energy&fuels

Article

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

Malcolm A. Kelland,* Erik G. Dirdal, and Lilian H. S. Ree

Read Online

ACCESS | Metrics & More | Article Recommendations

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]
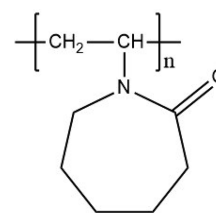

Figure 1. Structure of PVCap.

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

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 in 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
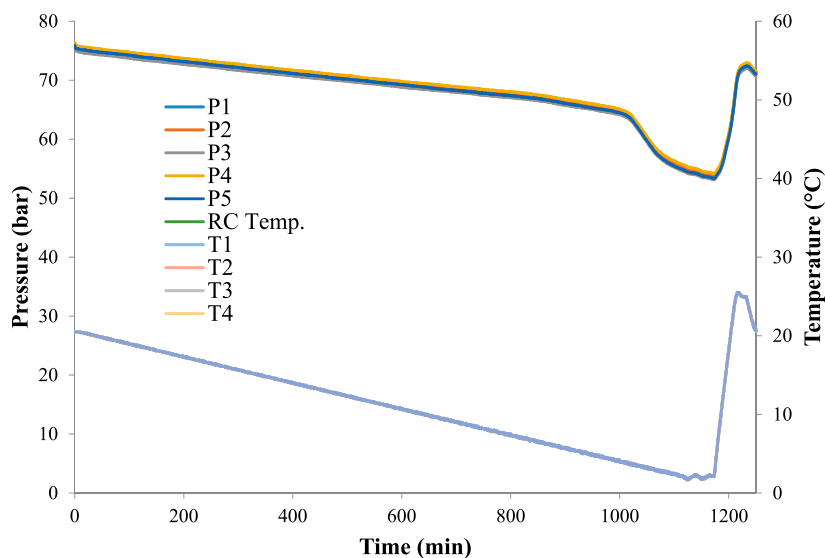
Figure 2. Results from five cells with 2500 ppm of PVCap and 5000 ppm of cyclohexanol as the synergist tested by the standard constant cooling experiment (RC Temp. = rocking cell bath temperature).
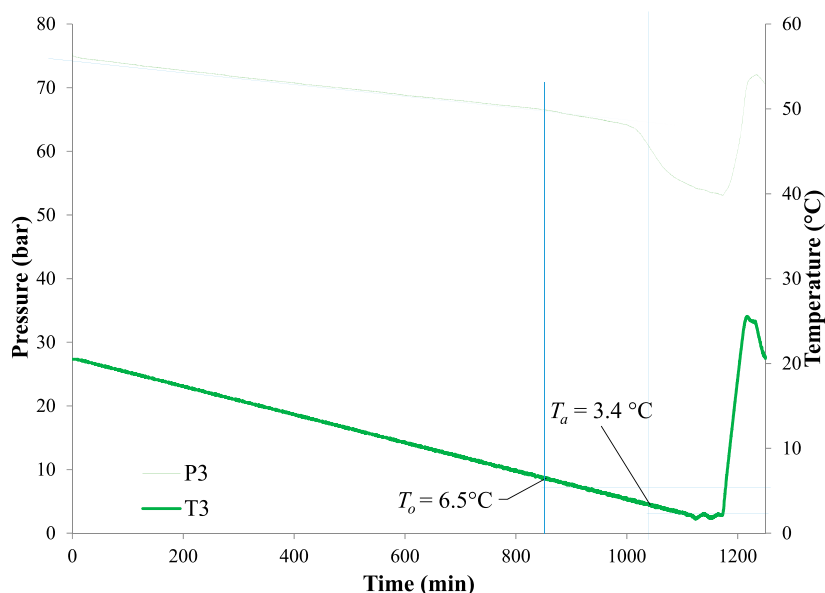
Figure 3. Standard constant cooling experiment for cell 3 containing 2500 ppm of PVCap and 5000 of ppm cyclohexanol as the synergist, where both T_o and T_a are determined.

