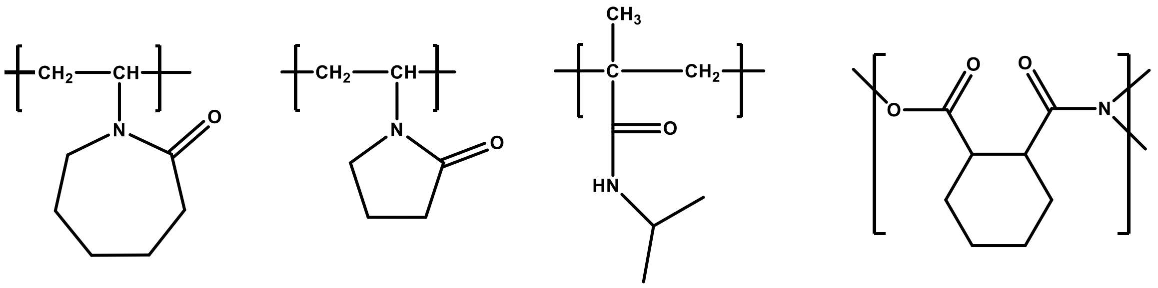

**Figure 1.** Structures of common KHIs, from left to right: PVCap, PVP, poly(*N-iso*-propylmethacrylamide) (PNIPMAM) (polyvinylic KHIs), and the esteramide unit in hyperbranched poly(ester amide)s.

Regarding the polymers, this is the main active compound and typically makes up 10−30 wt % of the KHI formulation.[20] Further, the polymer needs two structural features in order to perform good as hydrate inhibitors. This is achieved by incorporating hydrophilic and hydrophobic moieties into the polymer. The hydrophilic functional groups of the polymer consists usually of amide, imide, or amine oxide groups, moieties that are capable of making strong hydrogen bonds.[7,21,22] For the best performance of the polymer, the hydrophilic functional groups must be accompanied either directly or adjacent by a hydrophobic functional group.[23] These features consist of enabling the polymer to have both hydrophilic and hydrophobic capabilities making the polymer amphiphilic. The molecular weight of the polymer also determines how good it will perform as KHI, with a bimodal distribution of the molecular weight giving better nucleation inhibition.[24] However, it is beneficial that the majority of the polymer is of low-molecular weight, with a smaller portion being of higher molecular weight.[21] The bulk of commercially available KHI polymers and copolymers are based on the monomers *N*-vinylcaprolactam (VCap), *N*-vinylpyrrolidone (VP), and *N*-isopropylmethacrylamide, as well as hyperbranched poly(ester amide)s based on diisopropanolamine and various cyclic anhydrides (Figure 1).[7]

The mechanism behind the inhibition properties of these KHI polymers as well as the synergetic mechanism is not fully understood and highly debatable. The performance of KHI polymers have been ascribed to different mechanisms because there is no consensus within the hydrate community and ranges from labile cluster hypothesis, nucleation at interface hypothesis, local structuring mechanism, and the blob mechanism.[22,25] However, the KHI polymers are believed to kinetically interact with the hydrate formation process and are able to interfere with the hydrate nucleation step and/or the crystal growth process. Further, the KHI polymers are assumed to prevent the hydrate particles from reaching the critical size for continuous growth by binding onto the surface of hydrate particles at an early stage of nucleation and growth.[15,16] Hence, any nuclei with a radius smaller than the critical radius will re-dissolve in the liquid medium.[16,25,26] Thus, clusters of these molecules can either grow or shrink until they reach the critical size. Until they exceed the critical size, the agglomerates are in quasi equilibrium with each other and the labile clusters.[27] When clusters possessing the critical size, monotonic growth occurs. This phenomenon can also be interpreted as an excess in Gibbs free energy, $\Delta G$, between the small dissolved solid particles and the solvent in the solution.[28] $\Delta G$ becomes negative and the growth becomes spontaneous or catastrophic.[1] The hypothetical mechanisms behind the synergetic performance of the solvents, especially glycol ethers and alcohols, range from co-operative adsorption on the hydrate particles and/or water perturbation together with the KHI polymer, as well as giving a stronger adsorption of the KHI polymer on the surface of the aqueous phase where nucleation is expected to first occur by lowering the gas/liquid interfacial tension.[29−36]

One of the best KHIs currently available is poly(*N*-vinylcaprolactam) (PVCap), and several copolymers of VCap have also been applied in the field.[37] The majority of KHI polymers are based upon free radical polymerization of vinylic monomers, thus making the backbone polyvinyl. Free radical polymerization of two or more vinylic comonomers will cause the formation of statistical copolymers with no particular order of the comonomers.[38,39] Polymers and copolymers based on VCap are the most commonly used. Comonomers such as VP, *N*-vinylpyridine, *N*-methyl-*N*-vinyl acetamide, vinyl acetate, (acrylamide)propanesulfonic acid and (dimethylamino)-ethyl methacrylate have been investigated as KHIs.[16,40−43] Compared to other KHI polymer classes such as poly(alkyl methacrylamide)s, VCap-based KHI polymers are known to be particularly good at inhibiting hydrate crystal growth.[1,7,17] This means that once hydrate nucleation has started it may still be a long time before enough hydrate crystals have formed before catastrophic hydrate growth occurs using a VCap-based polymer. This can give the field operator a better opportunity to avoid completely plugging the flow line once hydrates are first suspected to be formed.

This gave us the incentive to investigate alternate caprolactam-based polymers. Interestingly, there exist very few reported studies on polymers containing caprolactam rings as KHIs, except for the VCap-based polymers. Our research group have previously attempted to react 2-aminocaprolactam with poly(dichlorophosphazene) in order to make poly(caprolactam-2-amino)phosphazene, which was water soluble as a homopolymer.[44] Another attempt was made by synthesizing acryloyloxyethylcaprolactam and acryloyloxymethylcaprolactam but it proved surprisingly difficult to make poly(*N*-acryloyloxyalkylcaprolactams), probably due to steric problems during the polymerization procedure (Figure 2).[44]

Both of the poly(caprolactam-2-amino)phosphazene and polyacryloalkylenecaprolactams had their drawbacks. Therefore, in the previous research, we synthesized 2-methacrylamidocaprolactam (2-MACap) from $\alpha$-amino-$\varepsilon$-caprolactam reacted with methacryloyl chloride, which was not water soluble as a homopolymer and needed to be copolymerized.[45] 2-MACap was copolymerized with the more hydrophilic monomers, *N*-methylmethacrylamide (MMA), *N*-methylol methacrylamide (MOIMA), VP, and *N*-vinyl-*N*-methylacetamide (VIMA) (Figure 3). Of these copolymers, 2-MACap/MMA (1:1) showed the best potential KHI potential. In addition, it had a fairly high cloud point at 1 wt % in deionized water (58 °C) and the KHI performance was improved with two solvent synergists.

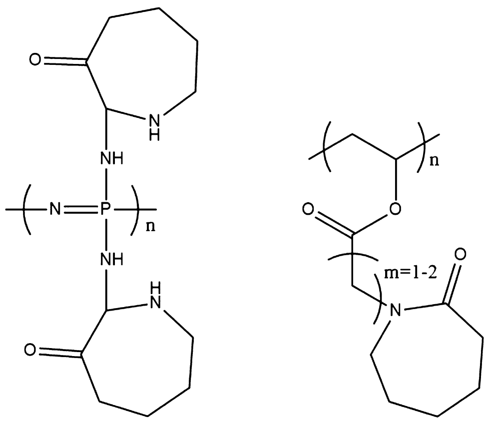

**Figure 2.** Poly(caprolactam-2-amino)phosphazene (left) and poly-acryloalkylenecaprolactams (right).

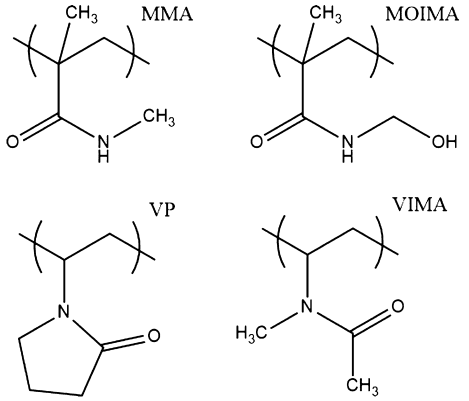

**Figure 3.** Hydrophilic comonomer units polymerized with 2-MACap from the previously study:[45] MMA, MOIMA, VIMA, and VP.

In this study, we continued our research on the new class of caprolactam-containing polymers to understand the structure−performance relationship better and find further improvements. We chose some new comonomers to copolymerize with 2-MACap that we postulated could either enhance the performance or raise the cloud point to more useful levels. We also investigated polymers with a new monomer 2-acrylamido-caprolactam (2-ACap) to determine if an extra methyl group in the polyvinyl backbone is favorable for KHI performance, as seen for *N*-alkyl methacrylamide polymers and poly(*N*,*N*-dimethylhydrazido methacrylamide)[46−48] (Figure 4). In addition, we have also investigated the synergetic properties of 2-MACap polymers with some molecules that are well-known synergists for PVCap to see if the performance improvements are similar with our new class of caprolactam-based polymers.

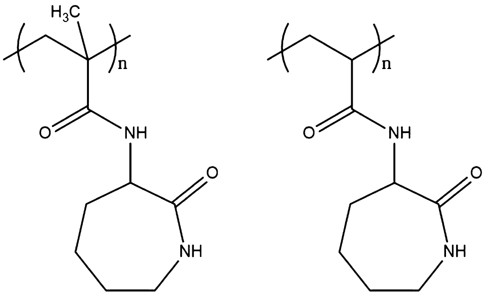

**Figure 4.** Poly(2-methacrylamido-caprolactam) [poly(2-MACap)] (left) and poly(2-acrylamido-caprolactam) [poly(2-ACap)] (right).

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** $\alpha$-Amino-$\varepsilon$-caprolactam was obtained from ABCR, Germany. Triethylamine and solvents used in this study were obtained from Merck. MOIMA was obtained from Evonik, Germany. MMA was obtained from Tokyo Chemical Industry (TCL). Methacryloyl chloride, *N*-vinyl-2-pyrrolidone, and VIMA were obtained from Sigma-Aldrich. All chemicals were commercially available and used without further purification. 1-Acryloylpyrrolidine (APYD),[49] *N*-methacryloylpyrrolidine (MAPYD),[50] and *N*-(pyrrolidine-1-yl)-methacrylamide (NPyMA)[51] were synthesized previously. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ascend NMR 400 MHz spectrometer at ambient temperature unless otherwise stated.

