

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

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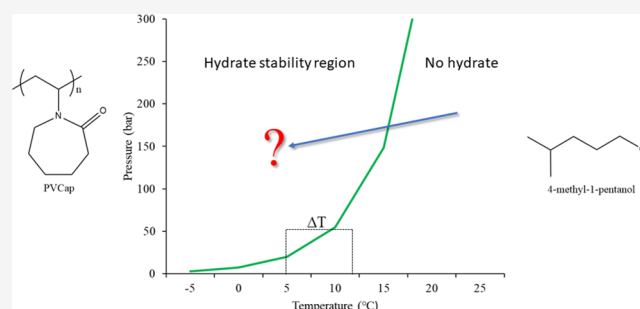
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ABSTRACT: Poly(*N*-vinylcaprolactam) (PVCap) and related copolymers have been used as kinetic hydrate inhibitors (KHIs) to combat gas hydrate formation in oil and gas field production flow lines. It is known that the addition of certain solvents to 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 hyper-branched 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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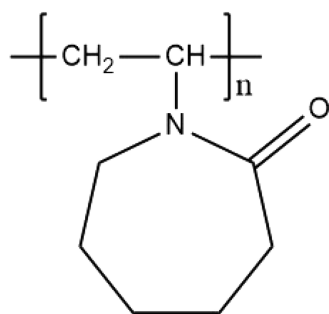


Figure 1. Structure of poly(*N*-vinylcaprolactam) (PVCap).

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 synergistic 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 synergistic 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 synergistic 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 cycloalkanes (five to seven carbon atoms) and their glycol ethers were also

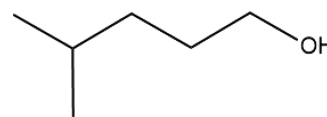


Figure 2. Structure of 4-methyl-1-pentanol (iHexOl).

powerful synergists. In addition, solvents with one or two glycol functional groups generally gave a better synergistic 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

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)-CH₂COOH ($M_n = 4006$ 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 ¹H 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

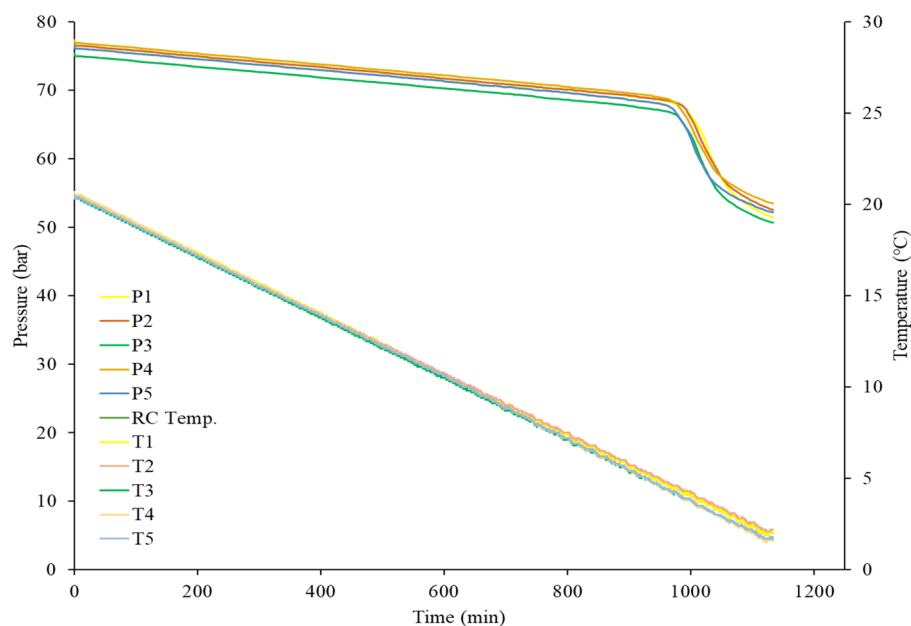


Figure 3. SCC tests results from all five cells, each containing in this example 2500 ppm PVCap and 5000 ppm 2-methyl-1-pentanol. “RC Temp.” is the temperature recorded in the cooling bath.

