

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

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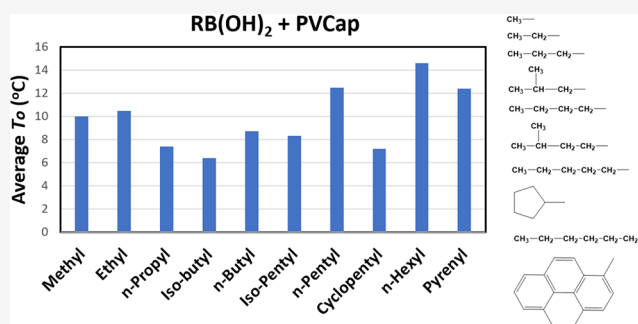
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ABSTRACT: A range of boronic acids have been investigated as synergists for the kinetic hydrate inhibitor (KHI) polymer, poly(*N*-vinylcaprolactam) (PVCap, $M_w \approx 10,000$ g/mol) using high pressure rocking cells, a natural gas mixture, and a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



1. INTRODUCTION

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

Most current commercial KHI polymers are water-soluble (or water-dispersible) polymers with multiple amide functional groups. They include homopolymers and copolymers of *N*-vinyl lactams, *N*-isopropylmethacrylamide (NIPMAM), and hyperbranched poly(esteramide)s^{3–6,10,11} (Figure 1). Many other classes of polymers, both amides and non-amide-based functional groups, have been investigated.^{2,4,6–12} In addition, a wide range of synergists or performance enhancers have been studied.^{2–4,13–16} Synergism occurs when the interaction or

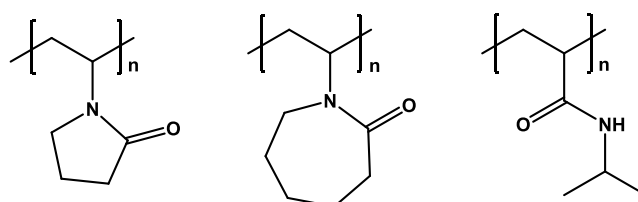


Figure 1. Monomer units in the structures of well-known classes of KHI polymers. From left to right: PVP, PVCap, and PNIPMAM.

cooperation of two or more substances produces a combined effect greater than the sum of their separate effects. Based on this definition, many chemicals currently called synergists are actually only performance enhancers as these chemicals by themselves have poor ability to prevent gas hydrate formation. However, the word “synergist” is being used to cover both terms as this is the general industry practice.

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Some of the first synergists to be discovered were the quaternary ammonium salts (Figure 2). They were found by

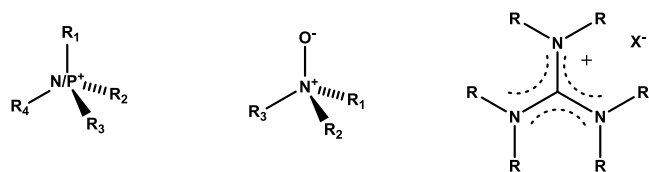


Figure 2. Tetraalkylammonium salts, trialkylamine oxides, and hexaalkylguanidinium salts.

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

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

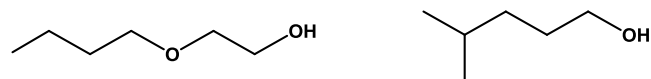


Figure 3. Butyl glycol ether (BGE, left) and 4-methyl-1-pentanol (iHexOl, right).

Recently, 4-methyl-1-pentanol (iHexOl) was shown to have excellent synergy with PVCap as well as several other KHI polymers (Figure 3).¹³ The authors speculated that the branched tail and maximum hydrophobicity without losing water solubility were key features. Interestingly, 1-pentanol was clathrated to form the sII hydrate when doped with ammonium fluoride.³⁰ This suggests that it may also be possible to enclathrate iHexOl and the reason why it is a good synergist, i.e., it is at the limit of the structural size to be able to form sII hydrate 5¹²6⁴ cages around it while being at the limit of water solubility (maximum hydrophobicity).

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

Boronic acids are based on boric acid [B(OH)₃] in which one of the three hydroxyl groups is replaced by an alkyl or aryl group.³⁵ The pKa of a boronic acid is about 9. They are known to be good Lewis acids. The unique feature of boronic acids is the ability to form reversible covalent complexes with sugars, amino acids, hydroxamic acids, and other functional organic classes.