**2.2. Synthesis of 2-MACap.** The synthesis was based on the described method,[52] by dissolving $\alpha$-amino-$\varepsilon$-caprolactam (1 g, 7.80 mmol) in dichloromethane (20 mL) in a 100 mL round-bottomed flask. Triethylamine (0.79 g, 7.80 mmol) was then added and the solution was cooled to 0 °C in an ice bath. Methacryloyl chloride (0.82 g, 7.80 mmol) dissolved in dichloromethane (10 mL) was added dropwise to the solution in the round-bottomed flask with vigorous stirring. The mixture was slowly heated to room temperature and stirred overnight. The reaction mixture was washed with NaCl brine. Then, the organic phase was extracted, washed with d. i. water, and dried with $Na_2SO_4$. The precipitated $NEt_3HCl$ (s) was filtered off and solvent was removed in vacuo on a rotary evaporator to yield 2-MACap. $^1H$ NMR confirmed that the resulting product was pure and was used for polymerizations without further purification.

**2.3. Synthesis of 2-ACap.** This synthesis was also based on the described method,[52] by dissolving $\alpha$-amino-$\varepsilon$-caprolactam (5 g, 39.01 mmol) in dichloromethane (20 mL) in a 100 mL round-bottomed flask. Then, triethylamine (3.95 g, 39.01 mmol) was added and the solution was cooled to 0 °C in an ice bath. Acryloyl chloride (3.53 g, 39.01 mmol) dissolved in dichloromethane (5 mL) was added dropwise to the solution in the round-bottomed flask with vigorous stirring. The mixture was slowly heated to room temperature and stirred overnight. The resulting white precipitate was filtered off and washed with dichloromethane. The combined solvents were then removed in vacuo on a rotary evaporator to yield 2-ACap. $^1H$ NMR confirmed that the resulting product was pure and was used for polymerizations without further purification.

**2.4. Poly(2-MACap), Poly(2-ACap), and Copolymer Synthesis Thereof.** From the first study, we found out that 2-MACap would not polymerize in 2-propanol, so dimethylsulfoxide (DMSO) was the preferred solvent used.[45] The resulting homopolymer was, however, not water soluble, as was also the case for 2-ACap. Therefore, copolymers were made for both these monomers. The polymerization synthesis was done in the same general manner for all copolymers. 2-MACap or 2-ACap (0.50 g, 2.50 mmol) was dissolved in DMSO (2 g) in a Schlenk flask with a magnet. The desired amount of the comonomer was added depending on the monomer ratio in the copolymer required. Then, AIBN (1 wt %) was added and the solution was flushed with dinitrogen using a standard pump-fill technique. While the solution was stirring, it was heated to 70 °C and left to react under the protection of dinitrogen overnight. Then, the copolymer solution was cooled to room temperature and the product was left in the solution. $^1H$ NMR showed that all the monomer was consumed.

The comonomers used to make copolymers of 2-MACap were methacrylamide (MAm), MMA, *N*,*N*-dimethylmethacrylamide (DMMAm), *N*-isopropylmethacrylamide (NIPMAm), *N*,*N*-dimethylhydrazidomethacrylamide (NDMHMAm), APYD, MAPYD, NPyMA, poly(ethylene glycol)monoethyl methacrylate (PEGMA-9), and VIMA (Figure 5).

**2.5. Gel Permeation Chromatography/Size Exclusion Chromatography Analysis.** Gel permeation chromatography/size exclusion chromatography (GPC/SEC) analysis was conducted in order to determine the molecular weight as well as the polydispersity index of

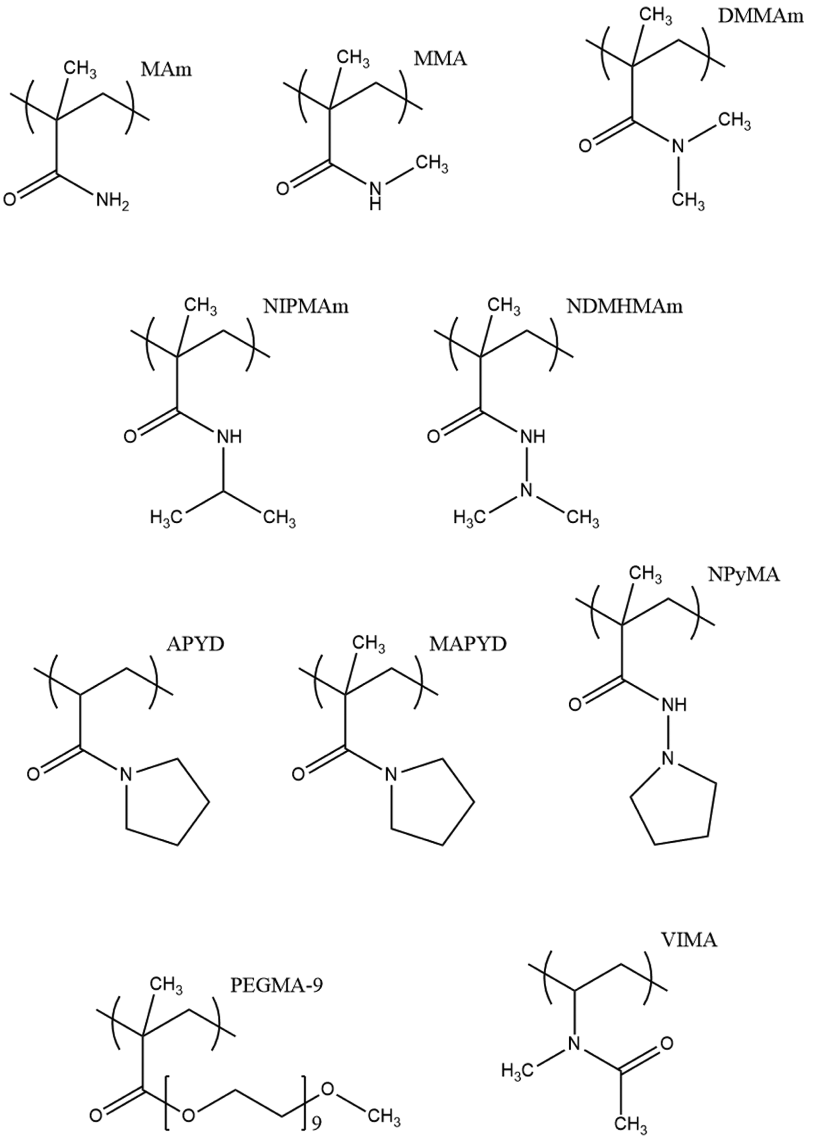

**Figure 5.** Structure of comonomer units used with 2-MACap copolymers: MAm, MMA, DMMAm, NIPMAm, NDMHMAm, APYD, MAPYD, NPyMA, PEGMA-9, and *N*-methyl-*N*-vinylacetamide (VIMA).

the polymers made. The apparatus used was a JASCO Chem NAV size-exclusion chromatography system. This system was equipped with PU-2080, AS-2055, CO-2065 RI-2031, and two commercial columns (TSKgel SuperH4000 and TSKgel GMHXL). The testing was done at 40 °C with dimethylformamide (DMF) as an eluent. Polystyrene standards were used for calibrating the molecular weights of the polymers.

**2.6. Cloud Point ($T_{cl}$) Measurements.** A sample of the polymer was dissolved in deionized water making a 2500 ppm concentration. This solution was then heated at approximately 2 °C/min. A visual observation was continuously done during heating, and the cloud point ($T_{cl}$) was determined at the temperature where the first sign of haze was observed. This was repeated minimum one more time for each polymer for the verification of the $T_{cl}$ temperature and to show reproducibility.

**2.7. Gas Hydrate KHI Performance Testing Using High-Pressure Apparatus.** The KHI performance testing was conducted in a multi-rocking cell apparatus, the Rocking Cell 5 (RC5) apparatus supplied by PSL Systemtechnik, Germany. This apparatus contains a cooling bath where five high-pressure stainless steel rocking cells, supplied by Svafas, Norway, are rocked. Both the cooling bath and the cells are equipped with temperature sensors in addition to each cell having pressure sensors. The cells have an internal volume of 40 mL and a stainless-steel ball inside each cell is used for agitating the test solution. A standard natural gas mixture (SNG), which preferentially forms a structure II gas hydrate as the most thermodynamically stable phase, was the gas used in these tests (Table 1).

The procedure for high-pressure KHI testing by the use of slow constant cooling (SCC), described previously, is summarized in the following:[53,54]

1. At least 1 day before initializing the test, the polymer, and if applicable the synergist, was dissolved to the desired concentration in deionized water.

### Table 1. Composition of the Synthetic Natural Gas Mixture (SNG) Used in the High-Pressure KHI Performance Testing

| component | mol % |
|---|---|
| methane | 80.67 |
| ethane | 10.20 |
| propane | 4.90 |
| iso-butane | 1.53 |
| *n*-butane | 0.76 |
| $N_2$ | 0.10 |
| $CO_2$ | 1.84 |

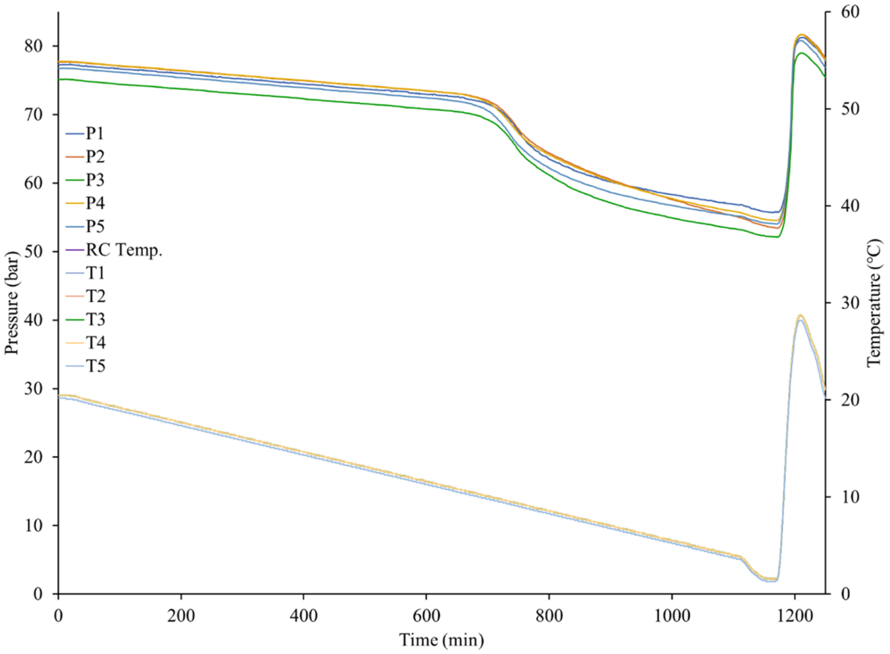

**Figure 6.** Graph containing the results from all five cells during a SCC experiment. In this example, each cell contained 2-MACap/MMA (1:2) copolymer in DMSO. RC temp. is the temperature recorded in the cooling bath.