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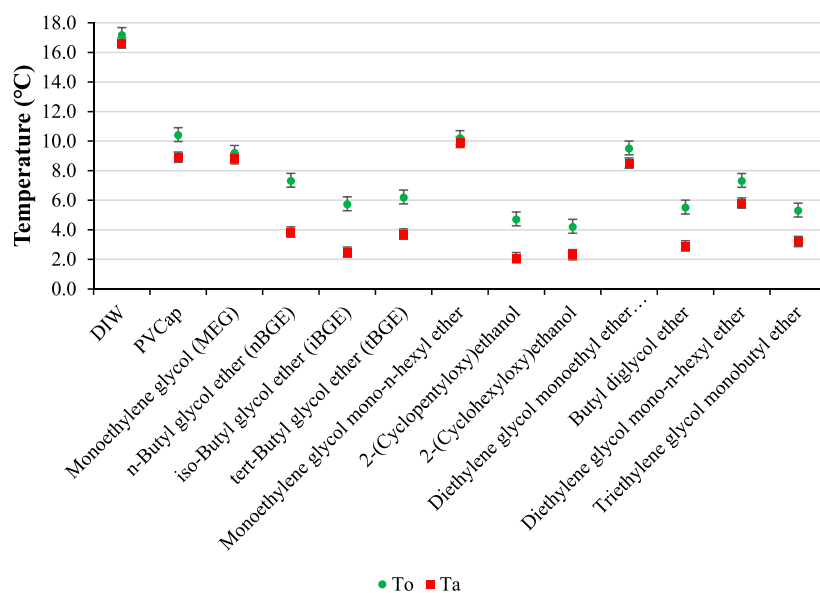
Figure 4. T_o and T_a values for PVCap (2500 ppm) with glycol ethers (5000 ppm).

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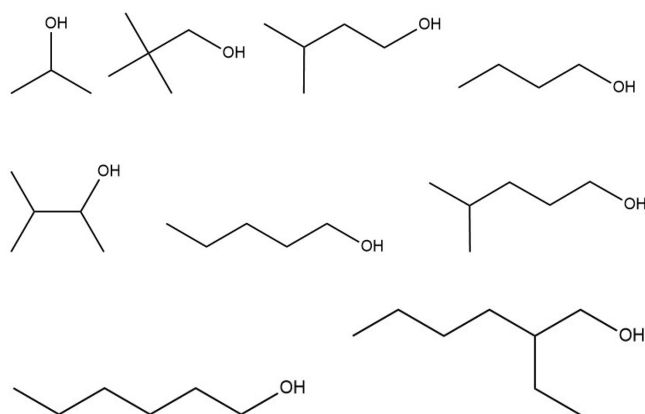
Figure 5. Structures for the acyclic alcohols investigated. From the top left to right: 2-propanol, 2,2-dimethyl-1-propanol, 3-methyl-1-butanol, 1-butanol, 3-methyl-2-butanol, 1-pentanol, 4-methyl-1-pentanol, 1-hexanol, and 2-ethyl-1-hexanol.

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.

