High-Performance Kinetic Hydrate Inhibition with Poly(*N*-isopropyl methacrylamide) and Triisopentylamine Oxide—Surprising Concentration-Dependent Results

Radhakanta Ghosh, Janronel Pomicpic, and Malcolm A. Kelland*

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ABSTRACT: Kinetic hydrate inhibitors (KHIs) are mostly used to prevent the deposition of gas hydrates in gas and condensate production flow lines. The main component in a KHI formulation is a water-soluble polymer, blended with solvents and other synergists to boost the performance. The performance limit in terms of subcooling and other factors restricts the application range of KHIs. Earlier, we reported on the synergetic performance of trialkylamine oxides with polyalkyl(meth)acrylamides using high-pressure steel rocking cell experiments. In particular, blends of poly(*N*-isopropyl methacrylamide) (PNIPMAm) in isobutyl glycol ether (iBGE) with triisopentylamine oxide (TiPeAO) gave exceptional KHI performance, better than what we have seen for any other KHI blend so far. Therefore, it is important to evaluate the limitations of this KHI. Here, we report the results of the KHI performance of this blend in more detail. The cloud point decreased with increasing salinity (0−15 wt % NaCl), but the blend remained soluble, giving excellent KHI performance even at the highest brine concentration. We also varied the concentration of the PNIPMAm/TiPeAO blend from 250 to 5000 ppm in deionized water in KHI slow constant cooling (SCC) tests using both a natural gas mixture [synthetic natural gas (SNG)] and methane gas. A unique concentration-dependent performance was discovered, wherein the performance decreased greatly above about 1500−2000 ppm, possibly due to aggregation of the polymer and amine oxide. This was observed for SCC tests with both SNG and methane, with the phenomenon being more pronounced for methane. In addition, an unusual double pressure drop was observed in SCC tests with methane and a blend of 5000 ppm PNIPMAm and TiPeAO. This study underlines the fact that overdosing of components in a synergistic blend can sometimes lead to detrimental effects on the KHI performance.
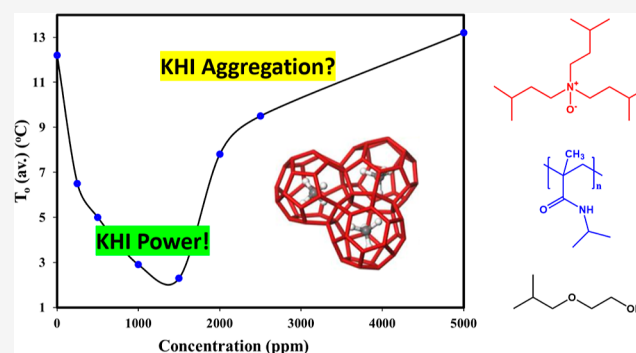
1. INTRODUCTION

Kinetic hydrate inhibitors (KHIs) have been used in the oil and gas industry to prevent the formation and plugging of gas hydrates in production flow lines.[1−5] They delay the hydrate nucleation and crystal growth processes. The delay time increases as the thermodynamic driving force for hydrate formation decreases. The driving force is a result of several factors, but the KHI concentration and the subcooling (ΔT) are often quoted as the main factors. Other factors include the pressure, the gas composition, salinity, the gas−oil−water ratio, and the presence of other production chemicals. The main component in a KHI formulation is one or more oligomers or polymers, which are water-soluble and have specific amphiphilic groups. For most commercial KHI polymers, the main hydrophilic group is the amide groups, usually bonded directly to hydrophobic groups of optimal size and shape. Depending on the polymer class, these hydrophobic groups are about three to six carbon atoms and can be alkyl groups, cycloalkyl groups, or part of a heterocyclic ring. Two of the commonest polymer classes deployed today are based on *N*-vinyl lactams [such as *N*-vinyl pyrrolidone or *N*-vinyl caprolactam (VP and VCap, respectively)] or *N*-isopropylmethacrylamide (NIPMAm).[6−16]

Trialkylamine oxides have previously been shown to be excellent hydrate growth inhibitors as well as synergists for VCap polymers.[17,18] Both tributylamine oxide (TBAO) and tripentylamine oxide (TPeAO) gave better synergy with PVCap than triisopentylamine oxide (TiPeAO) (Figure 1). We recently reported on the synergetic performance of trialkylamine oxides with polyalkyl(meth)acrylamides using a synthetic natural gas (SNG) mixture in high-pressure steel

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Figure 1. PNIPMAm and TiPeAO.

Table 1. Composition of SNG Mixture

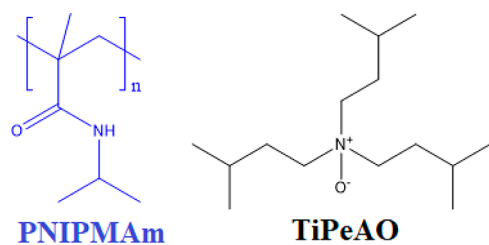| component	mol %
methane	80.67
ethane	10.20
propane	4.90
isobutane	1.53
n-butane	0.76
N_2	0.10
CO_2	1.84

rocking cell experiments.[19] We investigated poly(N-isopropyl methacrylamide) (PNIPMAm) (Figure 1) and polyacryloyl-pyrrolidine blends with trialkylamine oxides with one to five carbon atom alkyl groups. In contrast to the earlier results with PVCap, we found that TiPeAO was a better synergist for PNIPMAm than the isomeric TPeAO or TBAO. Di(isohexyl)-pentylamine oxide (nPe(iHex)$_2$AO) also performed exceptionally well as a synergist but would not be cost-effective for field use.)