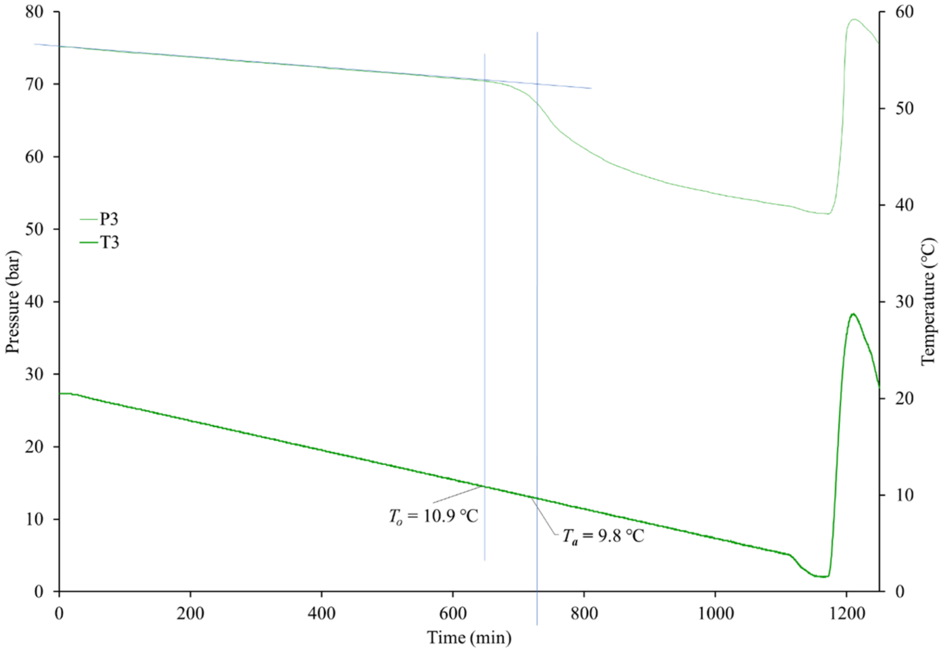

**Figure 7.** Graph from cell three during a SCC experiment with both $T_o$ and $T_a$ is determined. In this example, the cell contained 2-MACap/MMA (1:2) copolymer in DMSO.

2. Usually 20 mL of solution was added to each of the five cells, with the solution consisting of various additives dissolved in distilled water.
3. A sequence of vacuum and pressurizing with SNG was applied in order to replace the air with SNG in the cells. First, vacuum then pressurizing with SNG to 3−5 bar, and then depressurizing before a final round with vacuum.
4. The system was then pressurized to an experimental pressure of 76 bar with SNG.
5. The cells were cooled down and rocked with a cooling rate of 1.0 °C/h from 20.5 to 2.0 °C, and a rocking rate of 20 rocks per minute at an angle of 40°, respectively.

The hydrate equilibrium temperature ($T_{eq}$) at 76 bar have previously been determined to be 20.2 ± 0.05 °C by standard laboratory dissociation experiments warming at 0.025 °C/h for the last 3−4 °C. This correlated well with calculations done by Calsep PVTSim software.[55,56]

The initial pressure was 76 bar and the temperature were decreased from 20.5 to 2 °C during a SCC experiment (Figure 6). Because each cell is being a closed system, there will be a linear pressure decrease from which both the onset temperature for hydrate formation ($T_o$) and the rapid hydrate formation temperature ($T_a$) can be observed.

From this linear pressure decrease, $T_o$ is defined as the temperature at the first observable deviation from the linear pressure decrease. It is quite possible that the hydrate nucleation initiated at a molecular level

### Table 2. Summarized SCC KHI Test Results for the Copolymers with Cloud Points and GPC/SEC Data[a]

| copolymer | $T_{cl}$ (°C) | molecular weight (g/mol) | PDI | concentration (ppm) | $T_o$ (°C) | $T_a$ (°C) |
|---|---|---|---|---|---|---|
| poly(2-ACap) | <0 | 9600 | 1.94 | | | |
| poly(2-MACap) | <0 | 12 600 | 5.42 | | | |
| no additive | | | | | 17.2 | 16.6 |
| PVCap | | 10 000 | | 2500 | 10.4 | 8.9 |
| 2-MACap/MAm (1:1) | 33 | not soluble in DMF | 2500 | 10.3 | 9.0 | |
| 2-MACap/MMA (1:1) | 58 | 2100 (major), 120 800 (broad minor) | 1.16, 12.21 | 2500 | 8.8 | 8.1 |
| | | | | 5000 | 6.4 | 5.7 |
| 2-MACap/MMA (1:2) | 85 | not soluble in DMF | 2500 | 10.8 | 9.6 | |
| 2-MACap/DMMAm (1:1) | <2 | 2000 | 3.11 | 2500 | 10.7 | 9.9 |
| 2-MACap/NIPMAm (1:1) | 24 | 3200 | 5.01 | 2500 | 8.0 | 7.4 |
| 2-MACap/NDMHMAm (1:1) | >100 | 500 | 1.25 | 2500 | 12.0 | 11.8 |
| | | | | 5000 | 10.1 | 9.9 |
| 2-MACap/APYD (1:1) | 28 | 3300 | 4.39 | 2500 | 9.2 | 8.6 |
| | | | | 5000 | 6.7 | 5.8 |
| 2-MACap/MAPYD (1:1) | 24 | 1300 | 2.42 | 2500 | 8.4 | 8.1 |
| 2-MACap/MAPYD (1:2) | 20 | 2500 | 3.25 | 2500 | 10.8 | 10.3 |
| 2-MACap/NPyMA (1:1) | >100 | 800 | 1.25 | 2500 | 11.8 | 10.8 |
| | | | | 5000 | 9.4 | 8.3 |
| 2-MACap/PEGMA-9 (4:1) | 54 | 15 900 | 8.74 | 2500 | 10.3 | 9.0 |
| | | | | 5000 | 7.8 | 6.8 |
| 2-MACap/VIMA (1:1) | 28 | 61 500 | 2.93 | 2500 | 8.8 | 7.7 |
| 2-MACap/NIPMAm/VIMA (1:1:0.5) | 30 | 7800 | 4.37 | 2500 | 9.4 | 8.5 |
| 2-ACap/MMA (1:1) | 60 | 22 600 | 38.2 | 2500 | 9.7 | 8.8 |
| 2-ACap/MAPYD (1:1) | 24 | 4700 | 2.25 | 2500 | 10.4 | 10.0 |

[a] From the previous publications no additive, PVCap, 2-MACap/MMA (1:1) and 2-MACap/VIMA (1:1) are added for comparison.[45,58]

prior to this because this is the first macroscopic observation of hydrate formation done by an observation on a linear pressure decrease. However, these experiments are not capable of detecting nucleation, which possibly happens earlier. A rapid pressure decrease can be observed with varying intervals after $T_o$ have occurred. The temperature when the pressure decrease is at its steepest, that is, when the hydrate formation is at its fastest is defined as $T_a$ (Figure 7).

## 3. RESULTS AND DISCUSSION

**3.1. KHI Results from New Copolymers Based on 2-MACap and 2-ACap.** A series of new copolymers of 2-MACap were synthesized as well as the structurally similar 2-ACap. These copolymers gave a wide range in molecular weights. This meant that KHI performance comparison was not always easy to carry out because molecular weight is one of the structural parameters that affects the performance. Therefore, we have been cautious to only compare the performance of polymers with fairly similar molecular weight values. Past studies suggest that the majority of the polymers should have a low-molecular weight for optimal performance, perhaps only 8−10 repeat units and a molecular weight of 1200−2000 g/mol for most of the well-known KHI classes.[17,21]

To validate the KHI potential of the copolymers, they were evaluated using SCC tests (Table 2, Figure 8). Both the $T_o$ and $T_a$ values reported in the following are averages. The focus in this discussion will be on the $T_o$ value because this parameter refers to the first detection of hydrate formation after which crystal growth can potentially cause hydrate plugging irrespective of the growth rate. Therefore, the $T_a$ values, and the difference to the $T_o$ value can be used as an indicator of fast or slow hydrate growth in the system. Figure 8 gives average $T_o$ or $T_a$ values as well as the maximum spread in results obtained for each series. The standard deviation (assuming a normal distribution) for a set of $T_o$ or $T_a$ values is no more than 0.6 °C and usually less than 0.3 °C. Independent sample *t*-tests with equal variances for each polymer were used to identify statistical differences in the performance between $T_o$ and $T_a$ values of the different polymers. The predetermined significant level is often 0.05 and when the *p* value is less, this indicates that the observed result would be statistically significant.[57]

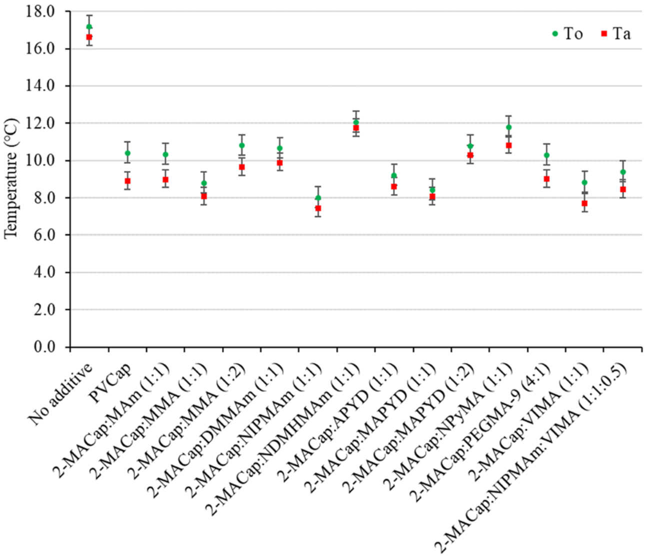

**Figure 8.** Graphical summary of SCC test results for 2-MACap copolymers at 2500 ppm. Both $T_o$ and $T_a$ values are given.

The results for no additive and PVCap are added to Table 2 and Figure 8 as comparisons for KHI performance. Only a few copolymers of 2-MACap were synthesized and tested as KHIs in the first study.[45] In this present discussion of the new copolymers tested, we take 2-MACap/MMA (1:1) from the previous study as the starting point as this gave the best performance. The first structural aspect investigated was the importance of the backbone methyl group coming from both comonomers. Therefore, one or both methyl groups needed to be removed from the two monomers and their relative performances compared.