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
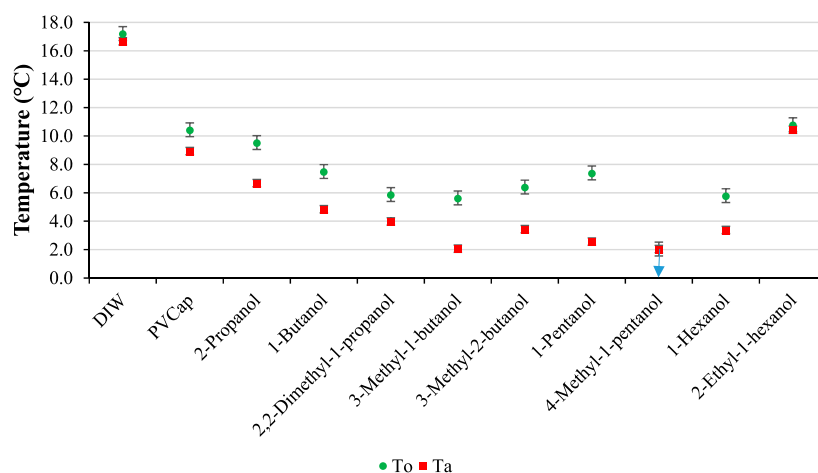
Figure 6. Graphical display of the synergetic effect of different acyclic alcohols (5000 ppm) with PVCap (2500 ppm).
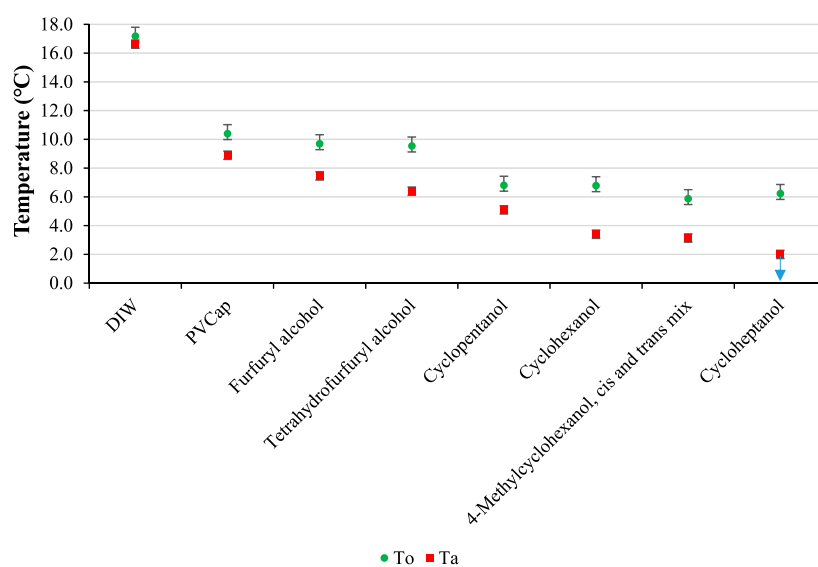
Figure 7. Graphic presentation of the performance of the cyclic alcohols, tetrahydrofurfuryl alcohol, and furfuryl alcohol (5000 ppm) as a potential synergist on the T_o value of PVCap (2500 ppm).

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 synthe-

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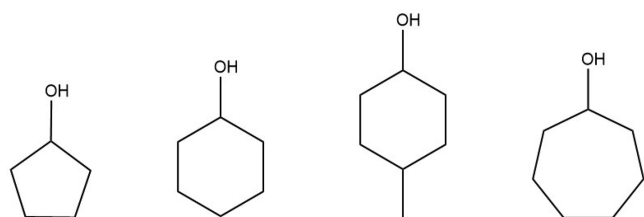
Figure 8. Structures of the cyclic alcohols tested as a potential synergist in this study. From left to right: cyclopentanol, cyclohexanol, 4-methylcyclohexanol, and cycloheptanol.

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.

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,
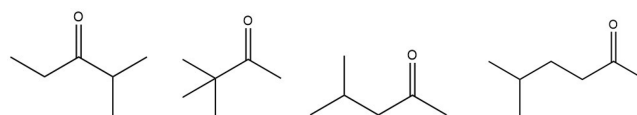

Figure 9. Structure of the various ketones investigated. From left to right: 2-methyl-3-pentanone, 3,3-dimethyl-2-butanone, 4-methyl-2-pentanone, and 5-methyl-2-hexanone.

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.

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

1660
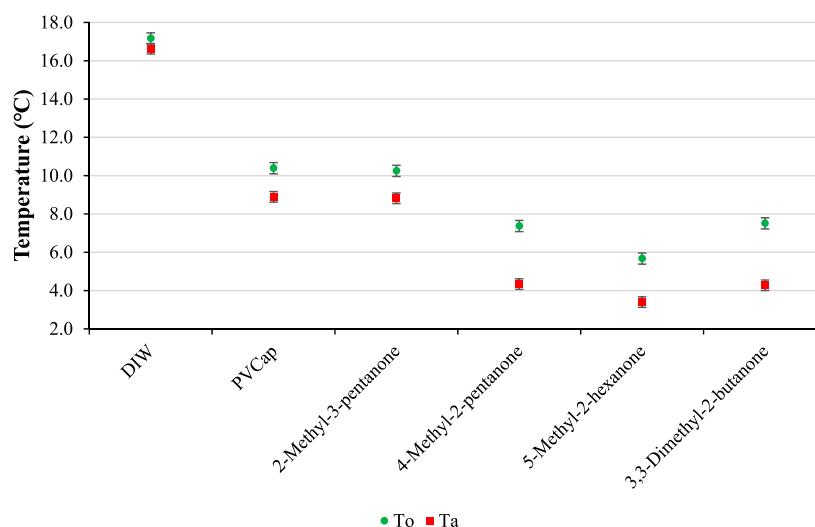
Figure 10. Graphical interpretation of the potential synergetic effect of different ketones (5000 ppm) on the T_o and T_a values of PVCap (2500 ppm).

