

Multi-functional Flow Assurance Chemicals: Corrosion and Kinetic Hydrate Inhibition from Maleic Anhydride:*N*-Vinyl Caprolactam Copolymers and Synergists

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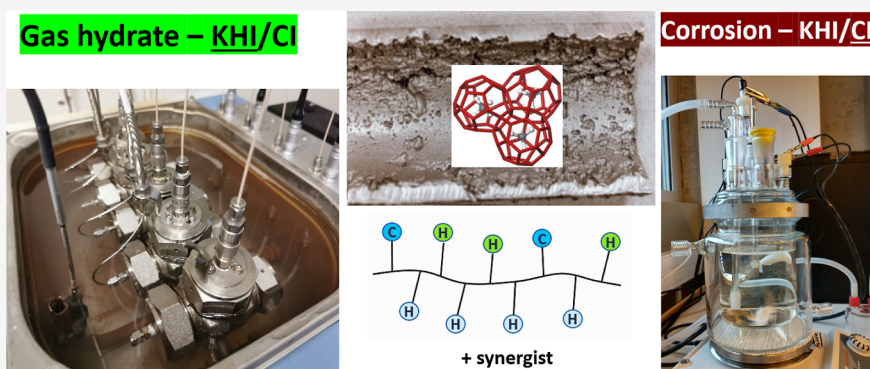


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ABSTRACT: Water-based flow assurance issues include corrosion, scale, and gas hydrate formation. Chemical solutions to mitigate these issues usually require separate inhibitors, which sometimes can lead to compatibility difficulties. Herein, we report studies on maleic-based copolymers to combat hydrate and corrosion with a view to optimizing for scale inhibition also. The product of maleic anhydride:*N*-vinyl caprolactam copolymer reacted with 3-dibutylaminopropylamine (MA:VCap-DBAPA) and its amine oxide derivative (MA:VCap-DBAPA-AO) were the kinetic hydrate inhibitor (KHI) polymers investigated. Due to limited CO₂ corrosion inhibition (CI) by the polymers alone, various oxygen-, sulfur-, and nitrogen-based additives were screened for improved CO₂ CI and possible KHI synergy. KHI performance screening tests were conducted under high pressure with a structure II-forming natural gas mixture in steel rocking cells using the slow (1 °C/h) constant cooling method. CO₂ corrosion inhibition was measured by linear polarization resistance in a stirred 1 L CO₂ bubble test apparatus using C1018 steel coupons and 3.6 wt % brine at 20.5 °C. Several sulfur-based additives improved the CI efficiency of the maleic polymers, especially butyl thioglycolate and 2-aminoethanethiol, without a negative effect on the KHI performance. For example, 2500 ppm MA:VCap-DBAPA plus 1000 ppm butyl thioglycolate gave an average hydrate onset temperature (T_o) of 4.4 °C (12.7 °C below the T_o for no additive) and 99.7% CI efficiency. In contrast to a classic fatty acid imidazolone surfactant corrosion inhibitor, butyl thioglycolate was also found to greatly enhance the CI efficiency of industrial KHIs, poly(*N*-vinyl caprolactam) (PVCap) and *N*-vinyl pyrrolidone:*N*-vinyl caprolactam copolymer, with no antagonism to the KHI performance of the polymer. In addition, butyl thioglycolate boosted the KHI performance of PVCap. The use of small synergists such as butyl thioglycolate avoids the use of classical surfactant corrosion inhibitors which can lead to tighter emulsions and poor overboard oil-in-water quality.

INTRODUCTION

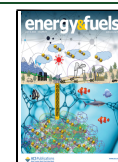
Production of oil and gas through flow lines presents several problems due to the presence of water. These include corrosion, scale, and gas hydrates.^{1–5} For most flow lines, operators choose to combat these issues with one or more chemical inhibitors. Co-injection of these inhibitors can present its own set of compatibility problems, including formulating several inhibitors to be stable and pumpable as a single fluid and the possibility of one inhibitor lowering the performance of another.^{6–8} Some compatible blends have been found, but there is scope for improvement.⁹

We envisaged that a possible way to treat all three production problems, corrosion, scale, and gas hydrates, was to use kinetic hydrate inhibitors (KHIs) that also function as corrosion and scale inhibitors (CIs and SIs). KHIs have been

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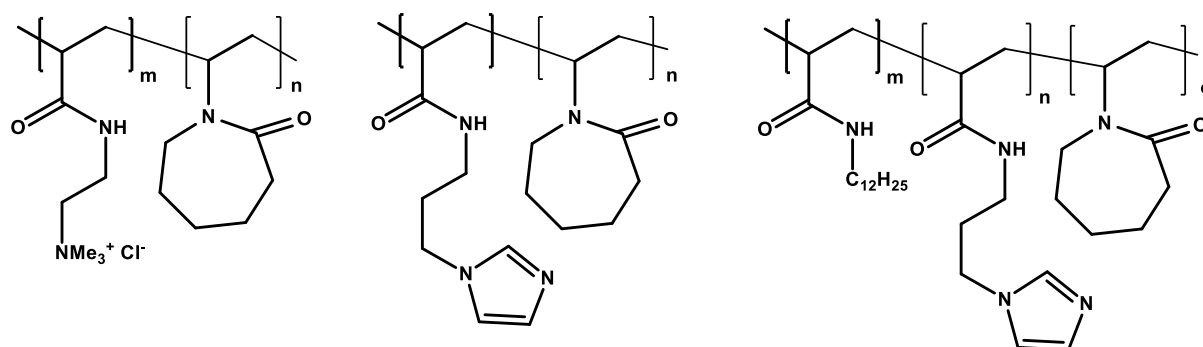