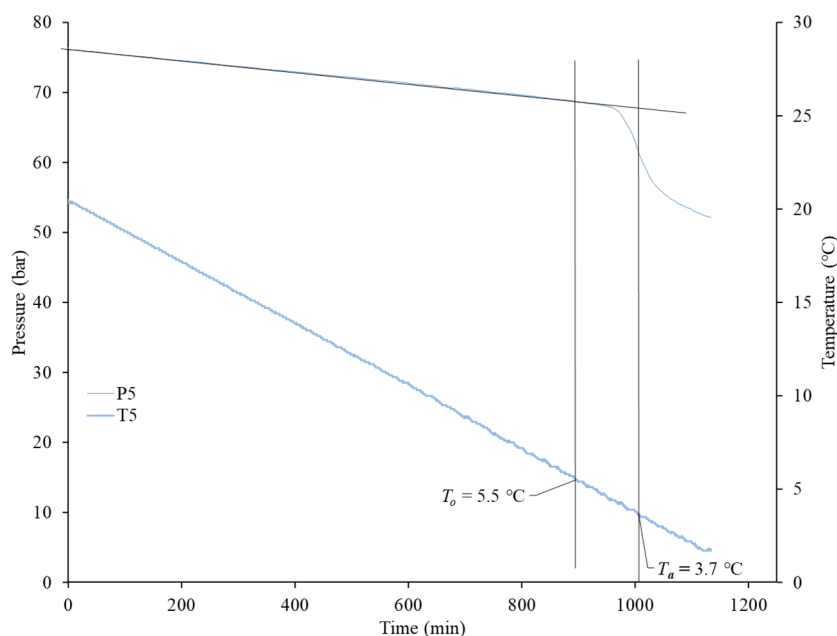


Figure 4. Graph from cell 1 with both T_o and T_a determined during an SCC experiment. In this example, the cell contained 2500 ppm PVCap and 5000 ppm 2-methyl-1-pentanol.

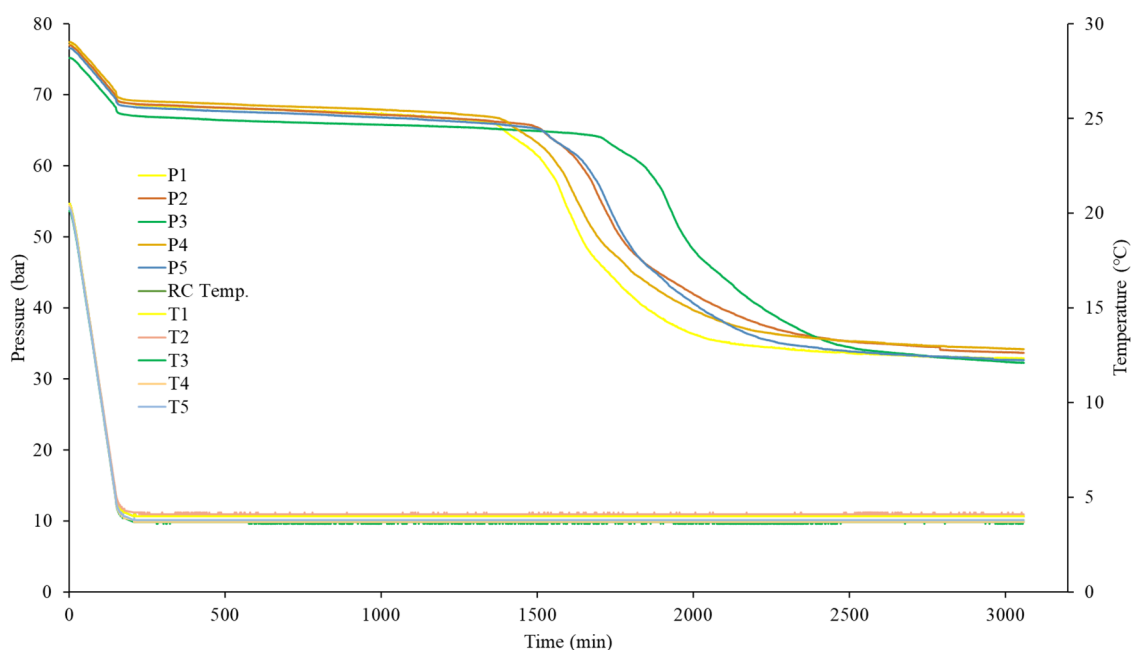


Figure 5. Graph containing results from an isothermal test for all five cells; in this example, the cells contained 2500 ppm PVCap and 2500 ppm iHexOl. “RC Temp.” is the temperature recorded in the cooling bath.