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.

■ AUTHOR INFORMATION

Corresponding Author

Malcolm A. Kelland − *University of Stavanger, Stavanger, Norway;* orcid.org/0000-0003-2295-5804; Email: malcolm.kelland@uis.no

Other Authors

Erik G. Dirdal − *University of Stavanger, Stavanger, Norway*

Lilian H. S. Ree − *University of Stavanger, Stavanger, Norway;* orcid.org/0000-0003-2357-4421

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.energyfuels.9b03994

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Sloan, E. D., Jr.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2007; DOI: 10.1201/9781420008494.

(2) Koh, C. A.; Sum, A. K.; Sloan, E. D. Gas hydrates: Unlocking the energy from icy cages. *J. Appl. Phys.* **2009**, *106*, 061101.

(3) Talley, L. D.; Mitchell, G. F. Application of Proprietary Kinetic Hydrate Inhibitors in Gas Flowlines. *Proceedings of the 1999 Offshore Technology Conference*; Houston, TX, May 3−6, 1999; OTC 11036, DOI: 10.4043/11036-MS.

(4) Koh, C. A. Towards a fundamental understanding of natural gas hydrates. *Chem. Soc. Rev.* **2002**, *31* (3), 157−167.

(5) Kelland, M. A. *Production Chemicals for the Oil and Gas Industry*, 2nd ed.; CRC Press: Boca Raton, FL, 2014; DOI: 10.1201/b16648.

(6) Carroll, J. J. *Natural Gas Hydrates: A Guide for Engineers*, 2nd ed.; Elsevier Gulf Professional: Amsterdam, Netherlands, 2009; DOI: 10.1016/B978-0-7506-8490-3.X0001-8.

(7) Sloan, E. D., Jr. Natural gas hydrates. *JPT, J. Pet. Technol.* **1991**, *43* (12), 1414−1417.

(8) Alapati, R.; Sanford, E.; Kiihne, E.; Vita, E. Proper Selection of LDHI for Gas Condensate Systems, in the Presence of Corrosion Inhibitors. *Proceedings of the Offshore Technology Conference*; Houston, TX, May 3−6, 2010; OTC 20896, DOI: 10.4043/20896-MS.

(9) Davies, S. R.; Boxall, J. A.; Koh, C. A.; Sloan, E. D.; Hemmingsen, P. V.; Kinnari, K. J; Xu, Z. G. Predicting Hydrate-Plug Formation in a Subsea Tieback. *Proceedings of the SPE Annual Technical Conference and Exhibition*; Denver, CO, Sept 21−24, 2008; SPE 115763, DOI: 10.2118/115763-MS.

(10) Lavallie, O.; Al Ansari, A.; O'Neill, S.; Chazelas, O.; Glénat, P.; Tohidi, B. Successful Field Application of an Inhibitor Concentration Detection System in Optimising the Kinetic Hydrate Inhibitor (KHI) Injection Rates and Reducing the Risks Associated with Hydrate Blockage. *Proceedings of the International Petroleum Technology Conference*; Doha, Qatar, Dec 7−9, 2009; IPTC 13765, DOI: 10.2523/IPTC-13765-MS.

(11) Davalath, J.; Barker, J. W. Hydrate Inhibition Design for Deepwater Completions. *SPE Drill. Completion* **1995**, *10*, 115.

(12) Mehta, A. P.; Hebert, P. B.; Cadena, E. R.; Weatherman, J. P. Fulfilling the Promise of Low-Dosage Hydrate Inhibitors: Journey from Academic Curiosity to Successful Field Implementation. *Proceedings of the 2002 Offshore Technology Conference*; Houston, May 6−9, 2002; OTC 14057, DOI: 10.4043/14057-MS.

(13) Kelland, M. A.; Svartaas, T. M.; Dybvik, L. Studies on New Gas Hydrate Inhibitors. *Proceedings of the SPE Offshore Europe Conference*; Aberdeen, U.K., Sept 5−8, 1995; SPE 30420, DOI: 10.2118/30420-MS.