Figure 1. Dual KHI-CIs, from left to right, PVCap-ATCH and PVCap-APIM, PVCap-APIM-C12.

used for over 25 years to prevent gas hydrate formation both in onshore and offshore production scenarios.^{10–21} The main component in KHI formulations is one or more water-soluble polymers with many amphiphilic groups. The solvent package often acts synergistically to boost the performance. KHIs are a class of low-dosage hydrate inhibitors and are usually added at 1000–10,000 ppm (0.1–1.0 wt %) to the produced water phase based on the active polymer. Admittedly, KHIs are limited in their performance with regard to the driving force in the system, usually to about 10–12 °C subcooling depending on the residence time of the fluids in the flow line, but this still gives a good range of applicable field cases.²²

Film-forming corrosion inhibitors (FFCIs) can be continuously injected to prevent acid gas corrosion (CO₂ but also H₂S), in which they are often added at concentrations of 10–500 ppm depending on the severity and type of steel.^{2,23} Most commercial FFCIs are blends of surfactants, such as imidazolines, amidoamines, phosphate esters, and quaternary ammonium salts, sometimes with added sulfur-based chemicals to enhance the performance. Therefore, a dual function KHI–CI does not have to be as efficient as typical commercial CI dosages since it will probably be injected at a much higher dosage to prevent hydrate formation. The same philosophy will also be true for scale inhibition, where commercial SIs are often added at dosages of 1–50 ppm.

All three classes of dual inhibitors have been reported previously. Examples of SI–CIs include polyaspartates, and examples of KHI–SIs are polyaspartamides. Examples of KHI–CIs include *N*-vinyl lactam copolymers, *N*-alkylacrylamide copolymers, and polyurethanes.^{24–30} The subject has been recently reviewed. A pioneering study by Sheng et al., and inspirational to our own studies, investigated the use of VCap copolymers as KHIs and CIs (Figure 1).³¹ They determined that copolymers with either (2-aminoethyl)trimethylammonium chloride hydrochloride (ATCH) or 1-(3-aminopropyl)imidazole (APIM) show the best potential for dual KHI and CI functionalities. However, if monomers with pendant C12 dodecyl alkyl chains were added, the CI performance increased but at the cost of the KHI performance. Sulfonate and phosphonate groups gave only a small improvement to the corrosion inhibition compared to the PVCap homopolymer. The entry point for these copolymers was VCap:sodium acrylate and required quite complex carboximide and *N*-hydroxysuccinimide chemistry.

As discussed above, the main component in KHIs is one or more water-soluble polymers and not classical single-chain surfactants, which often have emulsifying properties. Therefore, it may be better to deploy KHIs than surfactant-based

FFCIs such as imidazolines and quaternary ammonium salts (“quats”), which can adversely affect the oil–water separation process. There are many classes of polymeric CIs, although very few are used industrially.³² We have concentrated our efforts in designing tri-functional hydrate, corrosion, and scale inhibitors (KHI–CI–SIs) using maleic-based polymers as the starting material since maleic anhydride (MA) is cheap and readily available. There are also some reports of maleic polymers as CIs, but usually for aerobic corrosion conditions.^{33–36} The MA unit in a polymer also offers great flexibility and can be easily derivatized to contain a wide variety of functional groups. Maleic-based polymers are already used as SIs against carbonate and sulfate scales, and amide derivatives have been known as KHIs since the 1990’s.^{2,4,37–39} But these polymers would need adjusting to be able to function simultaneously as SI and KHI. Concerning our studies with maleic polymer chemistry to design a KHI–CI–SI, some of the published findings so far include the following (Figure 1):

- High KHI performance and cloud point for vinyl acetate:maleic anhydride (VA:MA) copolymers.^{40,41} For example, the reaction of the anhydride groups in the VA:MA 1:1 copolymer with a 60:40 mixture of cyclohexylamine:3-di-*n*-butylaminopropylamine (VA:MA-60%cHex-40%DBAPA, Mn = 11 kg/mol, 25 wt %) in *n*-butyl glycol ether (nBGE) gave better performance than previously reported maleamide polymers.
- Besides good KHI performance, the VA:MA-60%cHex-40%DBAPA copolymer also showed good CO₂ corrosion inhibition properties.⁴²
- MA:alkyl acrylates were shown to be poor KHIs, probably due to the lack of strong hydrogen-bonding groups such as amide or amine oxide. MA:tetrahydrofurfuryl (meth)acrylate copolymer (MA:THFMA) could be derivatized to a powerful KHI, first by reaction with DBAPA and then with H₂O₂ to give MA:THFMA-DBAPA-AO.⁴³
- Reaction of 3-(dibutylamino)-1-propylamine with MA:*N*-vinyl caprolactam (MA:VCap) copolymer followed by oxidation to give pendant dibutylamine oxide groups gave the best performing MA-based KHI reported to date, MA:VCap-DBAPA-AO.⁴⁴
- Reaction of the homopolymer polymaleic anhydride (PMA) with DBAPA or dibutylethanolamine and their amine oxide derivatives gave good KHI performance.⁴⁵