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

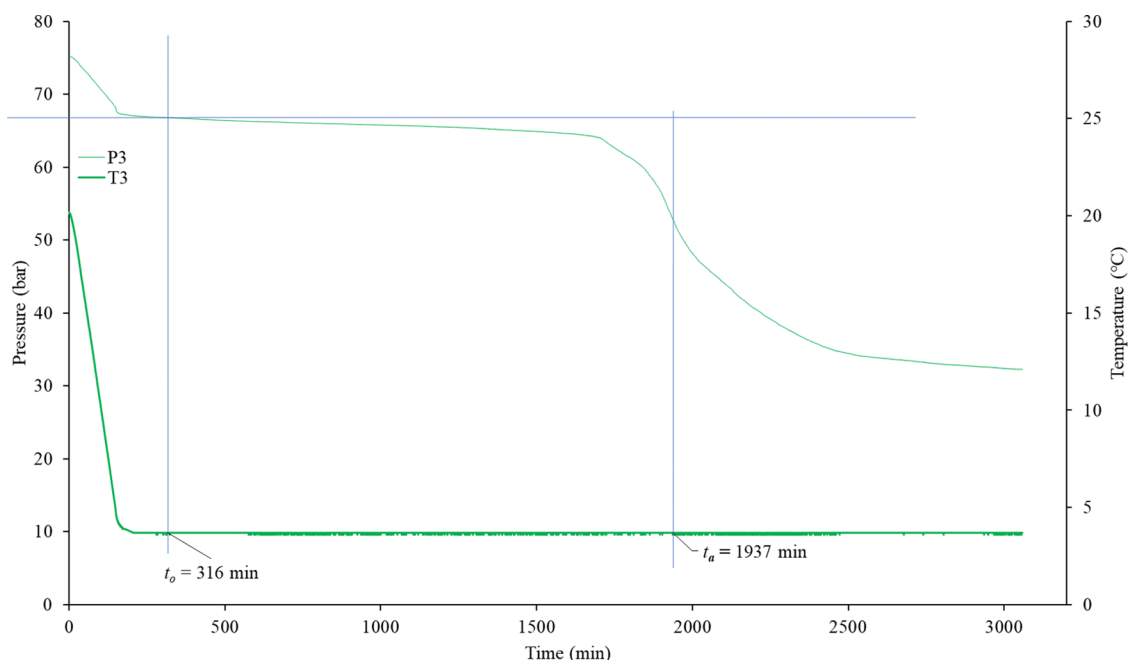


Figure 6. Graph from one cell with both t_o and t_a determined during an isothermal experiment. In this example, the cell contained 2500 ppm PVCap and 2500 ppm iHexOl.

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)		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	10,000	7.2	6.0

^aVolume 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

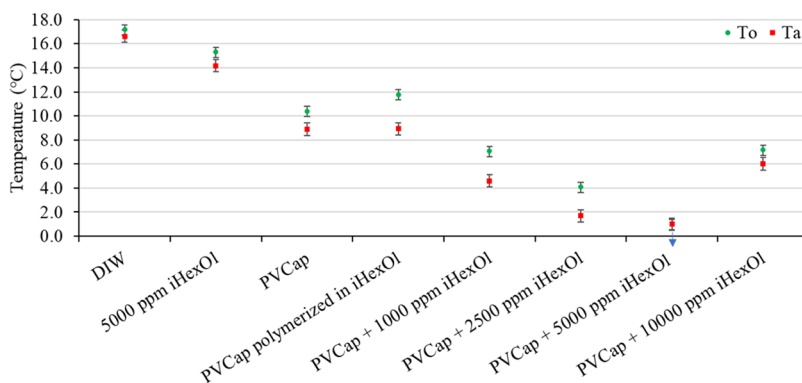


Figure 7. Summary of SCC test results for 2500 ppm PVCap with different concentrations of iHexOl, plus some comparative tests. Both T_o and T_a values are given.