(14) Ke, W.; Chen, D. A short review on natural gas hydrate, kinetic hydrate inhibitors and inhibitor synergists. *Chin. J. Chem. Eng.* **2019**, *27*, 2049−2061.

(15) Kelland, M. A. A review of kinetic hydrate inhibitors: Tailormade water-soluble polymers for oil and gas industry applications. In *Advances in Materials Science Research*; Wytherst, M. C., Ed.; Nova Science Publishers, Inc.: New York, 2011; Vol. 8.

(16) Perrin, A.; Musa, O. M.; Steed, J. W. The chemistry of low dosage clathrate hydrate inhibitors. *Chem. Soc. Rev.* **2013**, *42* (5), 1996−2015.

(17) Fu, S. B.; Cenegy, L. M.; Neff, C. S. A Summary of Successful Field Applications of A Kinetic Hydrate Inhibitor. *Proceedings of the 2001 SPE International Symposium on Oilfield Chemistry*; Houston, TX, Feb 13−16, 2001; SPE 65022, DOI: 10.2118/65022-MS.

(18) Kelland, M. A. History of the development of low dosage hydrate inhibitors. *Energy Fuels* **2006**, *20* (3), 825−847.

(19) Yousif, M. H. The Kinetics of Hydrate Formation. *Proceedings of the SPE 69th Annual Technical Conference and Exhibition*; New Orleans, LA, Sept 25−28, 1994; SPE 28479, DOI: 10.2118/28479-MS.

(20) Varma-Nair, M.; Costello, C. A.; Colle, K. S.; King, H. E. Thermal Analysis of Polymer-Water Interactions and Their Relation to Gas Hydrate Inhibition. *J. Appl. Polym. Sci.* **2007**, *103* (4), 2642−2653.

(21) Kamal, M. S.; Hussein, I. A.; Sultan, A. S.; von Solms, N. Application of various water soluble polymers in gas hydrate inhibition. *Renewable Sustainable Energy Rev.* **2016**, *60*, 206−225.

(22) Kirsh, Y. E.; Yanul, N. A.; Kalninsh, K. K. Structural transformations and water associate interactions in poly-N-vinyl-caprolactam-water system. *Eur. Polym. J.* **1999**, *35*, 305−316.

(23) Makogon, T. Y.; Larsen, R.; Knight, C. A.; Sloan, E. D., Jr. Melt growth of tetrahydrofuran clathrate hydrate and its inhibition: Method and first results. *J. Cryst. Growth* **1997**, *179*, 258−262.

(24) Lederhos, J. P.; Sloan, E. D. Transferability of Kinetic Inhibitors between Laboratory and Pilot Plant. *Proceedings of the SPE Annual Technical Conference and Exhibition*; Denver, CO, Oct 6−9, 1996; SPE 36588, DOI: 10.2118/36588-MS.

(25) Zhang, J. S.; Lo, C.; Couzis, A.; Somasundaran, P.; Wu, J.; Lee, J. W. Adsorption of Kinetic Inhibitors on Clathrate Hydrates. *J. Phys. Chem. C* **2009**, *113* (40), 17418−17420.

(26) Lee, W.; Shin, J. Y.; Cha, J. H.; Kim, K. S.; Kang, S. P. Inhibition effect of ionic liquids and their mixtures with poly(N-vinylcaprolactam) on methane hydrate formation. *J. Ind. Eng. Chem.* **2016**, *38*, 211−216.

(27) Yang, J.; Tohidi, B. Characterization of inhibition mechanisms of kinetic hydrate inhibitors using ultrasonic test technique. *Chem. Eng. Sci.* **2011**, *66*, 278−283.

(28) Anderson, R.; Tohidi, B. Water treatment. WO Patent 2015/022480, 2015.

(29) Clements, J.; Pakulski, M. K.; Riethmeyer, J.; Lewis, D. C. Improved poly(vinyl caprolactam) kinetic gas hydrate inhibitor and method for preparing the same. WO Patent 2015/022480, 2015.

(30) Ree, L. H.; Kelland, M. A. Investigation of Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly(N-isopropyl methacrylamide). *Energy Fuels* **2019**, *33*, 8231−8240.