As KHIs are limited in their application (subcooling and other factors), we wanted to start with a high-performing

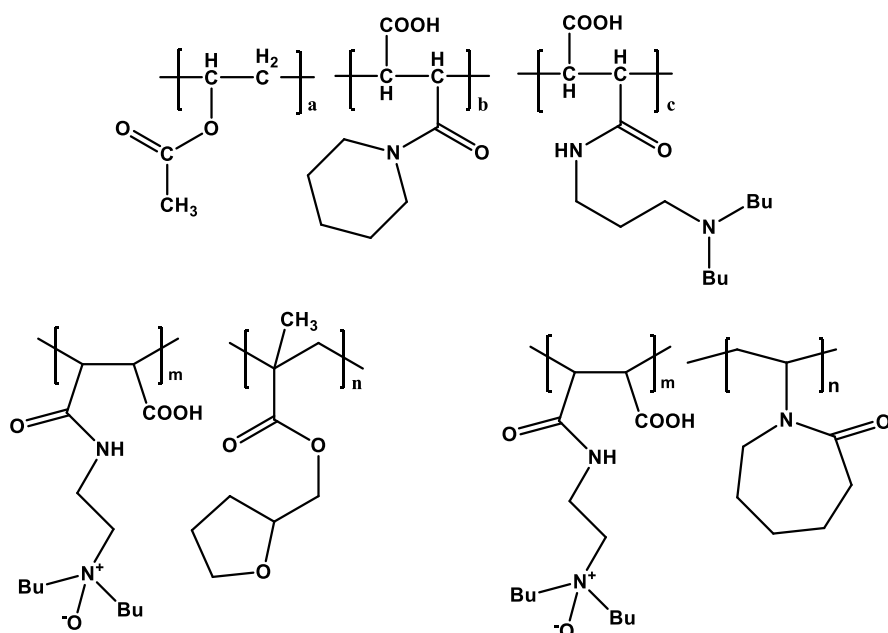


Figure 2. Maleic polymers with excellent KHI performance. VA:MA-60%CHex-40%DBAPA (top), MA:THFMA-DBAPA-AO (bottom left), and MA:VCap-DBAPA-AO (bottom right).

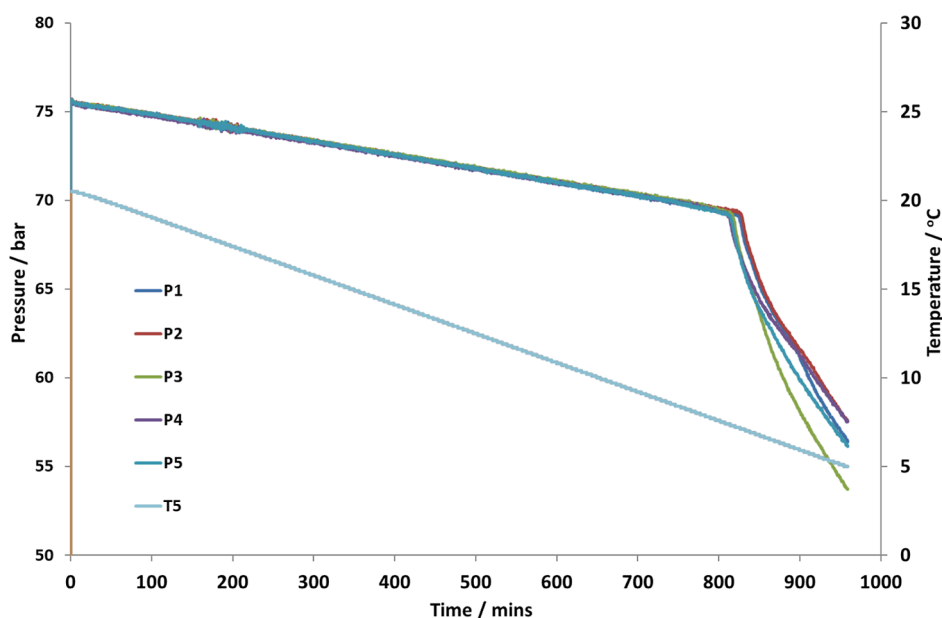


Figure 3. Summary graph of SCC in 5 cells. The temperature in cell 5 (T5) is shown only for clarity. Example is for 2500 ppm MA:VCap-DBAPA plus 1000 ppm thiobarbituric acid.

maleic-based KHI before modifying it to also inhibit corrosion and scale, since these modifications will probably reduce the KHI's efficacy to some degree. In addition to VCap, another monomer with similar activity and used in commercial KHI polymers is *N*-isopropylmethacrylamide (NIPMAm).^{46–49} Therefore, derivatives of MA:VCap copolymer and MA:NIPMAm copolymer seemed like good places to start with. (MA:NIPMAm copolymers as KHIs and Cis will be reported separately).

Of the maleic polymers in Figure 2, MA:Vcap-DBAPA and its amine oxide MA:Vcap-DBAPA-AO gave the best performance, significantly better than PVCap and with better brine compatibility. MA:Vcap-DBAPA-AO at 2500 ppm has $T_{d1} = 65$

°C in deionized water, 61 °C for 5% NaCl brine, and 35 °C for 15 wt % NaCl brine.⁴⁴ A summary of the best maleic-based KHIs (Figure 2) from earlier reports is given later in this report, along with a comparison with commercial PVCap and VP:VCap polymers.