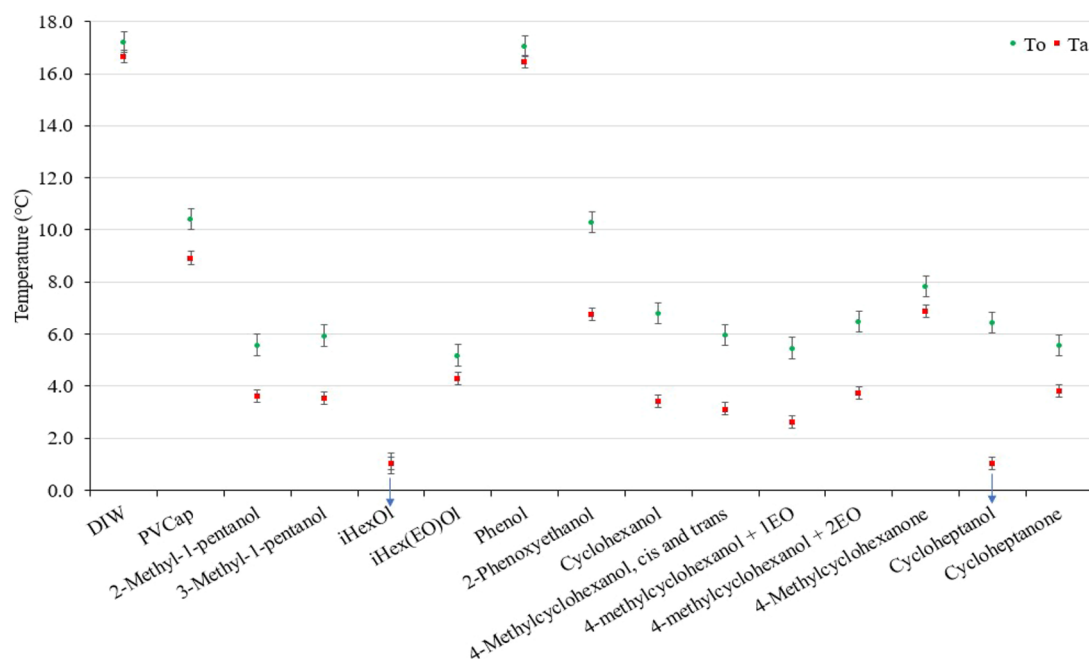


Figure 8. Graphical display of the T_o and T_a values for PVCap (2500 ppm) with different solvents added (5000 ppm).

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

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 (<i>cis</i> and <i>trans</i> mixture)	5.9	3.1
4-methylcyclohexanol (<i>cis</i> and <i>trans</i> mixture) + 1EO	5.4	2.6
4-methylcyclohexanol (<i>cis</i> and <i>trans</i> mixture) + 2EO	6.4	3.7
4-methylcyclohexanone	7.8	6.9
cycloheptanol	6.4	<3
cycloheptanone	5.5	3.8
<i>n</i> -butyl glycol ether (BGE)	7.3	3.8
butyl diglycol ether (DBGGE)	5.5	2.9
di(propylene glycol)butyl ether (DPGGE) isomer mix	5.5	<3
2- <i>n</i> -butoxyethyl acetate	5.5	<3

^aVolume of solution in the cells was 20 mL.

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.

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

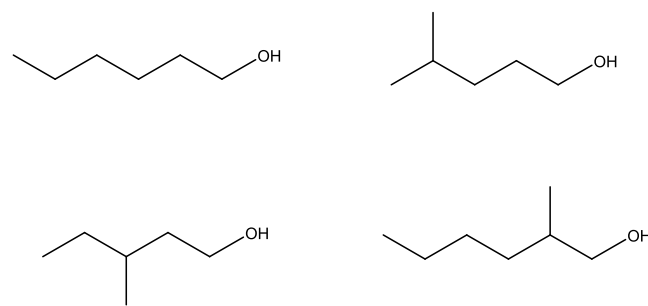


Figure 9. Clockwise from top left: 1-hexanol, 4-methyl-1-pentanol (iHexOl), 2-methyl-1-pentanol, and 3-methyl-1-pentanol.