The comonomers APYD and MAPYD were copolymerized with 2-MACap. Both comonomers have a pyrrolidine ring attached to the acrylamide. These cyclic structures have been reported to be beneficial for the KHI effect.[59,60] Further, this heterocyclic five-membered ring could potentially fit into the $5^{12}6^4$ cages of structure II gas hydrate. In addition, this ring is a common feature in a number of known KHI polymers, including poly(*N*-vinyl-pyrrolidone) (PVP) and poly(meth)-acryloylpyrrolidine.[51,61] We begin by discussing results with the simplest of them, APYD, which is an acrylamide with a pyrrolidine ring. Copolymerized with 2-MACap, making 2-MACap/APYD (1:1), the performance was adequate, giving $T_o$ value and $T_a$ value of 9.2 and 8.6 °C, respectively. We then investigated the methylated version, MAPYD. The copolymer 2-MACap/MAPYD (1:1) had an excellent KHI performance, resulting in a $T_o$ value of 8.4 °C and a $T_a$ value of 8.1 °C. Not only did this copolymer perform better than the non-methylated comonomer, but it had a performance among the best of the comonomers tested. However, both the $T_o$ value and the $T_a$ value between 2-MACap/MAPYD (1:1) and 2-MACap/MMA (1:1) was not found to be significantly different ($p > 0.05$ in a statistical *t*-test). The cloud point between the copolymers was different, with the MAPYD-containing copolymers having the lower value. The cloud point between MAPYD and APYD copolymers were more or less the same but perhaps slightly higher for the copolymer containing APYD.

Because both 2-MACap/MMA (1:1) and 2-MACap/MAPYD (1:1) had such a good KHI performance, we wanted to test them in a different ratio to see if this could possibly further enhance their performance and increase their cloud point. Because of the fact that poly(2-MACap) was not water soluble, the only way to change the ratio would be to increase the amount of MMA and MAPYD, respectively. 2-MACap/MMA (1:2) and 2-MACap/MAPYD (1:2) copolymers were synthesized and the results from both were clearly worse than the 1:1 ratio copolymers with the same monomers, and now on the same performance level with PVCap. Here, the ratio between the monomers were not optimal, and the hydrophilic to hydrophobic moiety of the copolymer was imbalanced. As it is for copolymers, in general, it is important to find the right ratio between the monomers used in order to obtain optimal results.[62] The cloud point for 2-MACap/MMA (1:2) had a profound increase compared to the 1:1 copolymer, but for 2-MACap/MAPYD (1:2), the cloud point had a slight decrease, compared to the 1:1 ratio of the same monomers (Table 2).

Continuing our investigation of the importance of a backbone methyl group, we synthesized 2-ACap, which when polymerized will be structurally the same as 2-MACap polymers but now without the methyl in the backbone (Figure 4). Poly(2-ACap) was insoluble as also found for poly(2-MACap), so copolymers were synthesized. There may be increased solubility at lower molecular weights as seen for some polymer classes with hydrophilic monomers. As comonomers with 2-ACap we used MMA and MAPYD because both of these gave excellent KHI performance results when copolymerized with 2-MACap (Table 2). Both 2-ACap/MMA (1:1) and 2-ACap/MAPYD (1:1) had a poorer result than their methylated counterparts indicating that adding a methyl group improved the inhibition performance. In addition, the cloud points of the 2-MACap and 2-ACap copolymers were virtually identical. Both the inhibition and cloud point trends correlate well with the findings for *N*-alkyl acrylamide polymers.[46] The beneficial extra methyl group in the polyvinyl backbone has also been recently demonstrated for poly(*N*,*N*-dimethylhydrazido methacrylamide) compared to poly(*N*,*N*-dimethylhydrazido acrylamide).[47,48] The steric effect of the methyl group opens the polymer structure and increases the surface-to-volume ratio, which is presumed to be the cause of the improved KHI effect. Further, it is essential for a good functionality of a KHI polymer that the bulk of the polymer has a low molecular weight. One possible way to achieve this is to polymerize monomers with the methyl group in the backbone. In radical polymerization or copolymerization, the acrylamide will form secondary radicals as the propagating end group, while methacrylamide form tertiary radicals as the propagating end group.[63] By nature, tertiary radicals are more stable than secondary radicals so they are thought to decrease the reactivity of the propagating end resulting in the polymerization rate to decrease. Moreover, the steric effect of approach of the monomer radical to monomer radical is always greater with regard to methacryl then acryl. This is in keeping with the fact that 2-ACap/MMA (1:1) and 2-ACap/MAPYD (1:1) had a higher molecular weight than the corresponding 2-MACap backbone-methylated copolymers.

From Table 2 and Figure 8, we can observe that all copolymers had an inhibition effect compared to PVCap, except when DMMAm and NPyMA were used as the comonomers. 2-MACap copolymerized with the simplest acrylamide-based comonomer, namely, MAm, making 2-MACap/MAm (1:1), had almost identical inhibition efficacy as PVCap. Both the $T_o$ value and the $T_a$ value between 2-MACap/MAm (1:1) and PVCap were not found to be significantly different ($p > 0.05$ in a statistical *t*-test). This copolymer was not totally dissolved (<95%) at a concentration of 2500 ppm. This could be caused by internal hydrogen bonding that might take place, polymer cross-linking, or some of the copolymers may have such a high percentage of the 2-MACap comonomer that it renders it water insoluble.

In the next part of our inquiry, we investigated other comonomers copolymerized together with 2-MACap to see if they could improve the KHI effect and increase the cloud point beyond 2-MACap/MMA (1:1) from the previous study. We selected the comonomers as they are hydrophilic and it was hoped they would not diminish the performance of poly-2-MACap, assuming it had been water soluble. Copolymerization could also possibly increase the KHI performance of homopolymers, as has been reported for VIMA/VCap copolymers.[17,37,64,65] Other vinyl lactam monomers have been copolymerized with amine-based monomers in order to obtain better KHI performance and potentially increase the cloud point.[41] The comonomers used with 2-MACap were all acrylamide based, with PEGMA-9 (an acrylate ester) and VIMA (a vinyl amide) as the only exceptions. This was done in the hope that these conjugated acrylamide monomers would have a polymerization rate fairly similar to that of 2-MACap, also an acrylamide.

Extending the complexity of the comonomer beyond MMA to introduce DMMAm results in the branching of the nitrogen on the amide, making 2-MACap/DMMAm (1:1). The resulting copolymer had limited solubility in water, which would explain why it gave lower performance compared to the 1:1 copolymer with MMA as the comonomer. Interestingly, increasing the hydrophobicity of the comonomer by using NIPMAm, gave the

Table 3. SCC Test Results with 2-MACap/MMA (1:1) and 2-MACap/MAPYD (1:1) with Different Synergists[a]

| copolymer | solvent synergist | concentration (ppm) | | $T_o$ (°C) | $T_a$ (°C) |
|---|---|---|---|---|---|
| | | polymer | synergist | | |
| 2-MACap/MMA (1:1) | | 2500 | | 8.8 | 8.1 |
| | TBAB | 2500 | 5000 | 7.8 | 6.6 |
| | TPAB | 2500 | 5000 | 9.7 | 7.0 |
| | TBPB | 2500 | 5000 | 8.8 | 7.3 |
| | HBuGCl | 2500 | 5000 | 6.4 | 4.5 |
| | *i*BGE | 2500 | 5000 | 6.2 | 5.4 |
| | 4-MePeOl | 2500 | 5000 | 4.6 | 3.8 |
| | iPeCOOH | 2500 | 5000 | 7.3 | 6.2 |
| | iPeCOONa | 2500 | 5000 | 6.9 | 5.9 |
| 2-MACap/MAPYD (1:1) | | 2500 | | 8.4 | 8.1 |
| | TBAB | 2500 | 5000 | 6.4 | 5.2 |
| | TPAB | 2500 | 5000 | 3.4 | 2.0 |
| | TBPB | 2500 | 5000 | 4.8 | 3.0 |
| | HBuGCl | 2500 | 5000 | 3.1 | 2.0 |
| | iPeCOOH | 2500 | 5000 | 11.9 | 11.2 |
| | iPeCOONa | 2500 | 5000 | 8.1 | 7.3 |

[a] Results with 2-MACap/MMA (1:1) with *iso*-butyl glycol ether (*i*BGE) and 4-MePeOl taken from the first study are added for comparison.[45]

copolymer 2-MACap/NIPMAm (1:1) with a higher cloud point of 24 °C. We assume there must be more going than just a straightforward increase in hydrophobicity compared to 2-MACap/DMMAm (1:1) for this cloud point increase to occur. For 2-MACap/NIPMAm (1:1), the impact was a clear improvement in the KHI properties, resulting in the $T_o$ value and $T_a$ value of 8.0 and 7.4 °C, respectively. The good performance is not only due to the 2-MACap monomer units but also NIPMAm, the homopolymer of which is known as a powerful inhibitor in its own right.[46,66,67] This result is in accordance with the good performing copolymers of MMA and MAPYD. The results for 2-MACap/NIPMAm (1:1) and 2-MACap/MMA (1:1) both the $T_o$ value and the $T_a$ value were found to be significantly different ($p < 0.05$ in a statistical *t*-test). However, for 2-MACap/NIPMAm (1:1) and 2-MACap/MAPYD (1:1) only, the $T_a$ value between them was found to be significantly different ($p < 0.05$ in a statistical *t*-test).

A cloud point of 24 °C for the 2-MACap/NIPMAm (1:1) copolymer was still too low for practical application. Therefore, a terpolymer, containing 2-MACap, NIPMAm, and VIMA as the monomers, was made in order to see if this could raise the cloud point without losing performance. VIMA was used because in the previous publication it was one of the copolymers that gave the best performance, in addition to reports that VIMA copolymerized with VCap increased the performance.[17,37,45] The resulting terpolymer was 2-MACap/NIPMAm/VIMA (1:1:0.5). The terpolymer had a slight increase in a cloud point to 30 °C, but the KHI effect for the terpolymer was less than the copolymers 2-MACap/NIPMAm (1:1) and 2-MACap/VIMA (1:1).

To avoid the low polymer cloud point using NIPMAm as a comonomer with 2-MACap, we investigated using a comonomer NDMHMAm. This comonomer has a hydrazide-bond where a carbon atom in the alkyl is replaced with a nitrogen atom. Homopolymers of this monomer were previously investigated as an alternative to PNIPMAm as well as copolymers with VCap.[47,54] A second hydrazide comonomer NPyMA, which contain a pyrrolidine ring, was also used to make a 2-MACap copolymer. The homopolymer PNPyMA has been reported to give good KHI results and no cloud point up to 95 °C in deionized water at 1 wt %.[51] Both 2-MACap/NDMHMAm (1:1) and 2-MACap/NPyMA (1:1) gave no cloud point even in boiling deionized water, which was a great improvement over 2-MACap/NIPMAm (1:1). However, although both copolymers gave a similar and reasonable performance (average $T_o$ 11.8 and 12.0 °C), the results were clearly worse than PVCap. The low performance could be related to the molecular weight being too low (500 and 800 g/mol), although it has been shown that PVCap with a molecular weight as low as these values can still give good KHI performance. A second reason for the mediocre performance of 2-MACap/NDMHMAm (1:1) and 2-MACap/NPyMA (1:1) may be the increased hydrophilicity of these hydrazide-based polymers. The past work has shown that many classes of KHI polymers perform the best when the cloud point is low, as long as the size and shape of the alkyl substituents are optimized.[64]

The last copolymer made with 2-MACap in this inquiry was by using PEGMA-9 as a large but hydrophilic comonomer. Under the test conditions, 2-MACap/PEGMA-9 (4:1) showed an inhibition effect similar to PVCap and 2-MACap/MAm (1:1). In fact, both the $T_o$ value and the $T_a$ values between 2-MACap/PEGMA-9 (4:1), PVCap and 2-MACap/MAm (1:1) were not found to be significantly different ($p > 0.05$ in a statistical *t*-test). The PEGMA comonomer had a strong effect on the hydrophilicity of the copolymer with 2-MACap. Just 20 mol % PEGMA turned an insoluble homopolymer into a water-soluble copolymer with cloud point 54 °C, also considerably higher than PVCap.