In fact, we obtained ground-breaking results in our rocking cells. For example, a blend of 1000 ppm PNIPMAm (M_w, 4300 g/mol) in isobutyl glycol ether (iBGE) with 1000 ppm TiPeAO gave no fast hydrate formation with added decane for over 48 h at 68 bar and 4 °C (ca. 15.5 °C subcooling). At this concentration, this represented the best result we had seen in over a decade of using our rocking cells with a wide range of polymers and synergists. The result was also far better than several commercial KHI formulations that we also investigated. This has led us, also at the request of several reviewers, to investigate the PNIPMAm (in iBGE)/TiPeAO synergistic system in more detail. Here, we present the results of our study wherein we investigated the effective PNIPMAm/TiPeAO ratio, the effect of salinity (0−15 wt % NaCl), and the performance using both a natural gas mixture and methane gas, as well as the cloud point of various blends at various salinities.

2. EXPERIMENTAL SECTION

2.1. Materials. PNIPMAm as 20.1 wt % in iBGE (M_w 4700 g/mol, PDI 1.6 by GPC analysis) was synthesized by the literature method.[19,20] TiPeAO was synthesized as previously reported.[19]

2.2. Kinetic Hydrate Inhibitor Performance Tests in High-Pressure Rocking Cells. All KHI performance experiments were carried out in a set of five high-pressure steel rocking cells, each with a volume of 40 mL and a steel ball for agitation, supplied by PSL Systemtechnik GmbH, Germany (Figure 2). The gas used was either a SNG mixture (Table 1), whose thermodynamically stable phase is
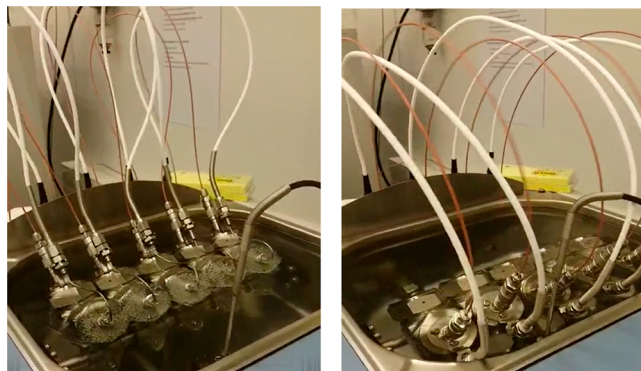
structure II hydrate, or methane gas, which forms structure I hydrate. Our standard slow constant cooling (SCC) test method was used for ease of comparison with past studies.[19,20] This usually allowed for the completion of five parallel tests in a 24 h period, giving a suitable number of data sets in 1−2 days in order to rank the KHI performances.[21]

The pressure was approximately 76 bar at the start of each SCC experiment using deionized water (DIW) and 110 bar for brine experiments. When using SNG, the average equilibrium temperature (T_{eq}) was 20.2 °C and 22.0 °C ± 0.05 °C for 76 bar and 110 bar, respectively. These values agreed well with the T_{eq} values calculated from Calsep's PVTSim software.[19] At 110 bar SNG with 5, 10, and 15 wt % sodium chloride brine, the T_{eq} values are approximately 20.0, 17.8, and 15.4 °C, respectively. For methane hydrate, T_{eq} at 110 bar is 15.7 °C in DIW.[22]

The standard constant cooling test (SCC) procedure was as follows.

1. Each 40 mL cell was charged with 20 mL of aqueous test solution at 20.5 °C.
2. Each cell was independently vacuumed and then filled with around five bar of gas (methane or SNG). The pressure was then released down to 1 bar (gas bled off), the vacuum procedure was repeated, and the cells were recharged with the appropriate hydrocarbon gas to the test pressure (76 or 110 bar). In this way, the air was removed.
3. The cells were rocked and cooled down gradually from 20.5 to 2 °C at a rate of 1 °C/h. The temperature and pressure data for each cell, as well as the bath temperature, were recorded.

Figure 3 illustrates a typical set of experimental data as a graph pressure and temperature vs time for all five cells. We determine two parameters from the data as shown in Figure 4. The first parameter is the gas hydrate onset temperature (T_o). T_o is taken as the temperature when the pressure first drops beyond the normal pressure drop due to the temperature drop in a closed system. Figure 4 shows a slight pressure drop at the very beginning as some of the hydrocarbon gas
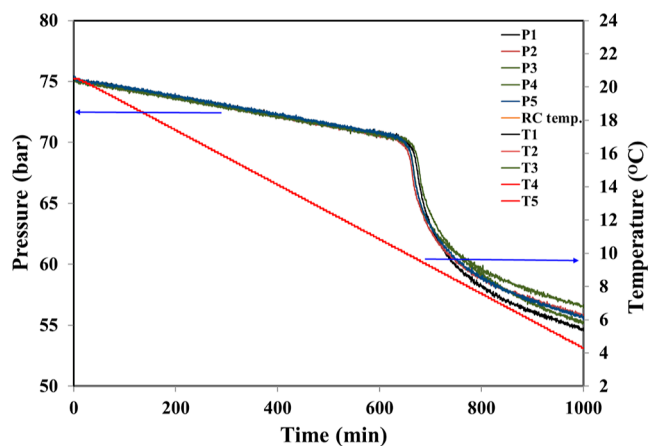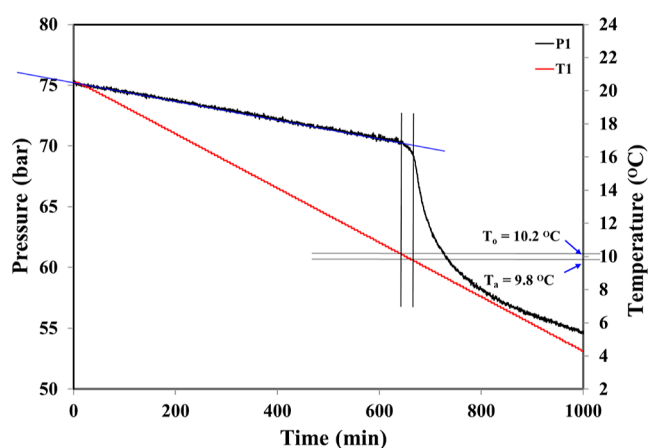

Figure 2. KHI test equipment showing the extreme rocking positions of the steel rocking cells placed in a cooling bath.