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).

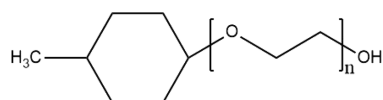


Figure 10. 4-Methylcyclohexanol and mono- and diglycol ethers ($n = 0-2$).

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 (DPGGE), 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

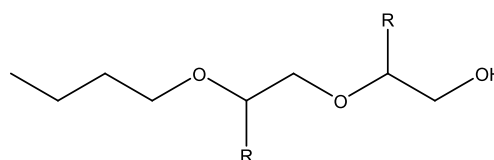


Figure 11. Butyl diglycol ether (DBGE) ($R=H$) and di(propylene glycol)butyl ether (DPGGE) ($R=CH_3$).

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.

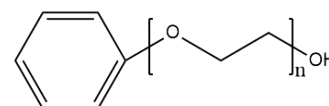


Figure 12. Schematic of phenol and 2-phenoxyethanol ($n = 0-1$).

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 π electron clouds in place of individual double and single bonds. These 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. 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)		t_o (min)	standard deviation for t_o	t_a (min)
polymer	synergist	polymer	synergist			
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

^an/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,

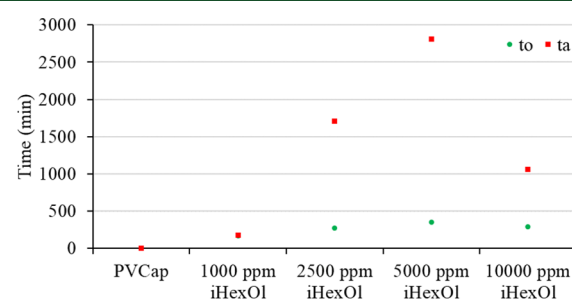


Figure 13. A graphical representation of the isothermal test results (68 bar, 4 °C) for 2500 ppm PVCap together with different concentrations of iHexOl, all with 20 mL of test solution (t_o and t_a overlap for PVCap and PVCap + 1000 ppm iHexOl).

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

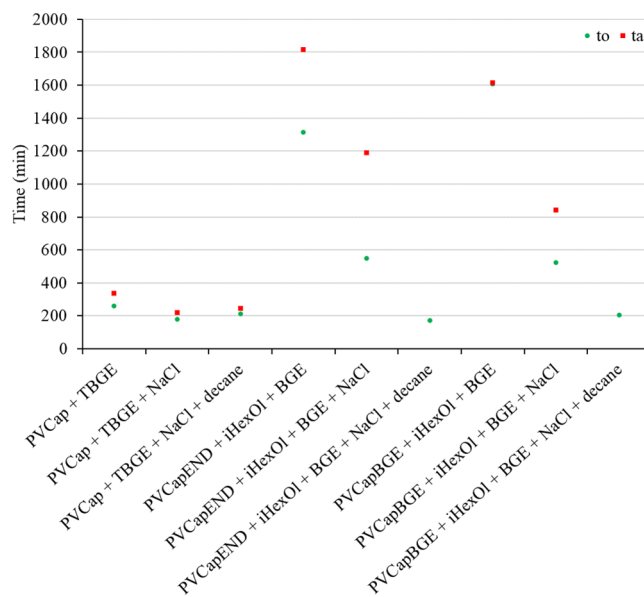


Figure 14. Isothermal test results at 68 bar, 4 °C. Concentrations were 7500 ppm polymer and 5000 ppm of all solvents as 15 mL aqueous solutions. Decane (1 mL) and/or 0.5 wt % NaCl was added where denoted.

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.

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)		t_o (min)	standard deviation for t_o	t_a (min)
polymer	synergist	polymer	synergist			
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

^aTest 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)		additive	t_o (min)	standard deviation for t_o	t_a (min)
polymer	synergist	polymer	synergist				
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

^a68 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)		volume (ml)	additive	T_o (°C)	T_a (°C)
KHI polymer	synergist	KHI polymer	synergist				
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 $S^{12}6^4$ 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 $S^{12}6^4$ 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 $S^{12}6^4$ 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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