Therefore, MA:VCap-DBAPA-AO seemed like a good starting point for adapting the polymer structure to function as a sweet (CO₂) corrosion inhibitor and possibly also as a scale inhibitor (calcite and barite). We assumed MA:VCap-DBAPA-AO would not be a good enough CO₂ CI by itself, which was corroborated by experimental evidence later in this paper. So, we envisaged several methods to incorporate CI

functionality, hopefully without losing any significant KHI performance. These included the following:

- Blending MA:VCap-DBAPA-AO with synergists that together give good CI performance without losing the KHI effect.
- Statistical or block copolymerization of MA:VCap with vinyl monomers with functional groups specially designed for the CI effect.
- End-capping MA:VCap-DBAPA-AO with functional groups for the CI effect.
- Reacting some of the anhydride groups in MA:VCap with amines with more active CI functional groups than those of DBAPA or DBAPA-AO.

The first method is reported here, i.e., to determine if the powerful KHI MA:VCap-DBAPA-AO copolymer could also be used to combat sweet corrosion and whether synergists could be found to enhance both the hydrate and corrosion inhibition. The other three methods above will be reported in a separate communication.

■ EXPERIMENTAL SECTION

Materials. Polyetherdiamine 230 (Jeffamine 230) was kindly supplied by Huntsman Corp. All other synergists were purchased from VWR (Avantor) or Merck and used as received. Poly(*N*-vinyl caprolactam) (PVCap) (Mw: approximately 2–4 kg/mol) and low-molecular-weight *N*-vinyl caprolactam:*N*-vinyl pyrrolidone (VP:VCap) copolymers were supplied from BASF as 41.1 and 53.8 wt % solutions in monoethyleneglycol (MEG) and water, respectively. For the PVCap, the MEG solvent was removed for this study by repeated precipitation of the polymer from aqueous solution above the cloud and deposition point (ca. 40 °C).

Polymer Synthesis. MA:VCap, MA:VCap-DBAPA, and MA:V-Cap-DBAPA-AO copolymers were made according to the literature method (Figure 3).⁴⁴ Polymer molecular weight analysis for all polymers was carried out by size exclusion chromatography using DMF solvent at 0.6 mL/min, 40 °C, using polystyrene standards. The apparatus used was a JASCO Chem NAV size exclusion chromatography system. This system was equipped with PU-2080, AS-2055, CO-2065, RI-2031, and two commercial columns (TSKgel SuperH4000 and TSKgel GMHXL).

KHI Experimental Test Procedure. KHI performance tests were carried out in five 40 mL stainless-steel cells that were rocked in a water bath with temperature controller. The rocking equipment was supplied by PSL Systemtechnik, Germany, and the cells by Swafas, Norway, were used to conduct KHI performance tests. Each cell contains a stainless-steel ball for agitating the test solution during rocking and pressure and temperature sensors. The cells were pressurized with synthetic natural gas (SNG, Table 1), which preferentially forms structure II gas hydrates as the most thermodynamically stable phase.

KHIs were evaluated for performance by the slow constant cooling (SCC) experimental method and are summarized as follows⁵⁰

1. Test chemicals were dissolved to the desired concentration in deionized water usually one day in advance of the test.
2. 20 mL of test solution was added to each of the five cells.
3. Using repeated vacuum and pressurizing with SNG, the air in the cells was replaced with SNG up to 76 bar.
4. The cells were rocked at a rate of 20 rocks per minute with an angle of 40° while being cooled at 1.0 °C/h from 20.5 to 2.0 °C.

As previously determined by standard laboratory dissociation experiments, the hydrate equilibrium temperature (T_{eq}) at 76 bar was found to be 20.2 ± 0.05 °C warming at 0.025 °C/h for the last 3–4 °C. This correlates well with calculations done using PVTsim software (Calsep, Denmark).⁵⁰ During cooling in SCC experiments, a linear pressure decrease occurs in the closed system until the first detected onset of hydrate formation (T_o) when the pressure drops faster due to consumption of SNG (Figures 3 and 4). The start of nucleation may possibly happen earlier than T_o . T_a is taken as the temperature when the pressure decrease is at its steepest, i.e., when the hydrate formation is at its fastest. In the example shown in Figure 4, T_o is 7.7 °C and T_a is 7.3 °C. The standard deviation (assuming a normal distribution) for a set of T_o or T_a values is no more than 0.6 °C and usually less than 0.3 °C. 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 are usually sufficient to get a significant difference at the 95% confidence level ($p < 0.05$).⁵¹

Corrosion Inhibitor Testing Equipment and Procedures.

The bubble testing equipment provided by Gamry Instruments and the CO₂ corrosion test method have been described before.⁴² The only change in this study was that a 100 mL three-neck round-bottom flask was used. The system is schematically illustrated in Figure 5. The three-electrode system consists of a working electrode that holds the 5 cm² C1018 mild steel metal coupon, a counter electrode, and a reference electrode. The reference electrode is a liquid junction Ag/AgCl electrode saturated with KCl with a potential of 199 mV vs NHE. The counter electrode is a cylindrical spectroscopic graphite rod with an area of 120 cm² counter electrode, and reference electrode, in which the working electrode holds the C1018 mild steel metal coupon. The coupon was prepared by cleaning with water and organic solvents, sonication, and polishing.