Figure 3. Pressure−time and temperature−time graphs obtained from SCC KHI experiments. Example shown is for 500 ppm PNIPMAm at 76 bar pressure SNG in DIW.

Figure 4. Example of T_o and T_a calculations in a standard constant cooling KHI experiment of 500 ppm of PNIPMAm at 76 bar pressure SNG in DIW.

Figure 5. Comparison study of KHI performance of different concentrations of PNIPMAm in the presence of various concentrations of TiPeAO synergists under 76 bar pressure of SNG gas.

dissolves in the aqueous phase. T_o occurs at 10.2 °C. In this test, there is a short period in which the rate of hydrate growth is slow, and at 9.8 °C we obtain the fastest pressure drop of the whole experiment. This is taken as T_a, such as $T_o - T_a$ gives a rough measure of the ability of the KHI to slow macroscopic hydrate crystal growth. The degree of scattering in T_o values ($\leq 20\%$) and T_a values ($\leq 15\%$) is due to the stochastic nature of gas hydrate formation and is as expected from previous studies.[19,20,23,24] The scattering still allows for a rough ranking of the performance of the KHI samples as long as sufficient tests are carried out for a statistically significant difference using a *t*-test. Depending on the variation in average T_o between samples, 5−10 tests suffice in most cases to get a significant difference at the 95% confidence level ($p < 0.05$).[25] Thus, it is possible to get statistically significant data in order to screen KHIs and compare the performance, in agreement with other KHI screening methods.[21]
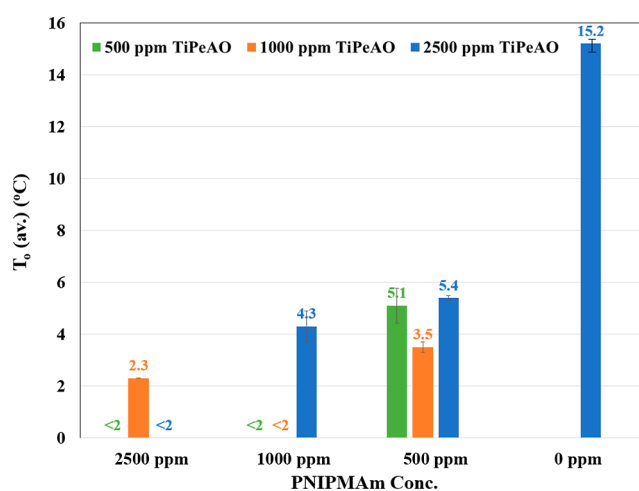
3. RESULTS AND DISCUSSION

3.1. Slow Constant Cooling Test Results with SNG.
The KHI performance for various ratios of PNIPMAm/TiPeAO was explored in SCC tests. A summary of the results at an initial pressure of 76 bar in DIW is given in Table 2 and illustrated in the graph in Figure 5. All average T_o and T_a values are based on results from five cells, except the blank tests with

Table 2. Summary of Slow Constant Cooling KHI (sII-Forming SNG) Test Results at 76 bar Pressure SNG in DIW[a]

[PNIPMAm] ppm	[TiPeAO] ppm	T_o (av.) °C	T_a (av.) °C	$T_o - T_a$ (av.) °C
		16.9	16.8	0.1
2500		4.2	3.7	0.5
	500	NH	NH	
	1000	2.3		
	2500	NH	NH	
1000		7.3	6.7	0.6
	500	NH	NH	
	1000	NH	NH	
	2500	4.3	2.0	2.3
500		10.2	9.8	0.4
	500	5.1	4.8	0.3
	1000	3.5	3.1	0.4
	2500	5.4	2.3	3.1

[a]NH means no pressure drop due to hydrate formation.

no additive, which are for 10 cells. The tests with no TiPeAO represent the use of only the low molecular weight PNIPMAm as a 20.1 wt % solution in an iBGE solvent. This solvent is a reasonable solvent in its own right, as shown from previous studies.[20,26,27] Thus, the tests with 2500 ppm PNIPMAm also have 12438 ppm of iBGE and give an average T_o value of 4.2 °C. Without iBGE, the T_o value is approximately 9.0−9.5 °C for 2500 ppm PNIPMAm (same molecular weight). The results in Table 2 indicate a generally low "$T_o - T_a$" value with low concentrations of TiPeAO synergist but increases with increasing synergist concentration. This trend fits with poor crystal growth inhibition by the PNIPMAm and good inhibition of TiPeAO as seen from THF hydrate crystal growth studies.[18,28]

The data in Table 2 also shows that the T_o and T_a values do not always follow a classic trend of decreasing with increasing KHI concentration. This was also shown in the first study with isothermal experiments.[19] An example from the table with 2500 ppm PNIPMAm is that 500 and 2500 ppm of TiPeAO gave no hydrates (NH) down to the minimum temperature of 2.0 °C, but hydrates did form at 2.3 °C with 1000 ppm TiPeAO. The point of T_a (rapid hydrate formation) was not reached in any of the five cells. A clearer example is for that of 1000 ppm PNIPMAM, which gave no sign of macroscopic hydrates with 500 and 1000 ppm but an average T_o of 4.3 °C was observed with 2500 ppm TiPeAO. This observation plus the fact that no macroscopic (detectable) amounts of hydrates were formed down to 2.0 °C in several experiments led us to investigate more extreme conditions, that is, higher pressure (110 bar) and varying salinity.