All of the above copolymers and the terpolymers were all sufficiently water soluble at 2500 ppm, and the results at this concentration are given. We speculate that there may be considerable internal hydrogen bonding, making the pendant groups less available for hindering gas hydrate nucleation or crystal growth. In the polymer and in the copolymers, there exists numerous options where internal hydrogen bonding can take place, between 2-MACap/2-ACap units, between copolymerization units, and between 2-MACap/2-ACap units and copolymerization units. In addition, hydrogen bonding can also occur between polymer strands. Moreover, polymerization rates of the monomers were different, and this could possibly make blocks of each monomer rather than an even distribution throughout the copolymer, causing some of the copolymer strands to exhibit low water solubility or even surfactant properties. This could also explain the solubility issues with some of the copolymers going from 2500 to 5000 ppm. Those copolymers that did show a sufficient solubility at 5000 ppm were also tested at this higher concentration, including 2-MACap/MMA (1:1), 2-MACap/NDMHMAm (1:1), 2-MACap/APYD (1:1), 2-MACap/NPyMA (1:1), and 2-MACap/PEGMA-9 (4:1). All copolymers had an improved inhibition effect at the higher concentration (Table 2).

**3.2. Synergists for 2-MACap Copolymers.** From the previous publication and other research, it is known that by adding certain solvents, it is possible that they can act as synergists with the KHI polymer, thereby improving the kinetic inhibition capabilities.[16,17,32,33,45,58,68−70] Knowing PVCap has many synergists, we wanted to investigate if 2-MACap copolymers, which also contain caprolactam rings, would show similar synergism. From the previous publications, we have shown that the acyclic aliphatic alcohol 4-methyl-1-pentanol (4-MePeOl) gave a good synergetic performance with the caprolactam-based KHI polymers PVCap and 2-MACap.[45,58,70] Here, we have broadened the field of the potential synergist using mixtures with 2-MACap/MMA (1:1) and 2-MACap/MAPYD (1:1). The synergists investigated were hexabutylguanidinium chloride (HBuGCl), tetrabutylphosphonium bromide (TBPB), tetrabutylammonium bromide (TBAB), tetrapentylammonium bromide (TPAB), sodium 4-methyl pentanoate (iPeCOONa), and 4-methylvaleric acid (iPeCOOH) (Table 3).

From Table 3, it can be observed that with the exception of iPeCOOH with 2-MACap/MAPYD (1:1), all synergists made this copolymer's KHI performance better than compared to PVCap. However, not all synergists improved the performance of the copolymers themselves.

Three of the synergists are onium salts (quaternary ammonium or phosphonium salts), which have good synergy with PVCap.[71−73] Interestingly, these synergists gave little performance enhancement to the 2-MACap/MMA (1:1) copolymer with only TBAB giving a significant improvement despite it being the least hydrophobic and weakest tetrahydrofuran hydrate crystal growth inhibitor of the three onium salts. In fact, the addition of TPAB worsened the average $T_o$ value relative to the copolymer alone. This behavior is more reminiscent of some corrosion inhibitors, which are known to be antagonistic to VCap-based KHI polymers.[74−78] The average $T_a$ value decreased for 2-the MACap/MMA (1:1) copolymer with all three synergists, which reflects their hydrate crystal growth inhibition abilities.

In contrast, the copolymer 2-MACap/MAPYD (1:1) gave a good synergetic effect with all three onium salts, significantly decreasing both the average $T_o$ and $T_a$ values. The addition of TPAB gave the best results, decreasing the average $T_o$ and $T_a$ from 8.8 to 8.1 °C for the polymer alone to 4.8 and 3.0 °C, respectively.

The onium salts are thought to exhibit good synergy with PVCap because of their different geometries (alkyl vs ring structure, respectively). Therefore, the onium salts and PVCap should attach to different sites on the hydrate crystal surface. This has been shown in molecular modeling by TBAB or TPAB penetrating $5^{12}6^4$ cavity on the 1,1,1 structure II hydrate surface.[14] The channels on the hydrate surface, where new $5^{12}6^4$ cages would normally form, are now occupied by two of the other butyl or pentyl groups. The possibility arises that these cages could partially form, trapping or imbedding the butyl or pentyl groups in the hydrate surface. TBAB or TPAB will not be able to embed themselves in the surface of the hydrate crystal as long as the critical nuclear size is not reached, and thus the growth of the nuclei is energetically unfavorable ($\Delta G$ is positive). In this case, the likelihood is toward the detachment of the onium salts. When the growth of the nuclei is energetically favorable ($\Delta G$ is negative), TBAB or TPAB can become embedded in the hydrate surface as partial hydrate cages form around the butyl or pentyl groups but further structure II growth is prevented by the remaining butyl or pentyl groups.[79] While the onium salts start to work after the growth of the nuclei is energetically favorable ($\Delta G$ is negative), PVCap attaches to several sites on the hydrate surface via caprolactam rings and prevents the declustering of subcritical nuclei. Crystal growth will become favorable once these nuclei reach a critical size, and at this stage the onium salts can embed on the hydrate surface and prevent further growth.[36] Based on this, we speculate that the reason for this surprising result was potentially caused by the pyrrolidine ring on the methacrylamide incorporating into the growing hydrate together with the caprolactam ring before the hydrate nuclei reach a critical size. After reaching critical size, TPAB embeds on the hydrate surface and prevents further growth. This means that the copolymer and the synergist operate on different aspects on the hydrate formation, thereby optimizing their combined inhibition. 2-MACap/MMA (1:1) does not have the extra pyrrolidine ring, so its mode of action might be too similar to TPAB and they end up outcompeting themselves for the same $5^{12}6^4$ cavity on the 1,1,1 structure II hydrate surface.

These multiple alkyl group in these quaternary ammonium or phosphonium salts could be increased by introducing them on guanidinium salts, which have three nitrogen atoms in the cationic center. The guanidinium salt HBuGCl also contains the butyl group so we wanted to see how this compound worked as a synergist with the copolymers, as it has been reported to give good synergy with PVCap.[80] The performance increased for both copolymers, with the most pronounced improvement for 2-MACap/MAPYD (1:1). For 2-MACap/MMA (1:1), the synergetic effect gave a $T_o$ value of 6.4 °C and $T_a$ value of 4.5 °C. The butyl groups have also performed well as a synergist when they are on a monoglycol ether, like *i*BGE. Together with PVCap, it has a good synergetic effect.[58] From the previous publication, we also observed this synergetic effect with 2-MACap/MMA (1:1).[45] When *i*BGE was added, it improved the performance of 2-MACap/MMA (1:1) resulting in the $T_o$ value and $T_a$ value of 6.2 and 5.4 °C, respectively. The $T_o$ value between 2-MACap/MMA (1:1) with *i*BGE and with HBuGCl was not found to be significantly different ($p > 0.05$ in a statistical *t*-test). The $T_a$ value between them indicates that the HBuGCl could be better at delaying catastrophic hydrate growth. HBuGCl with 2-MACap/MAPYD (1:1) had a much stronger synergy, with a $T_o$ value of 3.1 °C and $T_a$ value of 2.0 °C, similar values as those obtained with TPAB.

Previous works with alcohols has shown that branching of an acyclic aliphatic hydrocarbon "tail" can lead to better synergy than an unbranched tail. Thus, 4-MePeOl was tested with PVCap and 2-MACap/MMA (1:1) and gave excellent synergy for both polymers. For 2-MACap/MMA (1:1) with 4-MePeOl, an average $T_o$ value of 4.6 °C and $T_a$ value of 3.8 °C was the result.[45,58,70] To get a better understanding of the role the of the functional group, we changed the functional group from alcohol to a carboxylic acid in the compound iPeCOOH and tested it with the same copolymers. We also used the carboxylate form iPeCOONa, although the $CO_2$ in the gas mixture will buffer the effect of the higher pH.[51,54] Compared to the hydroxyl group in 4-MePeOl, the synergy was less pronounced for 2-MACap/MMA (1:1), with average $T_o$ value and $T_a$ values of 7.3 and 6.2 °C, respectively. A similar result was also found for iPeCOONa. Interestingly, both iPeCOOH and iPeCOONa were antagonistic with 2-MACap/MAPYD (1:1).

The synergy KHI test results highlight the difficulty in pre-determining, which molecules will enhance the performance of a given KHI polymer. Thus, while the onium salts gave good synergy with 2-MACap/MAPYD (1:1), they had only a weak effect on 2-MACap/MMA (1:1) and sometimes even antagonistic (e.g., TPAB). In contrast, iPeCOOH gave some synergy with 2-MACap/MMA (1:1) but was antagonistic with 2-MACap/MAPYD (1:1). Exactly what is happening in solution to cause these differences is hard to say, but it may be a combination of polymer−synergist interactions as well as competitive interactions to prevent hydrate nucleation and crystal growth.

## 4. CONCLUSIONS

2-ACap was synthesized for the first time and its homopolymer poly(2-ACap) was found to be insoluble in water. The KHI properties of a series of water-soluble 2-MACap and 2-ACap copolymers were investigated. All the copolymers showed KHI effects compared to no additive. The KHI performance of some of these copolymers exceeded that of PVCap of similar molecular weight. The copolymers that gave the poorest results were also the most hydrophilic with no cloud point, 2-MACap/NDMHMAm (1:1) and 2-MACap/NPyMA (1:1). Of the copolymers investigated, several gave a better KHI performance than PVCap, with the best results for 2-MACap/MMA (1:1), 2-MACap/NIPMAm (1:1), and 2-MACap/MAPYD (1:1). The performance also increased with increasing polymer concentration. As has been seen in previous methacrylamido-based polymers, a high percentage of backbone methyl groups led to improved performance. This was seen for 2-MACap/MAPYD (1:1) versus 2-MACap/APYD (1:1), as well as for 2-MACap/MAPYD (1:1) versus 2-ACap/MAPYD (1:1) and 2-MACap/MMA (1:1) versus 2-ACap/MMA (1:1).