The 100 mL flask was filled with 80 mL of 3.6% NaCl brine solution and saturated with very pure CO₂-gas (O₂ concentration <10 ppb) by introducing it through a gas dispersion tube directly into the solution at a high gas flow rate while stirring at 250–300 rpm for a minimum of 30 min before testing. The pH of the test solution was now about 4–5. The stirring rate was lowered to 200 rpm and the electrodes inserted and LPR measurements begun. The LPR measurement was carried out by introducing a potential to the metal sample of ± 20 mV relative to the metal sample's open circuit potential (E_{OC}). LPR measurements were manually repeated in 5 min time intervals to get a consistent measurement sequence. If the corrosion rate was less than 1.9–21 mmpy, the experiment was aborted and a new, prepared steel coupon was used, and the experiment was restarted. After 2 h or when the baseline corrosion rate was constant, the corrosion inhibitor solution was inserted with a syringe, and the LPR measurement continued for a minimum of 3 h or until a steady corrosion rate was obtained. For some of the best chemical combinations investigated, tests were continued for 24–48 h to observe any long-term changes in the corrosion rate.

The collected data were sorted so that anomalous readings due to pitting formation or an unstable system became more straightforward to identify and exclude before performing quantitative analysis. A graph was constructed showing the corrosion rate in both the absence and presence of inhibitors. Quantitatively, the percent inhibition efficiency (% η) was calculated as follows

$$\% \eta = \left(\frac{X_0 - X_1}{X_0} \right) \times 100\%$$

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

component	mol %
nitrogen	0.11
<i>n</i> -butane	0.72
isobutane	1.65
propane	5.00
CO ₂	1.82
ethane	10.3
methane	80.4

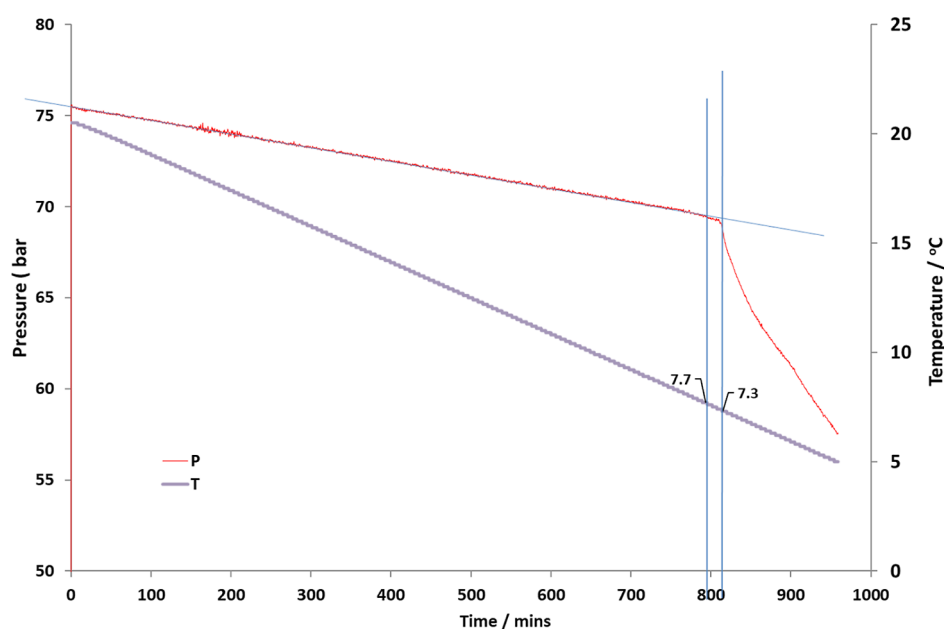


Figure 4. Determination of T_o and T_a values for one rocking cell constant cooling experiment. Example given is for 2500 ppm MA:VCap-DBAPA plus 1000 ppm thiobarbituric acid.



Figure 5. Assembled electrochemical bubble test cell for CO_2 corrosion inhibitor testing.

where $X_0 = 1.9\text{--}2.1$ mmpy was the steady-state corrosion rate without added inhibitor and X_1 was the steady-state corrosion rate with added inhibitor.

RESULTS AND DISCUSSION

KHI Performance Results—Polymer Only. Table 2 gives a brief summary of the KHI performance by SCC screening experiments of the best maleic-based KHIs from our group. The table includes data for the commercial KHI polymers, PVCap and VP:VCap as well as the subject KHI polymers for this study, MA:VCap-DBAPA and its amine oxide derivative MA:VCap-DBAPA-AO.^{40–44} We have also included the

Table 2. KHI Performance in SCC Tests for 2500 ppm of Various Polymers and Additives^{40–44}

polymer name	Mn (g/mol)	T_o (av.) [°C]	St. Dev. [°C]	T_a (av.) [°C]
no additive		17.1	0.5	16.9
PVCap	8000	9.7	0.3	9.4
PVCap + 500 ppm fatty acid imidazoline	8000/351	11.9	0.4	9.0
VP:VCap	2000–4000	8.5	0.5	6.4
VA:MA 40:60 CHex:DBAPA	10,000	6.2	0.3	5.5
MA:THFMeA-DBAPA	3900	6.9	0.3	6.1
MA:THFMeA-DBAPA-AO	4030	6.5	0.2	6.3
MAAcid:VCap	15,500	14.2	0.5	13.9
MA:VCap-DBAPA	16,600	5.6	0.4	5.4
MA:VCap-DBAPA-AO	17,300	3.9–5.2	0.4	3.7–4.5
PMA-DBAPA	2300	9.5	0.4	9.4
PMA-DBAPA-AO	2500	8.7	0.5	8.3
fatty acid imidazoline	351	17.6	0.4	17.5
butyl thioglycolate	141	16.9	0.4	16.0