(31) Cohen, J. M.; Wolf, P. F.; Young, W. D. Enhanced hydrate inhibitors: powerful synergism with glycol ethers. *Energy Fuels* **1998**, *12* (2), 216−218.

(32) Thieu, V.; Bakeev, K. N.; Shih, J. S. Method for preventing or retarding the formation of gas hydrates. U.S. Patent 6,451,891. 2002.

(33) Fu, B. The development of advanced kinetic hydrate inhibitors. In *Chemistry in the Oil Industry VII: Performance in a Challenging Environment*; Frampton, H., Craddock, H. A., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2002; pp 264−276.

(34) Cohen, J. M.; Young, W. D. Method for inhibiting the formation of gas hydrates. U.S. Patent 6,096,815. 2000.

(35) Mozaffar, H.; Anderson, R.; Tohidi, B. Effect of alcohols and diols on PVCap-induced hydrate crystal growth patterns in methane systems. *Fluid Phase Equilib.* **2016**, *425*, 1−8.

(36) Tohidi, F.; Anderson, R.; Tohidi, B. Evaluation of a Novel Water-Immiscible Kinetic Hydrate Inhibitor Formulation. *Energy Fuels* **2018**, *32*, 6518−6523.

(37) Qin, H.; Sun, C.; Sun, Z.; Liu, B.; Chen, G. Relationship between the interfacial tension and inhibition performance of hydrate inhibitors. *Chem. Eng. Sci.* **2016**, *148*, 182−189.

(38) Ruelle, P.; Kesselring, U. W. The hydrophobic propensity of water toward amphiprotic solutes: prediction and molecular origin of the aqueous solubility of aliphatic alcohols. *J. Pharm. Sci.* **1997**, *86* (2), 179−186.

(39) Foo, C. W.; Ruan, L.; Lou, X. The inhibition performance in relation to the adsorption of a polymeric kinetic inhibitor towards THF hydrates in the presence of methanol, ethanol and monoethyleneglycol. *J. Nat. Gas Sci. Eng.* **2016**, *35*, 1587−1593.

(40) Sefidroodi, H.; Chua, P. C.; Kelland, M. A. THF hydrate crystal growth inhibition with small anionic organic compounds and their synergetic properties with the kinetic hydrate inhibitor poly(N-vinylcaprolactam). *Chem. Eng. Sci.* **2011**, *66*, 2050−2056.

(41) Chua, P. C.; Kelland, M. A. Tetra (iso-hexyl) ammonium Bromide- The Most Powerful Quaternary Ammonium-Based Tetrahydrofuran Crystal Growth Inhibitor and Synergist with Polyvinylcaprolactam Kinetic Gas Hydrate Inhibitor. *Energy Fuels* **2012**, *26* (2), 1160−1168.

(42) Kelland, M. A.; Kvæstad, A. H.; Astad, E. L. Tetrahydrofuran hydrate crystal growth inhibition by trialkylamine oxides and synergism with the gas kinetic hydrate inhibitor poly(N-vinyl caprolactam). *Energy Fuels* **2012**, *26* (7), 4454−4464.

(43) Tohidi, B.; Burgass, R. W.; Danesh, A.; Østergaard, K. K.; Todd, A. C. Improving the accuracy of gas hydrate dissociation point measurements. In *Gas Hydrates: Challenges for the Future*; Holder, G. D., Bishnoi, P. R., Eds.; New York Academy of Sciences: New York, 2000; Vol. *912*, pp 924−931.

(44) Gjertsen, L. H.; Fadnes, F. H. Measurements and predictions of hydrate equilibrium conditions. In *Gas Hydrates: Challenges for the Future*; Holder, G. D., Bishnoi, P. R., Eds.; New York Academy of Sciences: New York, 2000; Vol. *912*, pp 722−734.

(45) Zhang, Q.; Kawatani, R.; Ajiro, H.; Kelland, M. A. Optimizing the Kinetic Hydrate Inhibition Performance of *N*-Alkyl-*N*-vinylamide Copolymers. *Energy Fuels* **2018**, *32*, 4925−4931.

(46) 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.

(47) National Center for Biotechnology Information (NCBI). 1-Hexanol—Compound Summary. *PubChem Database*; NCBI: Bethesda, MD, March 26, 2005.