Several known synergists for PVCap were investigated with two of the best 2-MACap copolymers, 2-MACap/MMA (1:1) and 2-MACap/MAPYD (1:1). Excellent synergy was obtained with 2-MACap/MAPYD (1:1) for several synergists but the effect on average $T_o$ values was sometimes quite different for 2-MACap/MMA (1:1), with TPAB even being antagonistic. Conversely, iPeCOOH gave some synergy with 2-MACap/MMA (1:1) but was antagonistic with 2-MACap/MAPYD (1:1). HBuGCl gave the most consistent synergetic effect for both copolymers. These results highlight the difficulty in pre-determining, which molecules will enhance the performance of a given KHI polymer, without doing the necessary experimental work.

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### Notes

The authors declare no competing financial interest.

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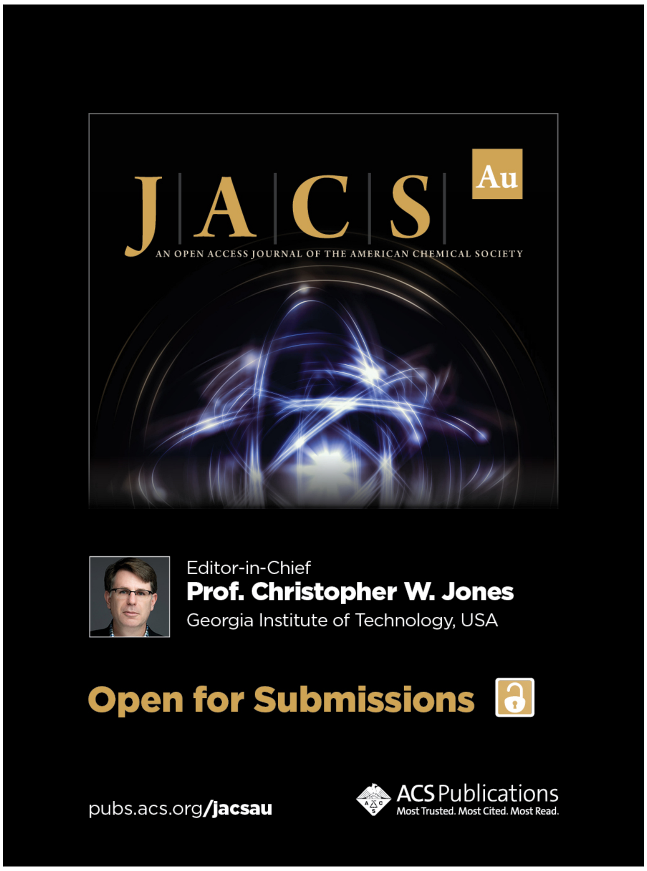

# Paper IX

High Cloud Point Polyvinylaminals as Non-Amide-Based Kinetic Gas Hydrate Inhibitors

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# High Cloud Point Polyvinylaminals as Non-Amide-Based Kinetic Gas Hydrate Inhibitors

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**ABSTRACT:** In recent years, we have explored non-amide-based classes of kinetic hydrate inhibitor (KHI) polymers to determine if the same level of performance can be achieved as commercial KHI polymers, which all contain amide groups. Here, we have investigated a series of polyvinylaminals as KHIs for the first time. These polymers with pendant alkyl or cycloalkyl groups of varying sizes and shapes were synthesized in a simple one-step procedure from polyvinylamine. Their performance as tetrahydrofuran (THF) hydrate crystal growth inhibitors and as high-pressure KHIs was studied with a structure II-forming natural gas mixture in both sapphire and steel rocking cells. A structure−performance analysis was carried out. The best KHI was obtained with a polyvinylaminal with pendant cyclohexyl groups and gave a similar performance to the well-known KHI poly(*N*-vinyl caprolactam) and without the disadvantage of a low cloud point.

## 1. INTRODUCTION

Plugging of flow lines by gas hydrates is one of the most serious production issues to consider during field development.[1] Various methods are available to avoid this problem, including the use of low-dosage hydrate inhibitors (LDHIs).[2,3] The two main subcategories of LDHIs are antiagglomerants (AAs) and kinetic hydrate inhibitors (KHIs). Both have limitations. KHIs are used to keep a flow line free from any amount of hydrate formation, whereas AAs allow hydrates to form in a controlled manner and keep them dispersed and transportable in the remaining produced fluids. The main limitation of KHIs is the subcooling limit to which they can be used. However, KHI products that can extend this limit would be very welcome as one need not worry about hydrate slurry transportation as with AAs, or melting the hydrates in the processing facilities.

The main constituents in kinetic hydrate inhibitor (KHI) formulations used in the oil and gas industries are water-soluble polymers.[4−8] The great majority of these are polyamides based on vinylic monomers such as *N*-vinyl lactams and *N*-alkyl(meth)acrylamides. Including hyperbranched polyester amides, these three classes represent the majority of all commercially available KHI polymers. Some non-amide-based KHIs have been investigated including poly(amine oxides), polyvinyloxazolines, and polyquaternaries, but as far as we are aware, none of them have been deployed in the field yet. Polyquaternaries based on 3-alkyl-1-vinylimidazolium bromide monomers have been reported but only showed good performance when used as synergists with polymers based on an *N*-vinyl caprolactam monomer or when copolymerized with this monomer (Figure 1).[9] 1-Vinyl imidazole and dimethylaminoethylmethacrylate bromide (DMAEMA) have also been used in KHI polymers.[10−12]

In this study, we investigate a new class of nonamide KHI polymer for the first time: polyvinylaminals. They have been shown to be useful as flocculants and epoxy resin and polyurethane cross-linking agents, and are easily made in one step from commercial polyvinylamine (Figure 2).[13,14] The authors proposed that two amines separated by three carbon atoms (i.e., 1,3-diamines) are involved in the reaction with an aldehyde to give six-ring hexahydropyrimidine groups.[15] Support for this reaction comes from the reaction of 1,3-diaminopropane with alkylamines, which are known to produce hexahydropyrimidines.[16,17] However, if two amines separated by two carbon atoms (i.e., 1,2-diamines) react with an aldehyde, imidazolidine rings can be formed.[18] Polyvinylaminals were not expected to show good biodegradability due to an all-carbon backbone; therefore, this was not investigated. The focus of this study was to determine whether nonamide polymers can perform as well as the classic amide-based polymers.

Previously, we have synthesized polyvinylamides from polyvinylamine.[19] However, the size of the pendant alkyl groups for the homopolymer in this class is limited to three carbon atoms (*iso*- or *n*-propyl) due to solubility problems with larger groups. Polyvinylaminals have cyclic aminal (or aminoacetal) groups with two nitrogen atoms and offer the possibility of quaternizing one or both of these atoms to produce cationic groups (Figure 3).[20,21] The charge on the polymer allows for larger pendant alkyl groups. This could be important as studies on other classes of LDHIs have shown that hydrophobic groups larger than propyl can give improved

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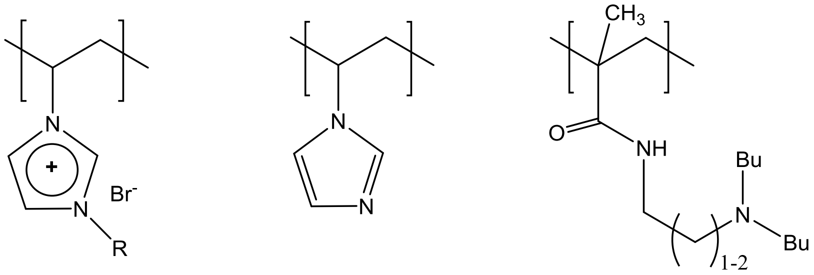

**Figure 1.** Monomer units for 3-alkyl-1-vinylimidazolium bromides, 1-vinyl imidazole (VIM), and *N*-dibutylaminoalkylmethacrylamides.

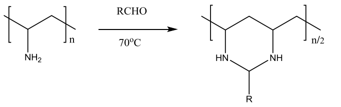

**Figure 2.** General synthesis of polyvinylaminals.

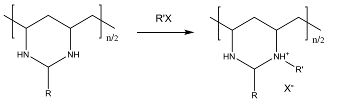

**Figure 3.** Protonation (*R* = H) or alkyl quaternization of polyvinylaminals.

performance, e.g., pendant dibutylamine groups (or the quaternized versions) in dibutylaminoalkyl(meth)acrylamide-based polymers, butyl, pentyl, *iso*-hexyl, and t-heptyl groups in quaternary ammonium salts, and some polyamine oxides (Figure 1).[9,22−26]

## 2. EXPERIMENTAL METHODS

**Materials.** Solvents and commercial aldehyde products (99% pure) were used as received from the suppliers (VWR and Sigma-Aldrich), without any further purifications. 2-Propanol (>99 %) was supplied by VWR. Low-molecular-weight poly(*N*-vinylcaprolactam) (PVCap), 41.1 wt % in monoethyleneglycol, was supplied by Ashland chemical company under the tradename Luvicap EG. Poly(*N*-vinylpyrrolidone) (PVP, $M_W$ = 4000 g/mol) was supplied by BASF. Polyvinylamine was supplied as the hydrochloride salt by BASF under the tradename Lupamin 1595 ($M_W$ < 10 000 g/mol, pH 7.5) as a 10 wt % aqueous solution. 4-Methylpentanal (*iso*-hexanal) was synthesized by a literature method via reduction of 4-methylpentanitrile with diisobutylaluminum hydride.[27]

**Synthesis of Polyvinylaminals.** To 2.00 g of a solution of 10 wt % polyvinylamine in water were added 0.5 or 1.0 molar equivalents of aldehyde per amine group and 1.00 g of 2-propanol. The flask was sealed and stirred at 70 °C for 18 h. A light orange-brown solution was formed in the normal case, which was used for KHI testing. In some cases with more hydrophobic aldehydes, an orange-brown layer separated from a colorless layer. When these polyvinylaminal products were diluted with water or tetrahydrofuran (THF)/water to KHI test concentrations (2500−5000 ppm), both layers were found to be fully water soluble, with no cloud point up to 95 °C.

**Tetrahydrofuran Hydrate Crystal Growth Experimental Method.** The tetrahydrofuran (THF) hydrate crystal growth rate experiments were carried out as previously reported.[28−36] An outline of the procedure is as follows: THF and water were mixed in the molar ratio 1:17, and sodium chloride was added and dissolved by stirring to give a final salt concentration of 36 000 ppm (3.6 wt %). This solution (80 mL) was added to a 100 mL glass beaker and placed in a cooling bath (accuracy ±0.05 °C) set to −0.5 °C. Taking into account the added salt, this gave a theoretical subcooling for THF hydrate of about 3.4 °C. The solution was stirred every 5 min for 20 min. A hollow glass tube was filled with crushed ice (kept at −20 °C) and the tip of the tube was placed vertically into the THF/salt solution. The ice initiates nucleation of THF hydrate at the tip. The tube was removed from the solution after 1 h. The THF hydrate crystals growing only from the tube tip were quickly cut off and weighed, having first removed any liquid from the crystals with a dry absorbent cloth or tissue. This gave the rate of growth of THF crystals in grams over 1 h. The average growth rate of 5−8 experiments was recorded, in which the spread in growth rates was about 20−25%. The test requires salt because if no salt is added to the mixture, THF hydrate formation becomes too fast due to high subcooling. This makes it hard to differentiate the ranking of the crystal growth inhibition of the additives. At temperatures above 0 °C, the ice in the glass tube (which we used to initiate THF hydrate formation) melts and falls out of the tube.