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

2. EXPERIMENTAL METHODS

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

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

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

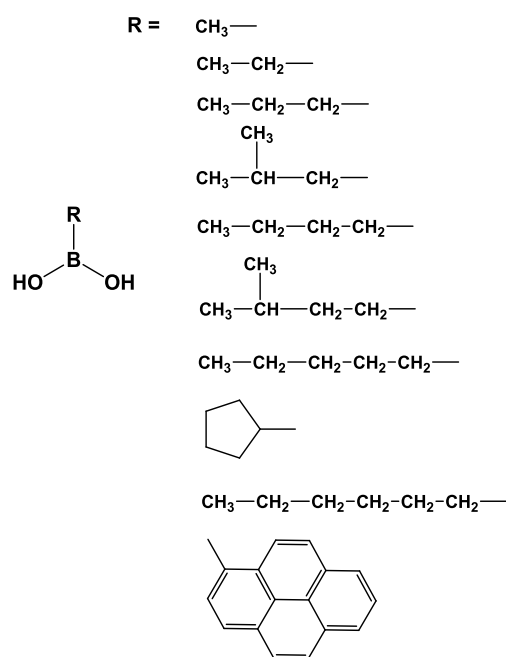


Figure 4. Boronic acids used in this study.

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

component	mol %
methane	80.67
ethane	10.20
propane	4.90
isobutane	1.53
<i>n</i> -butane	0.76
N ₂	0.10
CO ₂	1.84

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

Figure 5 shows an example of the results from a run with five cells of a mixture of 2500 ppm PVCap with 5000 ppm *n*-butylboronic acid, and Figure 6 shows the result and analysis for one individual cell from

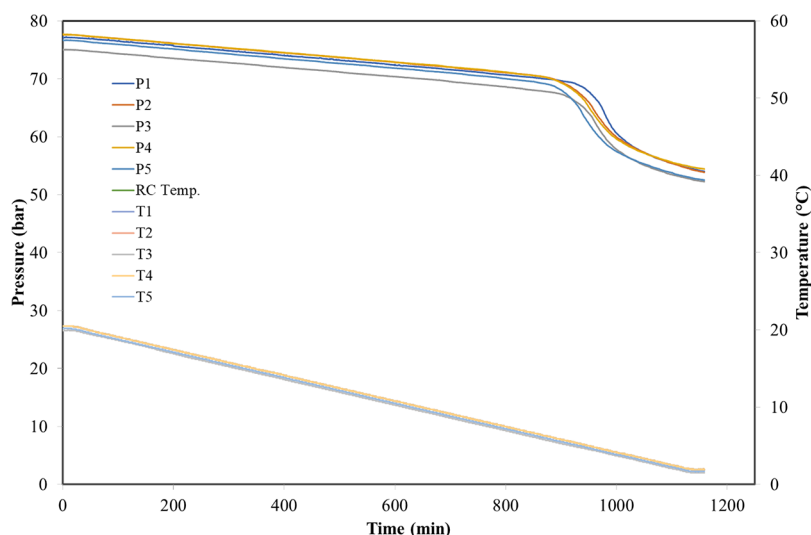


Figure 5. Results from five cells after a standard slow constant cooling experiment with 2500 ppm PVCap + 5000 ppm *n*-butylboronic acid.