homopolymers of polymaleic anhydride reacted with DBAPA and its amine oxide derivative (PMA-DBAPA and PMA-DBAPA-AO, respectively). These two homopolymers gave similar KHI performance to PVCap but poorer than the best MA-based copolymers. Results for the film-forming CI, fatty acid imidazoline are also in Table 2. The fatty acid imidazoline had no KHI effect by itself but had a negative effect on PVCap, raising the average T_o value significantly from 9.7 to 11.9 °C. Computer simulations on the formation of methane hydrate with 1-(2-aminoethyl)-11-alkyl-imidazoline showed a significant hydrate kinetic inhibition effect.⁵² This was mainly attributed to the hydrophobic group displacing the methane molecules and destroying the stability of water cages or separating the methane from the water molecules to markedly reduce their interactions. However, the simulations considered the interaction of the imidazoline at the pipe wall and not other factors such as the surfactant's ability to increase the gas solubility in the water phase.

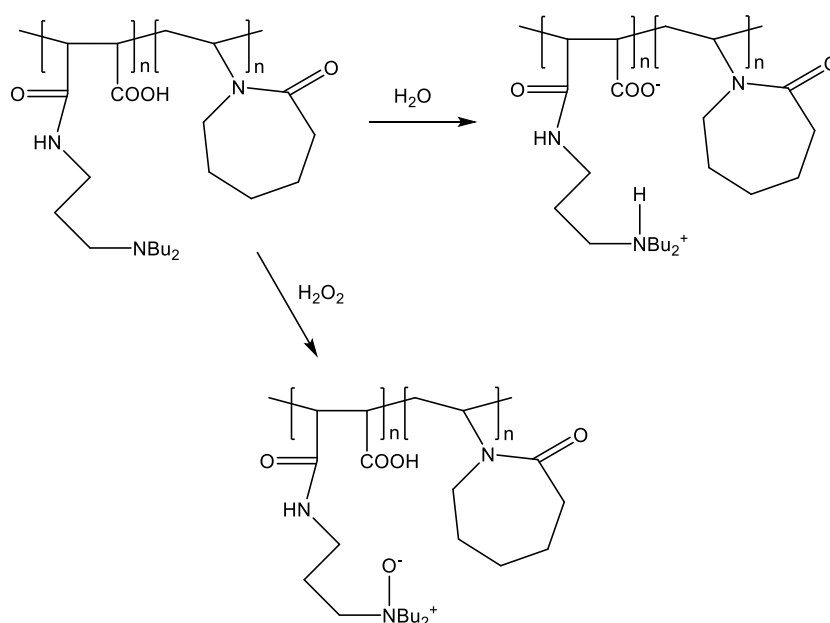


Figure 6. Reaction of the MA:VCap copolymer with either water or with DBAPA and subsequent formation of the amine oxide polymer (MA:VCap-DBAPA-AO).

Table 3. Effect of Concentration on KHI Performance^a

polymer	concentration/ppm			
	0	1000	2500	5000
MA:VCap-DBAPA	17.1/16.9 °C	8.8/8.0 °C	4.8/4.5 °C	5.6/4.0 °C
MA:VCap-DBAPA-AO		8.4/7.7 °C	4.3/3.7 °C	5.2/3.3 °C
VP:VCap		10.5 °C	8.5/6.3 °C	6.4/4.2 °C

^aAverage T_o/T_a values given.

Butyl thioglycolate, which is discussed later as a corrosion inhibitor and KHI synergist, also had negligible KHI effect by itself. The results for MA:VCap-DBAPA-AO have been given as a range as we made six batches and the KHI performance varied somewhat between batches and with the person who made them. One possible reason for the variation is partial hydrolysis of the precursor MA:VCap copolymer before reaction with DBAPA. This would give some maleic acid groups which would not react with DBAPA at the conditions used. When discussing blends and synergists with any one KHI polymer, we always kept to the same polymer batch for the best comparison.

Before investigating synergists for MA:VCap-DBAPA and MA:VCap-DBAPA-AO, we carried out tests at a variety of concentrations for both polymers. We point out that MA:VCap-DBAPA can exist in aqueous solution as the ionized form, as shown in Figure 6. Both MA:VCap-DBAPA and MA:VCap-DBAPA-AO can therefore have pendant quaternary nitrogen atoms. The results for average T_o and T_a values are given in Table 3, and the average T_o values are shown graphically in Figure 7. We have added results for VP:VCap for comparison, showing the improved performance of the maleic polymers.⁵³ The excellent performance of MA:VCap-DBAPA-AO has been proposed previously as being due to a synergistic effect between the caprolactam groups and the dibutylamine oxide groups.⁴⁴ The average T_o value for MA:VCap-DBAPA-AO increased slightly from 3.9 °C (but within acceptable standard deviation limits) from the earlier study to 4.3 °C as several batches were made and tested giving a new average. We