3.2. Higher-Pressure KHI Tests with SNG and Varying Brine Concentrations.
These SCC tests were carried out at an initial pressure of 110 bar and 0−15 wt % NaCl. Since the salinity was up to 15 wt % NaCl, we first need to check the solubility and compatibility of the polymer/synergist blends. In general, the cloud points of thermoresponsive polymers such as PNIPMAm decrease with increasing NaCl salinity, according to the Hofmeister rules.[29−32] For field application, it is preferable if the KHI has a cloud point (Tcl) higher than the maximum temperature encountered in the flow line (usually at the well head) or in the processing equipment. This will ensure that KHI polymer fouling will probably not be an issue.

C

We checked the compatibility and Tcl of blends of the PNIPMAm with the iBGE solvent and TiPeAO synergist. Separate solutions of either iBGE or TiPeAO or a mixture give no clouding in 500−2500 ppm brine solutions with 0−15 wt % NaCl. Table 3 summarizes our investigation of Tcl values for

Table 3. Cloud Points (Tcl) of PNIPMAm Polymer (in iBGE) with TiPeAO Synergist Blends in DIW

[PNIPMAm] ppm	[TiPeAO] ppm	Tcl °C
10,000	10,000	29
5000	5000	35
2500	2500	39
1500	1500	45
1000	1000	49
500	500	57
250	250	>85[a]

[a]Difficult to determine visually due to low concentration.

decreasing concentrations of both polymers and synergists in DIW. The Tcl values were found to increase with decreasing polymer/synergist concentrations. For brines, we investigated a 1000 ppm PNIPMAm (in iBGE) + 1000 ppm TiPeAO blend, as this had been shown to have exceptional KHI performance in the first study (Figure 6).[19] As expected, Tcl decreased with
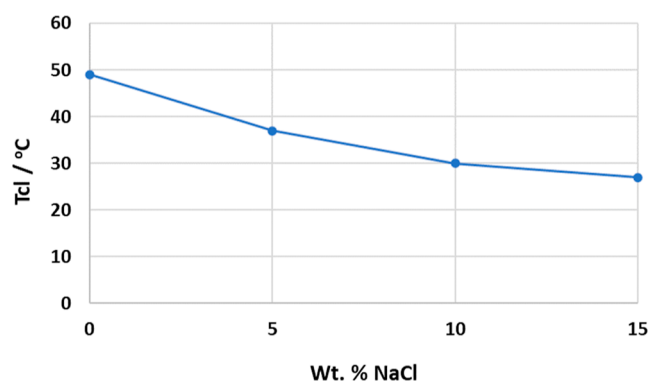
Figure 6. Cloud points of 1000 ppm PNIPMAm + 1000 ppm TiPeAO in varying brine salinity.

increasing salinity, but the blend was still fully soluble below 27 °C, even in a 15 wt % NaCl solution. These cloud points in DIW or brines are not optimal for many fields with high well head temperatures, but we expect that the introduction of small amounts of a more hydrophilic comonomer could be carried out in the polymerization process to raise the Tcl values (and/or fouling temperatures), hopefully without significant loss of performance. Exploring these copolymer options was beyond the scope of this study. Alternative methods of preventing KHI polymer deposition have been reported.[33,34]

Table 4 and Figure 7 summarize the KHI SCC test results at 110 bar SNG using varying NaCl brine concentrations. It should be noted that increasing NaCl concentration reduces the thermodynamic driving force (subcooling) for hydrate formation. For example, at 110 bar, 10 wt % NaCl and 15 wt % NaCl drop the Teq for sII hydrate by about 5 and 8.1 °C, respectively, compared to DIW as calculated by PVTSim software (Calsep). The driving force at 15 wt % NaCl is lowered so much that even 1000 ppm PNIPMAm without TiPeAO synergist gave no hydrates down to 2 °C in any test.

We initially chose to use PNIPMAm concentrations from 250 up to 1000 ppm since higher concentrations were expected to give no hydrates in many tests, which would not allow a comparison of performance. (However, later, we did carry out sets of tests with both 2500 and 5000 ppm of PNIPMAm and TiPeAO. This was because of the results obtained with methane gas. This is discussed later in this report.) Notably, TiPeAO always improved the KHI performance (lowered the average T_o value) at all polymer concentrations up to 1000 ppm (Figure 7). In general, we found that as the NaCl salinity increased (and subcooling decreased), it became easier to obtain a NH (no hydrates) result at all test temperatures down to 2.0 °C. Within the range 250−1000 ppm, 1000 ppm gave the highest average "$T_o − T_a$" values (0.6 °C), but this is not significantly different from the other concentrations. As with the tests at 76 bar SNG, these "$T_o − T_a$" values were small, but this was also because the maximum TiPeAO synergist concentration was now 1000 ppm.

3.3. SCC KHI Tests with Methane Gas. The results are summarized in Table 5. In comparison to the tests with an initial pressure of 110 bar SNG, it should be borne in mind that the subcooling for sI hydrate with methane gas is only about 6.2−6.3 °C less at this pressure.