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

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

3. RESULTS AND DISCUSSION

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

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

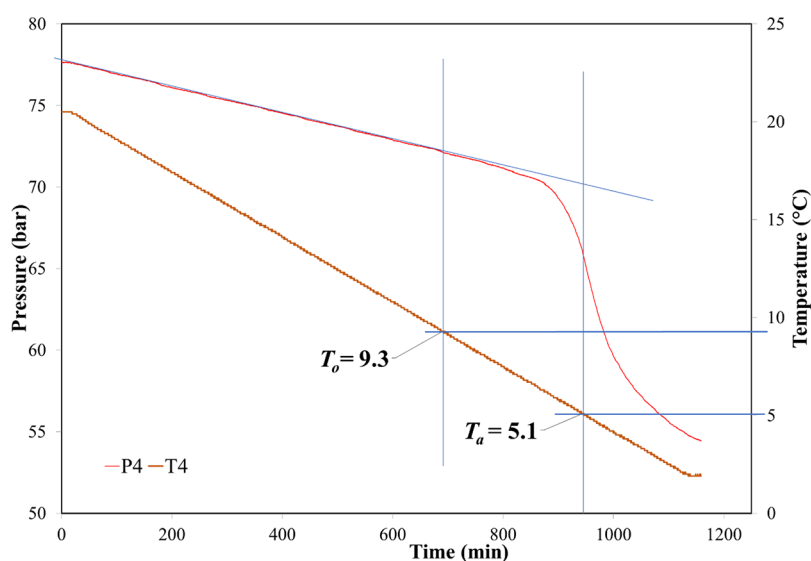


Figure 6. Determination of T_o and T_a for cell 3 after a slow constant cooling experiment with 2500 ppm PVCap + 5000 ppm *n*-butylboronic acid.

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

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

^a1 mL of decane added.

From the results with 2500 ppm PVCap + 5000 ppm alkylboronic acid, we see that there is no significant performance enhancement with the methyl or ethyl derivatives (Table 2 and Figure 7). For the larger alkyl groups, we observed that some alkylboronic acids enhanced the KHI performance, while others even decreased the performance.

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

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

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

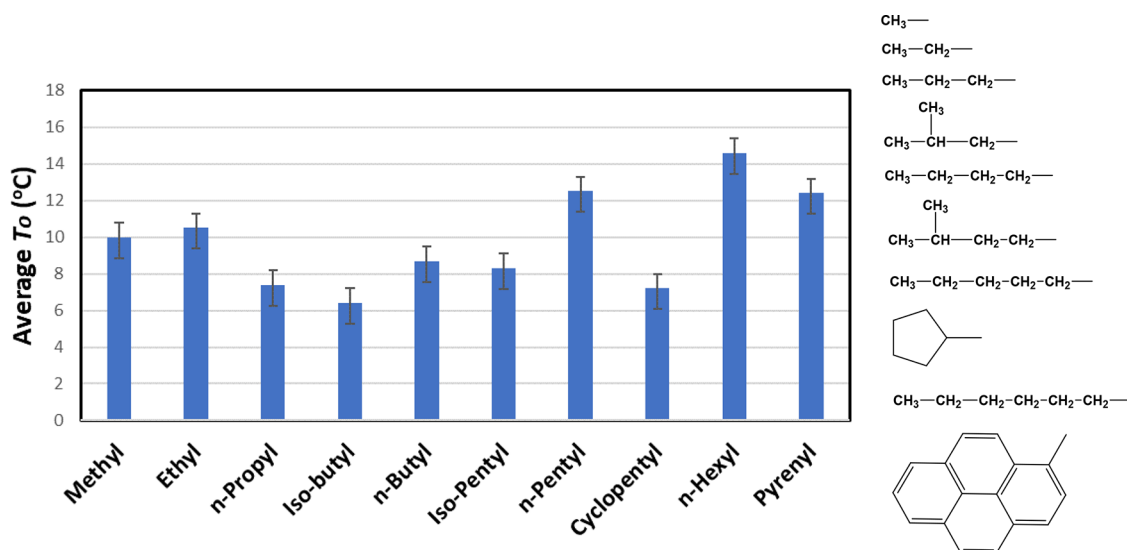


Figure 7. Average onset temperatures (average T_o) with error bars for 2500 ppm PVCap and 5000 ppm alkylboronic acids.

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

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

We carried out a few other synergy tests with varying ratios of PVCap and iso-butylboronic acid (Figure 8). Using 2500

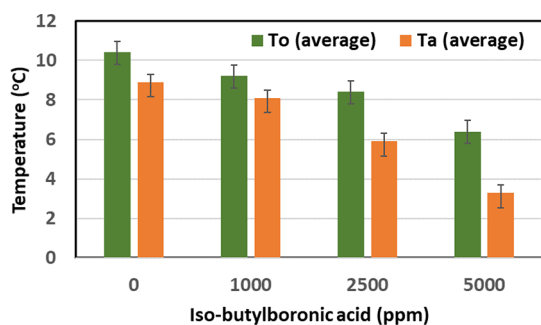


Figure 8. Effect on average T_o and T_a values with error bars of varying concentrations of iso-butylboronic acid with 2500 ppm PVCap.

ppm PVCap but only 2500 ppm iso-butylboronic acid, the average T_o dropped to 8.4 °C. With an even less synergist, 1000 ppm, the T_o value dropped to 9.2 °C. With 1000 ppm PVCap and 5000 ppm iso-butylboronic acid, the average T_o dropped only a little to 7.1 °C. Thus, within these concentration ranges, we observe that increasing either the

KHI polymer or synergist concentration gives improved performance.