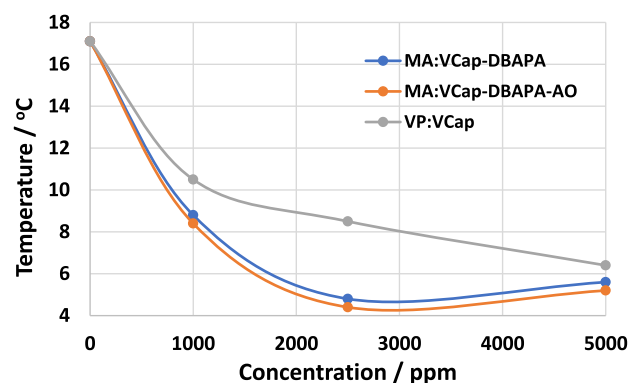


Figure 7. Effect of concentration vs KHI performance (average T_o values only given for clarity).

observed a small decrease in performance for the T_o values for both maleic polymers when doubling our standard concentration of 2500 to 5000 ppm. The 5-cell test was repeated on the same polymer batch to give 10 individual experiments giving a statistically significant result. We have very occasionally seen this trend of increased T_o values at higher polymer concentrations before, but only for very few polymers or blends of polymers and non-polymeric synergists. Recently, a decrease in performance above a concentration limit was seen for a VP:VCap copolymer, although the trend was dependent on the subcooling.⁵⁴ However, in our SCC and within the range 1000–5000 ppm, we did not observe any loss of performance with increasing concentration (Table 3, Figure 7).

We speculate there is some kind of concentration-dependent polymer aggregation occurring, akin to the critical micelle concentration observed for many surfactant classes.

KHI Performance Results—Polymer with Added Synergists. The additives for combining with the maleic polymers that we picked for this study are given in [Tables 4](#)

Table 4. KHI Results for 2500 ppm MA:VCap-2-DBAPA-AO Polymer ($T_{cl} = 65\text{ }^{\circ}\text{C}$ in DIW) with 1000 ppm Synergists

synergist	T_o (av.) [$^{\circ}\text{C}$]	St. Dev. [$^{\circ}\text{C}$]	T_i (av.) [$^{\circ}\text{C}$]
5th batch polymer only	5.2	0.4	4.5
decane/toluene 1:1 mix, 1 mL	4.5	0.5	3.7
fatty acid imidazoline	6.1	0.4	4.7
iHexOl	deposit formed when mixed, not tested		
2,4,7,9-tetramethyl-5-decyne-4,7-diol	4.4	0.5	4.3
cycloheptanol	4.3	0.3	3.8
butyl lactate	4.0	0.2	3.4
thioglycolic acid	7.6	0.3	7.1
butyl thioglycolate	4.4	0.3	3.6
1-butylimidazole	3.7	0.4	3.0
3,6-dioxo-1,8-octanedithiol	7.7	0.5	5.6
polyetherdiamine, Mw: 230 g/mol	6.7	0.9	4.3
polyethyleneglycol Mw: 400 g/mol	4.2	0.4	3.5
polypropyleneglycol 400, Mw: 400 g/mol	4.6	0.5	4.2
polyglycerine, Mw: 1000 g/mol	3.8	0.2	3.2
polyethyleneimine, Mw: 2000 g/mol	4.9	0.2	4.1
polylysine, Mw: 5000 g/mol	4.8	0.2	4.0
polyguanidine, Mw: 2000 g/mol	5.5	0.8	4.4
6th batch polymer only	6.1	0.5	5.1
mercaptoacetic acid	5.7	0.6	4.0
mercaptoethanol	6.0	0.6	5.0
2-aminoethanethiol	4.2	0.8	3.5
butyl thioglycolate	5.1	0.6	4.1

Table 5. KHI Results for 2500 ppm MA:VCap-2-DBAPA with 1000 ppm Synergists

synergist	T_o (av.) [$^{\circ}\text{C}$]	St. Dev. [$^{\circ}\text{C}$]	T_i (av.) [$^{\circ}\text{C}$]
no synergist	4.8	0.3	4.5
fatty acid imidazoline	6.7	0.3	6.0
ammonium thiocyanate	5.9	0.4	4.8
thioglycolic acid	5.5	0.3	5.0
1-butyl imidazole	4.3	0.4	3.9
butyl thioglycolate	4.7	0.3	4.2
butyl lactate	6.2	0.3	5.0
polyglycerine, Mw: 1000 g/mol	4.5	0.2	4.1
polypropylene glycol 400, Mw: 400 g/mol	4.6	0.3	4.2

and [5](#). We used both MA:VCap-DBAPA and the amine oxide derivative MA:VCap-DBAPA-AO, as we weren't sure at the start of the project which of the two polymers would be optimal for obtaining both good KHI and CI performance. Both polymers already contained nBGE solvent, which has been shown to have a small but significant synergistic effect for these maleic polymers.⁴⁰ As blends with these polymers, we chose additives that we thought would improve the corrosion

inhibition of the polymer or could possibly improve the KHI's performance. We usually added 1000 ppm synergist to 2500 ppm polymer in order to see more clearly the effect of the KHI synergism, although a lower concentration might have worked just as well for corrosion inhibition. Those synergists that were tested with both MA:VCap-DBAPA and MA:VCap-DBAPA-AO gave similar KHI and CI performance enhancement. For this reason, we did not carry out every KHI or CI test in the matrix of polymer (amine or amine oxide) plus synergist, as we assumed the two polymers behaved similarly with a range of synergists.