**High-Pressure Rocking Cell Kinetic Hydrate Inhibitor (KHI) Performance Tests.** To determine the KHI performance ranking of the additives, we used two different types of rocking cell equipment. One equipment was a set of five high-pressure 40 mL steel rocking cells; the other equipment was a set of six high-pressure 20 mL sapphire rocking cells[37,38] (Figures 4 and 5). All cells contained a steel ball for extra agitation. All equipment was supplied by PSL Systemtechnik GmbH, Germany.

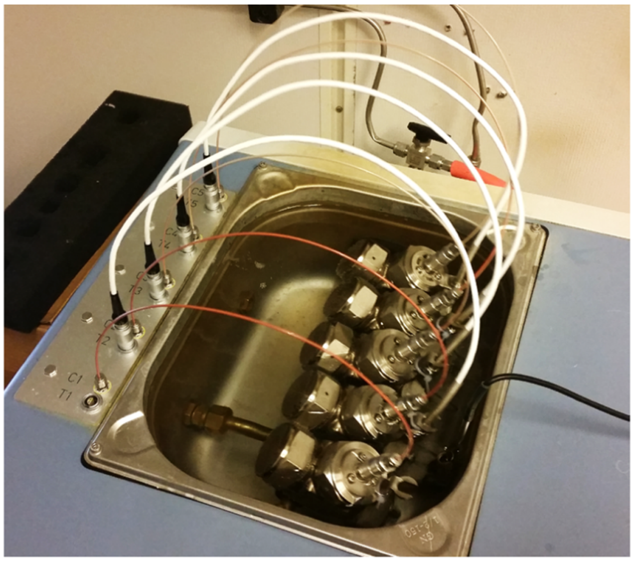

**Figure 4.** RC5 rocker rig showing the five steel cells in a cooling bath.

The reason for using two sets of cells was due to maintenance needed on one rig, which meant that we had to move the study to the other rig. To be able to compare the results in the two rigs, we conducted tests on some polymers in both rigs and found that there was general agreement within a 95% confidence limit. We used the same synthetic natural gas mixture that forms structure II hydrate as the thermodynamic stable phase in both sets of equipment. The composition is given in Table 1. We also used our standard slow constant cooling (SCC) test method in both sets of equipment, which we have used in many previous studies, mostly in the steel cells.[39] We

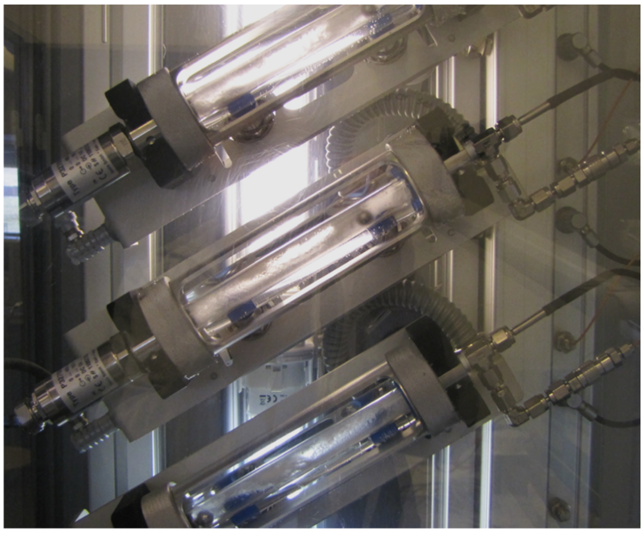

**Figure 5.** RCS20 rocker rig showing hydrate formation in three of the six sapphire cells.

**Table 1. Composition of the Synthetic Natural Gas (SNG) Mixture Used in the KHI Experiments**

| component | mol % |
|---|---|
| methane | 80.67 |
| ethane | 10.20 |
| propane | 4.90 |
| isobutane | 1.53 |
| *n*-butane | 0.76 |
| $N_2$ | 0.10 |
| $CO_2$ | 1.84 |

also used the same gas/water volume ratio, 50:50, in all tests. We have purposely kept to the same method and equipment to allow easy comparison of results from many classes of additives. The cooling rate (1 °C/h) is slower than that observed under real field conditions, but it is not our intention to determine the field KHI performance of the additives but only to provide a ranking in KHI performance. We have found that a series of tests using a slow ramping or cooling method enables better differentiation in performances than using a faster cooling method.[1] Di Profio[40] recently showed that slow ramped cooling experiments gave good reproducibility and recommended lowering the temperature by 0.5 °C every 3 h. However, KHI experiments at this rate could take several days for good additives as the subcooling would be high before hydrates would form. The cooling rate in our method is a good enough compromise to screen new additives to give a rough idea of their KHI performance potential.

The pressure was approximately 76 bar (accuracy ± 0.1 bar) at the start of each SCC experiment. The hydrate equilibrium temperature (HET) at this pressure was determined by standard laboratory dissociation experiments at a warming rate of 0.025 °C/h for the last 3−4 °C.[41,42] Five repeat tests were carried out, which gave 20.2 ± 0.05 °C as the HET.[39] This value was found in both steel and sapphire cell rocking rigs and agrees very well with a calculated HET value of 20.5 °C at 76 bar using Calsep's PVTSim software.

The constant cooling test procedure was as follows:

(1) Deionized water (20 mL) containing the chemicals to be tested was added to each cell. If the sample to be tested was in two layers (see the section on Synthesis of Polyvinylaminals), the sample was vigorously shaken before the correct aliquot was diluted with water to the test concentration.
(2) Air in the cells was removed using a vacuum pump and refilled with SNG to 2 bar. The procedure was repeated twice.
(3) The cell was pressurized to 76 bar with the SNG and rocked at 20 rocks/min at a 40° angle.
(4) The rocked cells were cooled from 20.5 °C at a rate of 1 °C/h down to 2 °C.
(5) The temperature and pressure for each cell, and the cooling bath temperature, were logged on a computer.

A typical graph of pressure and temperature data versus time for one of the five cells is shown in Figure 6. A thorough explanation of our interpretation of such data has been reported previously.[43] From this data, we determine the onset temperature ($T_o$) (first detection of hydrate formation from the pressure drop) and the temperature at which fast hydrate formation is observed ($T_a$). The $T_o$−$T_a$ value gives an indication of the ability of the additive to slow the growth of SII gas hydrate formation but depends on the subcooling at $T_o$. Comparisons of $T_o$−$T_a$ are only valid between tests when $T_o$ is similar. Figure 6 illustrates how we determine the $T_o$ value (here 10.8 °C) and the $T_a$ value (here 10.3 °C). In this study, at least six identical experiments for any one product were conducted. Due to the stochastic nature of gas hydrate formation, there is some degree of scattering in $T_o$ and $T_a$ values, which is never more than 20% for $T_o$ and 15% for $T_a$. A more thorough investigation of the reproducibility under various test conditions in this multicell rocker rig was carried out by Lone et al.[38] *P*-values from statistical *t*-tests lower than 0.05 were considered as an indication of a significant difference in two sets of $T_o$ or $T_a$ values.[44]

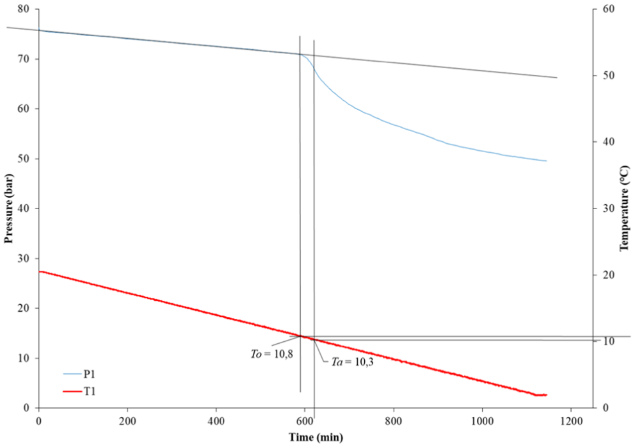

**Figure 6.** Typical pressure and temperature graphical data for a slow constant cooling rocker rig KHI experiment, showing the determination of $T_o$ and $T_a$.

## 3. RESULTS AND DISCUSSION

A series of polyvinylaminals was synthesized by the reaction of polyvinylamines of varying molecular weights with alkylamines. NMR spectroscopy of the polymers was inconclusive as to the formation of the aminal groups as the lines were very broad, typical for polymers. However, as further proof of the formation of the aminal group, beyond the references given in the Introduction section, we carried out the reaction of pivaldehyde with 1,3-diaminopropane and obtained 2-tert-butylhexahydropyrimidine in quantitative yield as judged by comparison of our $^1H$ and $^{13}C$ NMR spectroscopic analyses with the reported values (Figure 7).[17]

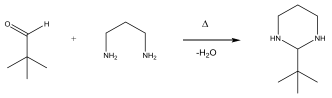

**Figure 7.** Synthesis of 2-tert-butylhexahydropyrimidine.

Table 2. THF Hydrate Crystal Growth Results[a]

| polyvinylaminal | concn. (ppm) | pH | g/h | crystal shape |
|---|---|---|---|---|
| no additive | | 7 | 1.59 | rhombic |
| | | 3 | 1.30 | rhombic |
| tetrabutylammonium bromide | 4000 | 7 | 0.45 | distorted rhombic |
| tetrapentylammonium bromide | 4000 | 7 | 0.04 | very distorted |
| polyvinylamine, $M_W$ 10 000 g/mol | 4000 | 7 | 1.81 | rhombic |
| polyvinylaminal/*n*-butanal | 4000 | 6.5 | 0.72 | rhombic |
| polyvinylaminal/*n*-pentanal | 2000 | 3 | 0.80 | mostly rhombic |
| | 4000 | 7 | 0.34 | hexagonal plates |
| | | 3 | 0.23 | hexagonal plates |
| polyvinylaminal/*n*-hexanal | 2000 | 3 | 1.25 | rhombic crystals + hexagonal plates |
| | 4000 | 7 | 0.65 | rhombic crystals + hexagonal plates |
| | | 3 | 0.38 | hexagonal plates |
| polyvinylaminal/cyclopentanecarboxaldehyde | 4000 | 7 | 0.58 | rhombic crystals + hexagonal plates |
| polyvinylaminal/cyclohexanecarboxaldehyde | 4000 | 7 | 0.39 | hexagonal plates |
| | | 3 | 0.33 | hexagonal plates |

[a] Average of minimum six tests per chemical.