A blank test with additives gave an average T_o of 12.2 °C. For the methane tests with 250, 500, 1000, and 1500 ppm of both PNIPMAm and TiPeAO, in DIW, we obtained average T_o values of 6.5, 5.0, 2.9, and 2.3 °C, respectively. The same test concentrations from Table 5 with SNG at 110 bar in DIW gave average T_o values of 9.1, 7.1, and 3.4 °C, respectively. Thus, the trend is for lower T_o values with increasing KHI concentration, which is what is usually found for KHIs. If we plot this as subcooling values in Figure 8 we see that the subcooling at T_o is always greater for the SNG than methane, which relates to the thermodynamically preferred hydrate structure (sII vs sI, respectively).

However, Table 5 shows some clear exceptions to the trend of increasing performance with increasing concentration, and that is with 2000, 2500, and 5000 ppm of both polymer and synergist.

Chronologically, the first tests we carried out above 1500 ppm were tests at 2500 ppm of both PNIPMAm and TiPeAO. The average T_o and T_a values were 9.5 and 8.5 °C, respectively, from 10 cells, all carried out by the same researcher and using the same batches of chemicals. These values were far higher than the tests at 1500 ppm. Later, we carried out tests at 2000 ppm and again obtained average T_o and T_a values higher than at 1500 ppm (7.8 and 7.4 °C, respectively). This was not a complete surprise because we had encountered and reported significantly lower induction times in isothermal tests using 2500 ppm PNIPMAm and 2500 ppm TiPeAO than with a mixture of 1000 ppm of each additive.[19] Second, as shown in Table 4, using SCC tests with SNG at 76 bar and a blend of 2500 ppm of PNIPMAm and 2500 ppm TiPeAO, we did not obtain as good KHI performance results as with 1000 ppm of each additive (average T_o was 4.2 °C vs 3.4 °C, respectively).

To be sure of the result at 110 bar methane, a different researcher in our laboratory repeated the SCC tests with fresh solution in five more cells. This time we obtained a similar result of $T_o = 8.8$ °C from five tests, which was statistically acceptable (at the 95% confidence level from the standard deviations) to the first 10 tests by the first researcher. The T_a values were even closer, being 8.5 and 8.0 °C from the two sets

Table 4. Summary of Slow Constant Cooling KHI (sII-Forming SNG) Test Results at 110 bar Pressure SNG in NaCl Brine Solution[a]

[PNIPMAm] ppm	[TiPeAO] ppm	[NaCl] (wt %)	T_o (av.) °C	T_a (av.) °C	$T_o - T_a$ (av.) °C
-			19.3	18.9	0.4
		5	16.2	16.0	0.2
		10	13.0	12.9	0.1
		15	10.3	10.2	0.1
1000			10.1	9.8	0.3
		5	6.9	6.4	0.5
		10	3.8	3.2	0.6
		15	NH	NH	
	1000		3.4	2.8	0.6
		5	NH	NH	
		10	NH	NH	
		15	NH	NH	
500			11.8	11.5	0.3
		5	8.1	7.8	0.3
		10	4.5	4.1	0.4
		15	2.0	<2	
	500		7.1	6.7	0.4
		5	NH	NH	
		10	NH	NH	
250			14.0	13.7	0.3
		5	10.4	10.1	0.3
		10	6.1	5.7	0.4
		15	2.1	2.0	0.1
	250		9.1	8.8	0.3
		5	5.3	4.8	0.3
		10	NH	NH	

[a]NH means no pressure drop due to hydrate formation.
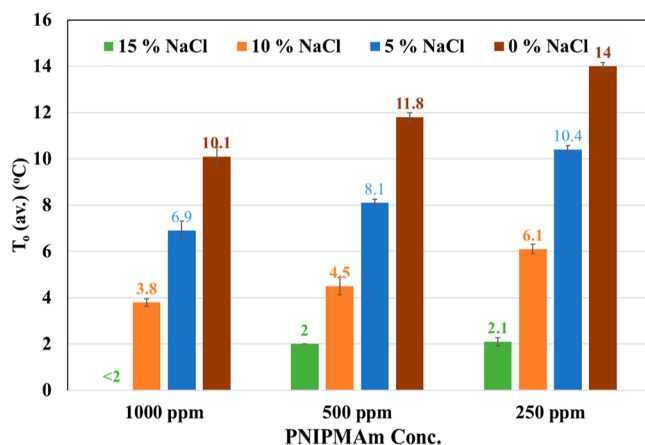
Figure 7. Comparison study of KHI performance of different concentrations of PNIPMAm in the presence of various concentrations of NaCl brine solution under 110 bar pressure of SNG gas. (1000 ppm PNIPMAm in the presence of 15% NaCl brine has T_o values less than 2 °C.)

of tests. The second researcher carried out further tests at 2000 and 5000 ppm, again using the same batches of chemicals. These are also listed in Table 5, and all the average T_o values are plotted in Figure 9. The trend was that the average T_o and T_a values increased when the concentration increased from 2000 to 2500 to 5000 ppm. The most surprising result was at 5000 ppm which gave an average T_o value of 13.2 °C, which was 1 °C higher than no additive! we have not seen this type of worsening performance at increasing concentrations between polymers and solvents such as alcohols and glycols. We are also

not aware of any such reports from other groups. So, we assume the poor performance must be due to the TiPeAO possibly forming aggregates with the polymer. This is discussed in more detail later. Interestingly, the cloud point of 5000 ppm PNIPMAm and 5000 ppm TiPeAO was found to be 32 °C, which is only a little lower than typical values for PNIPMAm homopolymers.