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

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

We also added decane to the cyclopentylboronic acid synergy tests. Ten experiments were conducted on both the decane and decane-free systems. This time, no improvement in performance from the addition of decane was observed. Both gave the same average T_o value of 7.2 °C, although the average T_a value was 1.8 °C lower for the decane system. Cyclopentylboronic acid is more hydrophobic than iso-butylboronic acid, which would explain the difference in results with these two synergists. Since the equilibrium temperature is reduced in this system, we presumed that a little cyclopentylboronic acid may have partitioned to the decane phase, lowering its activity

in the water. This effect would counteract the lower equilibrium temperature. To check this experimentally, we stirred 0.1 g of cyclopentylboronic acid in 10 mL of hexane in a sealed vessel for 18 h. Careful decantation of the solvent and drying of the remaining solid showed that approximately 4–5% of the acid had partitioned into the hexane. Hexane has similar polarity to decane. Therefore, we assume that a small portion of this boronic acid also partitioned to decane in the high pressure KHI tests.

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

It is interesting to compare the synergistic effects of boronic acids with organic acids as synergists for PVCap. There appear to be no studies reported of small organic acids as synergists with any KHI polymer. The closest study was with several sodium alkyl carboxylate salts.²⁶ As organic acids are weak, a minor percentage of these organic carboxylates will be in the acid form in water. Alkylboronic acids are weak acids, but organic acids are a little more dissociated in water. The pKa of small boronic acids is ~9. As mentioned earlier, we measured the pH of 5000 ppm iso-butylboronic acid to be ~5. However, they can form tetrahedral boronate complexes with pKa ~7.³⁵ The pKa value of small organic acids is about 4.8, meaning that they are more deprotonated, making aqueous solutions more acidic than for boronic acids.

In this study, we investigated a few organic acids and their sodium salts (Table 2). We used only tail-branched organic acids as we were confident from studies with several other classes of synergists that this was beneficial over acids with a straight chain of carbon atoms. The equivalent organic acid of iso-butylboronic acid can be thought of as 3-methylbutanoic acid with the same chain length between the OH group and the end of the alkyl group. 3-Methylbutanoic acid has a carbon chain length of 4 carbon atoms, with tail-end branching. In Table 2, we see that it gave reasonable synergy with PVCap, lowering the T_o value for PVCap alone from 10.4 to 8.2 °C. This is better synergy than observed for the shorter acid, 2-methylpropanoic acid. When we increased the alkyl chain length to 5 carbon atoms, for 4-methylpentanoic acid, this molecule was observed to be antagonistic to the performance of PVCap, giving an average T_o value of 14.2 °C. (The solubility of 4-methylpentanoic acid in water at room temperature is 5.3 g/L or 5300 ppm). This trend is very

similar to that of the alkylboronic acids if we equate the B–OH moiety to the C–OH moiety (Figure 9). We tested one more

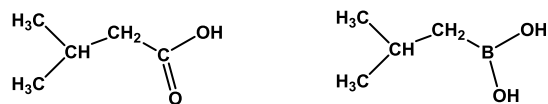


Figure 9. 2-Methylbutanoic acid (left) and iso-butylboronic acid (2-methylpropyl boronic acid) (right).

organic acid with a double-branched tail, 3,3-dimethylbutanoic acid. This acid has the same carbon chain length of 4 carbon atoms as 2-methylbutanoic acid. Surprisingly, this acid did not improve the performance of PVCap but was weakly antagonistic.

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

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

4. CONCLUSIONS

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

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

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

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Notes

The authors declare no competing financial interest.

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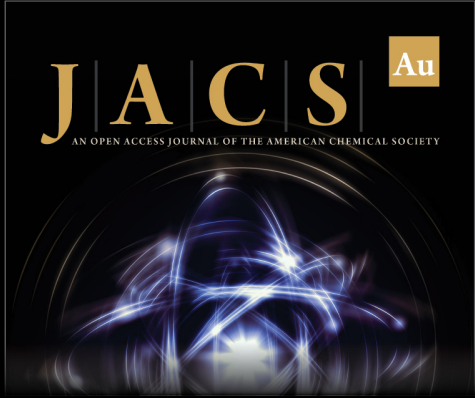
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