**THF Hydrate Crystal Growth-Inhibition Experiments.** Due to the possibility of quaternization of the amine groups, we reasoned that the polyvinylaminals may be good hydrate crystal growth inhibitors like some of the tetraalkylammonium salts.[28,45] THF hydrate is an easy medium on which to test the crystal growth-inhibition ability at atmospheric pressure. It was originally used by Shell energy company to determine the optimum quaternary ammonium groups for surfactant antiagglomerants (AAs).[46,47] A summary of the THF hydrate crystal growth inhibition experiments is given in Table 2. The use of no additive gave an average growth rate of 1.75 g/h, forming a cluster of regular rhombic pyramidal crystals at the end of the tube. The pH of this solution was about 7, but since we were investigating protonated polyvinylaminals, we also carried out tests at pH 3. The growth of THF hydrate crystals was still high but a little less than that at pH 7. Presumably, a higher concentration of hydronium ions ($H_3O^+$) and larger protonated water clusters found in the acidic solution slow the hydrate growth rate, possibly also by protonating the water molecules at the THF hydrate crystal surface. Under the same conditions, PVCap at 4000 ppm gives no THF hydrate growth at all.[36]

For the polyvinylaminals at pH 7, some gave similar performance to tetrabutylammonium bromide (TBAB) but none of them performed as well as tetrapentylammonium bromide (TPAB), which is one of the best quaternary ammonium salt THF hydrate growth inhibitors.[28,46] The best results were obtained with the *n*-pentanal and cyclohexanecarboxyaldehyde derivatives. As far as we know, cyclopentyl and cyclohexyl groups in nonpolymeric quaternary ammonium salts have not been investigated as hydrate growth inhibitors. Some of the polyvinylaminals were also tested at pH 3 and most gave a small but not dramatic improvement in performance. Presumably, protonation of some of the amine groups to give quaternary ammonium groups is only a minor advantage for hydrate growth inhibition with this class of polymers.

Often, both rhombic crystals (with no additive) as well as hexagonal plates showing preferential crystal facial inhibition were obtained. In general, as the concentration increased with the best inhibitors, we observed more and thinner hexagonal plates. An example of hexagonal plates is shown in Figure 8 for the cyclohexanecarboxaldehyde derivative at pH 3. Aqueous solutions of this polymer at 4000 ppm polymer were a little cloudy at pH 7, but solubility increases at pH 3, again indicating quaternization of at least some of the polymer amine groups.

Figure 8. Hexagonal THF hydrate plates from a test with 4000 ppm of polyvinylaminal/*n*-hexanal at pH 3.

**High-Pressure Slow Constant Cooling Gas Hydrate KHI Experiments.** The high-pressure KHI test results are summarized in Table 3. As explained earlier, we conducted tests in both steel and sapphire rocking cells. The results in this table for PVP 15K ($M_W$ 8000 g/mol) and PVCap ($M_W$ 10000 g/mol), with similar molecular weights to the polyvinylaminals, are taken from previous work.[48−50] In general, there was good agreement for the polymers tested in both sets of equipment. The variation in the $T_o$ values in our rocking cell equipment has been reported many times before as about ±10−15% and this study was no exception.[36−38]

Table 3. Constant Cooling Test Results[a]

| polyvinylaminal | test concn. (ppm) | pH | $T_o$ (°C) | $T_a$ (°C) | cell type |
|---|---|---|---|---|---|
| no additive |  | 7.0 | 17.1 | 16.6 | steel |
|  |  | 7.0 | 16.8 | 16.4 | sapphire |
| PVP-K15 $M_W$8000 g/mol | 2500 | 7.0 | 11.6 | 10.9 | sapphire |
|  |  | 7.0 | 11.1 | 9.9 | steel |
| PVCap, $M_W$ 10 000 g/mol | 2500 | 7.0 | 9.6 | 9.2 | steel |
|  |  |  | 9.9 | 8.9 | sapphire |
| polyvinylamine, $M_W$ 10 000 g/mol | 2500 |  | 16.9 | 16.8 | sapphire |
| polyvinylaminal/butanal | 2500 | 6.5 | 15.1 | 15.0 | sapphire |
| polyvinylaminal/*iso*-pentanal (3-methylbutanal) | 2500 | 6.5 | 11.6 | 11.2 | steel |
|  |  |  | 11.8 | 11.5 | sapphire |
|  | 5000 | 6.5 | 10.0 | 9.7 | sapphire |
| polyvinylaminal/pivaldehyde (2,2-dimethylpropanal) | 2500 | 6.5 | 15.2 | 15.1 | sapphire |
| polyvinylaminal/*n*-pentanal | 2500 | 6.5 | 11.8 | 11.7 | sapphire |
|  |  | 2.9 | 11.5 | 11.4 | sapphire |
| polyvinylaminal/*n*-hexanal | 2500 | 6.5 | 11.9 | 11.8 | sapphire |
| polyvinylaminal/*iso*-hexanal (4-methylpentanal) in iPrOH (8 tests) | 2500 | 6.5 | 10.3 | 10.0 | steel |
| polyvinylaminal/cyclopentanecarboxaldehyde | 2500 | 6.5 | 11.6 | 11.5 | sapphire |
| polyvinylaminal/cyclohexanecarboxaldehyde | 2500 | 6.5 | 9.8 | 9.4 | steel |
|  |  |  | 10.4 | 10.2 | sapphire |
|  |  | 3.1 | 11.2 | 10.8 | sapphire |
|  | 5000 | 6.5 | 7.0 | 6.5 | steel |
|  |  |  | 7.6 | 7.1 | sapphire |

[a] Average of six tests. All samples were made with polyvinylamine ($M_W$ 10 000 g/mol) in $H_2O$/iPrOH unless otherwise stated.

Polyvinylamine ($M_W$ 10 000 g/mol), the starting material for making the polyvinylaminals, showed no KHI effect as was expected for a very hydrophilic polymer with no pendant hydrophobic groups. As many previous studies have shown, an effective KHI polymer requires pendant hydrophobic groups of a certain size (preferably containing three to six carbon atoms) and neighboring hydrophilic groups to maintain water solubility.[51] All commercial KHI polymers have these structural properties.

All of the polyvinylaminals derived from polyvinylamine showed some KHI activity, which increased with the size of the pendant alkyl or cycloalkyl groups as long as water solubility was not lost. Thus, the butanal ($R$ = *n*-propyl in Figure 2) and pivaldehyde ($R$ = t-butyl in Figure 2) polyvinylaminals gave the poorest KHI performance, with average $T_o$ values of 15.0 and 15.1 °C, respectively. Branching the end of the butanal derivative using 3-methylbutanal (*iso*-pentanal) gave a more hydrophobic group and better kinetic inhibition efficacy. The average $T_o$ value dropped to 11.6 °C in the steel rocking cells and 11.8 °C in the sapphire cells. The same trend was seen for polymers made using pentanal and 4-methylpentanal (*iso*-hexanal), with the latter giving the lowest average $T_o$ values of the polymers with acyclic groups. We believe that the reason for these observations is that the alkyl branching gives an end group that gives a better van der Waals interaction with open hydrate cavities than the straight-chain alkyl group, which has been seen in previous studies.[28,50] These cavities can be formed on the hydrate particle surface, causing growth inhibition, or a hydrate cavity could be created around the alkyl group by free water molecules, leading to nucleation inhibition. Either way, this leads to better kinetic inhibition.

Another class of hydrocarbyl fragments with good van der Waals interactions either with hydrate cavities or creating cavities in the water solution are cycloalkyl groups. We know that cyclopentane forms structure II hydrates, as can cyclohexane with the help of a gas like methane.[52] Therefore, we also investigated two polymers with cycloalkyl groups made by reacting the base polyvinylamine with cyclopentanecarboxaldehyde or cyclohexanecarboxaldehyde. The five-ring polyvinylaminal gave a similar performance to the pentanal derivative, but the six-ring polyvinylaminal with pendant cyclohexyl groups gave the best performance of all of the new polymers tested. At 2500 ppm and pH 6.5 (initial pH before pressurizing the cells), the average $T_o$ values were 9.8 °C in the steel rocking cells and 10.4 °C in the sapphire rocking cells. There was no statistically significant difference between these results. The actual pH under pressure during the test was probably a little lower due to the dissolution of the acid gas $CO_2$. When the solution was adjusted to pH 3.1 (by addition of aq. HCl) and retested in the sapphire cells, the average $T_o$ value increased to 11.2 °C, which was significant ($p$ = 0.03 in the *t*-test). We speculate that the slightly poorer performance might be attributed to increased protonation of the amine groups at the lower pH, making the polymer less hydrophobic. Previous results from our group suggest that increased hydrophobicity with hydrocarbyl groups of the correct size and shape can improve KHI performance as long as water solubility is not lost.[51] When the cyclohexanecarboxaldehyde polyvinylaminal derivative was tested at 5000 ppm and pH 6.5, the average $T_o$ values decreased significantly to 7.0 °C (steel cells) and 7.6 °C (sapphire cells). An increase in performance with an increase in concentration for KHI polymers is a typical occurrence.[23,44,53]

There are some previous studies on KHIs showing the usefulness of the cyclohexyl group. For example, the best KHI performance for a series of poly(ethylene citramide)s was found for the polymer with pendant cyclohexyl groups.[53] Related polytartramides also perform well with cyclohexyl groups.[54] The six-ring cyclohexyl group is also present in hyperbranched poly(ester amide) KHIs.[55] However, only four carbon atoms in the ring are available for hydrophobic interactions as the polymer is made using hexahydrophthalic anhydrides. Cyclohexyl groups are also useful in solvent synergists for *N*-vinyl caprolactam or isopropylmethacrylamide polymers.[56]

## ■ CONCLUSIONS

A series of water-soluble polyvinylaminals with pendant alkyl and cycloalkyl groups were prepared. Under acidic conditions, the amines can be protonated to give quaternary groups. The best polyvinylaminals functioned as THF hydrate crystal growth inhibitors, but not as powerfully as poly(*N*-vinylcaprolactam) (PVCap). The best results were observed for the pentanal and cyclohexanecarboxyaldehyde derivatives. In gas hydrate experiments with a gas that preferentially forms structure II hydrate, several polyvinylaminals gave good KHI performance. Branching of the end of the pendant alkyl groups improved the inhibition performance. As with the THF hydrate tests, the polyvinylaminal with pendant cyclohexyl groups gave good results, but now, the performance was similar to PVCap. The contrasting results of these polymers on the two clathrate hydrate systems indicate that nucleation inhibition is probably also taking place in the gas hydrate system with the polyvinylaminal derivative for this polymer to surpass the performance of PVCap.

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### Notes

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