In addition, at 5000 ppm each of PNIPMAm and TiPeAO, the pressure drop plot was very unusual for all five cells (Figure 10). At an average temperature of 13.2 °C, the pressure trace dropped until it was most rapid at 12.6 °C, which we assume must be due to hydrate formation. However, the pressure drop was about 1 bar, and there appeared to be no further pressure drop due to hydrate formation until a new average T value of 7.6 °C. The determination of T_o, T_a, and T for one experiment is shown in Figure 11. Here we see the small initial pressure drop before a larger pressure drop after a long delay and at about 5 °C more higher subcooling. We thought this result might be due to the temporary blocking of the pressure sensor by hydrates. So, we carried out an identical test in a second series of five cells, and this time we obtained the same behavior. There was an initial pressure drop that began at average T_o = 13.4 °C and a larger pressure drop at T = 7.7 °C, confirming the first result. This was not seen in any SCC test in this or other studies, so we do not think it is due to a temporary hydrate blockage. The reason for the double pressure drop behavior is currently unclear, although we have seen analogous results for unpublished isothermal KHI experiments in our rocking cells using a PVCap polymer in an oxygenated organic solvent. A possible speculation is that a small amount of meta-stable hydrates forms under non-

Table 5. Summary of Slow Constant Cooling KHI (Structure I, Methane Hydrate) Test Results at 110 bar Pressure Methane in DIW/NaCl Brine Solution[a]

PNIPMAm] ppm	[TiPeAO] ppm	[NaCl] (wt %)	T_o (av.) °C	T_a (av.) °C	$T_o - T_a$ (av.) °C
5000	5000	0	13.2	12.7	0.5
			13.4	13.1	0.3
2500	2500	0[b]	9.5*	8.5	1.0
			8.8*	8.0	0.9
		5	4.9	4.3	0.6
		10	NH		
2000	2000	0	7.8	7.4	0.3
1500	1500	0	2.3	2.2	0.1
		5	NH		
1000	1000	0	2.9	2.6	0.3
			2.3	2.0	0.3
		5	NH		
500	500	0	5.0	4.7	0.3
		5	NH		
250	250	0	6.5	6.2	0.3
		5	3.3	2.4	0.9
		10	NH		
0	0	0	12.2	12.0	0.2

[a]NH means no pressure drop due to hydrate formation, * indicates 10 cells' average. All concentrations are active concentrations of polymer or synergist. [b]Two sets of data were obtained by two different researchers.
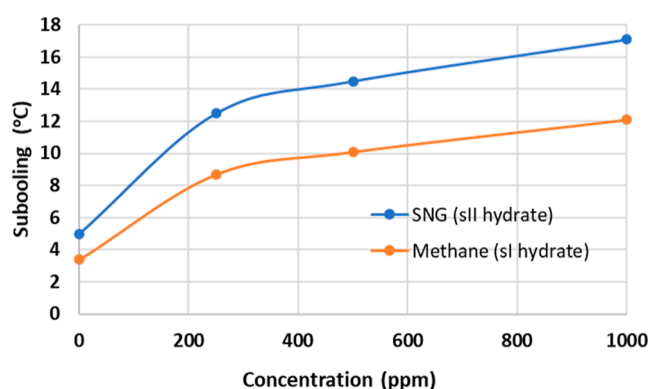
Figure 8. Average subcooling values at T_o for equal concentrations of PNIPMAm and TiPeAO in DI water. Methane tests were performed at 110 bar and SNG tests at 76 bar.
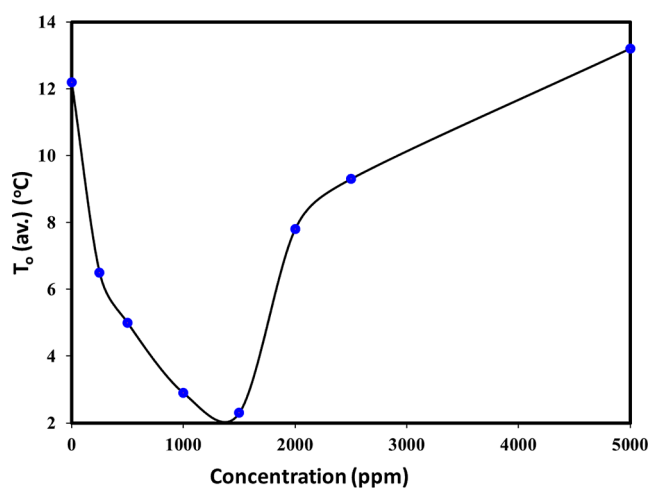
Figure 9. Effect of concentration on KHI performance for equivalent concentrations of PNIPMAm and TiPeAO in DI water with methane gas at 110 bar in SCC tests. T_o is average onset temperature.

equilibrium conditions, perhaps sII hydrates, which are then inhibited from further growth. Then, at temperature T = 7.6 °C (see Figure 11), the amount of nuclei to form sI hydrate has grown to a threshold value and hydrates begin to grow again. The temperature difference between T_o and T is about 5.1 °C, which fits quite well with the difference in equilibrium temperature of ca. 6.2−6.3 °C at 110 bar for sI and sII hydrates.

As these SCC test results with high and equal concentrations of PNIPMAm and TiPeAO with 110 bar methane were so different from the normal KHI behavior, we made a thorough check of the test procedure. Contamination of the cells was ruled out as results before and after this blend fitted the expected trends for those chemicals, and no surfactants and/or strong film forming chemicals, such as corrosion inhibitors, were in use at that time. Also, repeated results by the second researcher at 1000 ppm of both chemicals in the PNIPMAm/TiPeAO blend gave typical results (T_o av. = 2.3 °C) in keeping with earlier results (T_o av. = 2.9 °C) by the first researcher (Table 5).

A significantly lower KHI performance, but only at intermediate concentrations, has been reported for a VP/VCap copolymer in BGE solvent using a methane-propane blend. The full concentration range was 100−51000 ppm. The effect was only pronounced at medium-to-high subcoolings.[35] Our results showed a continued decrease in KHI performance above 1500 ppm and up to 5000 ppm. Perhaps if we had continued up to higher concentrations, the performance may have increased again. Although this makes the KHI concentration economically less viable for practical purposes in the field, we do intend to carry out these studies along with a range of other experiments and modeling designed to probe the solution behavior. This is discussed further on in this section and in the conclusion.

3.4. Further SCC KHI Tests at Higher Concentrations with SNG. We wanted to check that the loss of performance at high and equal-weight concentrations of PNIPMAm and TiPeAO with methane gas was not a one-off phenomenon.
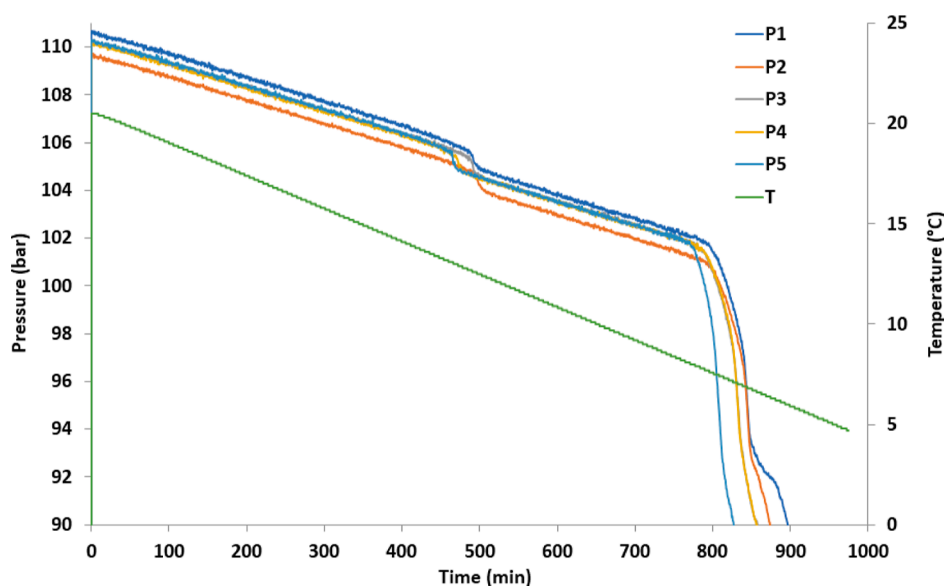
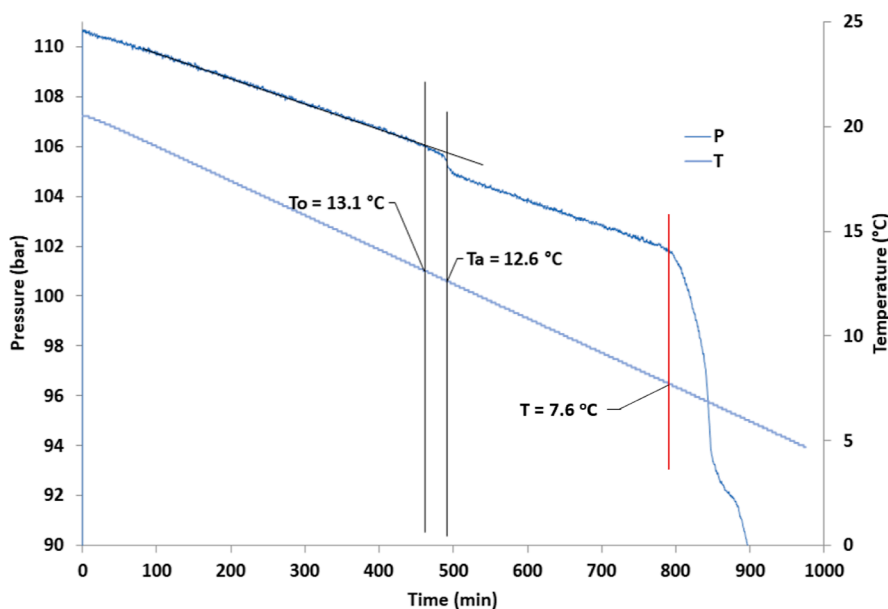**Figure 10.** SCC tests at 110 bar methane gas with 5000 ppm PNIPMAm and 5000 ppm TiPeAO.

Figure 11. Determination of all pressure drop temperatures, T_o, T_a, and T, for one SCC test at 110 bar methane gas with 5000 ppm PNIPMAm and 5000 ppm TiPeAO.

Therefore, for further confirmation, we carried out additional tests with the PNIPMAm/TiPeAO blends using SNG at 110 bar. Originally, we had only done tests up to 1000 ppm, as summarized earlier and in Table 4 and Figure 8. The additional tests were at 1500, 2500, and 5000 ppm, with five, ten, and five tests at the respective concentrations. The full set of results for average T_o values at all concentrations used are plotted in Figure 12. The behavior was seen to mimic that obtained for methane gas. We observed an increase in performance up to a concentration of 1000 ppm (average T_o = 3.4 °C). Then the performance was a little worse at 1500 and 2500 ppm, but at 5000 ppm the average T_o value rose significantly to 9.9 °C.

Although the trend for the experiments with both methane and SNG is similar, there are two noticeable differences. First, for the SNG system, the performance at 5000 ppm of each of PNIPMAm and TiPeAO was still quite good, whereas for the

methane system, the average T_o value was similar to no additive. This is hard to explain, but one possibility is that the loss of performance is more extreme for the methane system, giving preferentially sI hydrate due to the higher symmetry and faster kinetics with sI hydrate formation. The other difference is that we did not observe a double pressure drop for the tests at 5000 ppm of the mix of chemicals with the SNG. We saw a typical graph one pressure drop due to hydrate formation, such as in Figures 3 and 4. The only change in parameters between the two sets of data is the gas type (SNG vs methane) and the onset temperature (T_o = 9.9 and 13.3 °C, respectively). Since the temperatures are fairly similar, we assume this difference of behavior must stem from the gas type and the amount and type of gas hydrates formed. We are currently investigating the cause of this effect in other gas hydrate experiments as well as computer simulations, and we hope to report on these later.
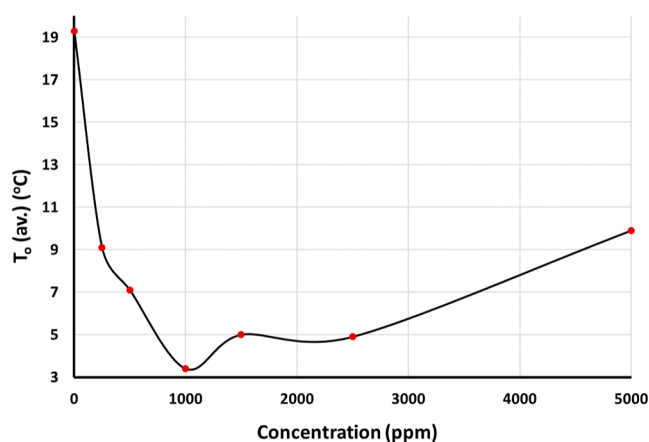
Figure 12. Effect of concentration on KHI performance for equivalent concentrations of PNIPMAm (20.1% in iBGE) and TiPeAO in DI water with SNG gas at 110 bar in SCC tests. T_o (av.) is the average onset temperature.

As mentioned earlier, we currently have no detailed explanation as to why the higher concentrations of PNIPNAm and TiPeAO gave worse results, but we have now given several confirming results of the phenomenon, and we are currently investigating this further. For now, we can only speculate that amide-amine oxide interactions between PNIPMA and TiPeAO may possibly reach a threshold (like a critical micelle concentration for surfactants) that could cause an aggregation of these species, rendering them less available for hydrate inhibition. Aggregation would make less polymer surface available for interaction with water and hydrate particle surfaces, lowering the kinetic inhibition effect. Computer molecular dynamics and dynamic light scattering of aqueous trimethylamine oxide with PNIPAm have been reported, but not for larger trialkylamine oxides, nor for PNIPMAm. The combined study for TMAO and PNIPAM, which serves as a model protein, showed a preferential association of TMAO at the PNIPAM surface.[36] However, the TMAO hydration shell as a sheet of water molecules was always maintained, and therefore no direct TMAO−PNIPAM interaction was observed.[37] These interactions could be very different for the more hydrophobic TiPeAO amine oxide with PNIPMAm, and we are currently pursuing such studies in collaboration with another research group. Other evidence of aggregation interactions between small hydrogen-bonding molecules and water-soluble polymers that also affect the lower or upper critical solution temperature has been reported.[38] For example, effects have been seen for addition of small amounts of isobutyric acid (IBA) to aqueous solutions of polypropylene oxide (PPO).[39] These results illustrate that hydrogen bonding and a polymer's capability to maintain its hydration shell are the key factors in polymer responsiveness to external triggers, and this may be the case for aqueous solutions of PNIPMAm and TiPeAO.

4. CONCLUSIONS

This study concerns the synergetic performance of monoamine oxides in certain KHI polymer blends. In particular, building on a recent study, we have investigated in greater detail the synergetic KHI performance of blends of TiPeAO and PNIPMAm in iBGE. We expanded the high-pressure rocking cell tests to include a wider range of concentrations and synergetic ratios. Tests were conducted with both SNG and

methane gas and with varying brine concentrations. Generally, this blend shows remarkable KHI performance in a range of conditions. At some conditions, this blend performed better than any other KHI blend we have tested in our steel rocking cells since we began using them about 12 years ago. Thus, we believe that this blend is capable of being used in field applications at quite high subcoolings where either sI or sII hydrate is the preferred thermodynamic phase.

However, a word of caution needs to be added. Surprisingly, overdosing the KHI blend (for example, 2000+ ppm each of PNIPMAm and TiPeAO) was shown to give a worse performance both for tests in methane and SNG. We speculate that some kind of polymer-amine oxide aggregation takes place at higher concentrations, reducing the performance. In addition, the SCC tests with 5000 ppm of both polymer and amine oxide using methane at 110 bar gave an unusual double pressure drop.

Due to the rarity of these phenomena, we plan using other laboratory instruments such as a tensiometer, laser light scattering equipment, NMR spectroscopy, as well as computer simulations to investigate the aqueous solution properties. We also plan to probe these phenomena by broadening the KHI experiments. This will include tests at other concentration ratios (including molar concentrations), other polymer molecular weights, related *N*-alkylacrylamido polymers, other amine oxides, other solvents, and different KHI test methods.

■ AUTHOR INFORMATION

Corresponding Author

Malcolm A. Kelland − *Department of Chemistry, Biological Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, Stavanger N-4036, Norway;* ⊙ orcid.org/0000-0003-2295-5804; Phone: +47 51831823; Email: malcolm.kelland@uis.no

Authors

Radhakanta Ghosh − *Department of Chemistry, Biological Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, Stavanger N-4036, Norway;* Present Address: Reliance Industries Limited, Vadodara Manufacturing Division, Gujarat, India; ⊙ orcid.org/0000-0002-3384-028X

Janronel Pomicpic − *Department of Chemistry, Biological Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, Stavanger N-4036, Norway*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.energyfuels.2c03963

Notes

The authors declare no competing financial interest.

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