The KHI performance of the MA:VCap-DBAPA-AO copolymer alone is based on two separate batches, called batches 5 and 6. Many synergists were evaluated with batch 5, and these are listed at the top of [Table 4](#). This batch 5 copolymer when tested alone gave an average T_o of 5.2 $^{\circ}\text{C}$. When this batch ran out, we used a new batch (6) which gave an average T_o of 6.1 $^{\circ}\text{C}$. A possible reason for the discrepancy was discussed above and may be related to partial hydrolysis of the MA:VCap precursor. For comparison purposes, it is important to stick to the same polymer batch when evaluating potential synergists. That is why values for both batches are given when used alone.

Fatty imidazolines are good film-forming CIs and are known to reduce the performance of some KHI polymers, as we saw with PVCap in [Table 2](#).^{2,6,7} We also found this to be true for the maleic polymers, as the results in [Tables 4](#) and [5](#) show, although we did add 1000 ppm of the imidazoline, which is higher than typical CI field dosages.

Several small, oxygenated molecules that have been identified as good KHI synergists for VCap and NIPMAM-based polymers are butyl lactate, 4-methyl-1-pentanol (iHexOl), and the acetylenic diol gemini surfactant 2,4,7,9-tetramethyl-5-decyne-4,7-diol.^{55–57} These were tested as possible synergists for the maleic polymers. The alcohol iHexOl was found to be incompatible with MA:VCap-DBAPA-AO. Cycloheptanol, butyl lactate, and the acetylenic diol were compatible but gave no significant performance enhancement. It is possible they could improve the CI performance of the maleic polymer, but we were more interested in nitrogen- and sulfur-based molecules, as these are the main components in film-forming flow line CIs.^{58–62} Polypropyleneglycol 400 (PPG) gave no synergy at 1000 ppm but has been reported to enhance the performance of the VP:VCap copolymer at higher concentrations.⁶³ In addition, the corrosion inhibition results show that none of the oxygenated additives were able to significantly enhance the CI performance of the maleic polymers alone.

Sulfur-based chemicals are often added to classic nitrogen-based CO_2 corrosion inhibitors, whereas this is less necessary for sour corrosion due to the presence of H_2S and other sulfide species.² Examples are mercaptoacetic acid, mercaptoethanol, and thioglycolic acid.^{2,64} Some of the non-polymeric sulfur- as well as nitrogen-based synergists that were investigated have small alkyl groups, which we assumed could be suitable for KHI synergy ([Figure 8](#)), just as butyl glycol ether is a synergist for PVCap or PNIPMAM. VCap-based polymers show synergy with molecules, particularly those with C4–7 alkyl or cycloalkyl groups.⁵⁴ As [Tables 4](#) and [5](#) show, some synergists such as 1-butyl imidazole, isobutylthiazole, and butyl thioglycolate lowered the average T_o value for one or both of the maleic polymers by about 1 $^{\circ}\text{C}$. Therefore, these molecules were made candidates for CI tests. [Figure 8](#) gives the structures of

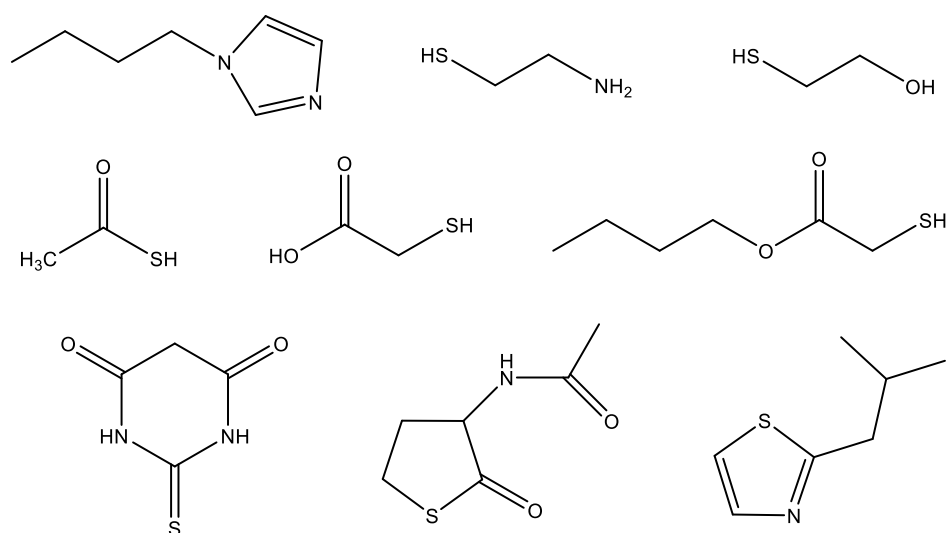


Figure 8. Row 1: 1-butyl imidazole, 2-aminoethanethiol (cysteamine), and mercaptoethanol (thioethanol). Row 2: thioacetic acid, thioglycolic acid (mercaptoacetic acid), and butyl thioglycolate. Row 3: thiobarbituric acid, 3-acetamidotetrahydro-2-thiophenone, and 2-isobutylthiazole.

Table 6. Summary of CO₂ Corrosion Inhibition Efficiency Results for Various Additives or MA:VCap-DBAPA with Various Synergists^a

main additive	synergist	concn. ppm	inhibition efficiency %	S.D. %
fatty acid imidazoline		100	76.5	5
		500	85.4	8
	thioglycolic acid	500 + 100	75	6
	acetic acid	100 + 33	62	8
	LAWS	100 + 10 mL	79	7
PEG 400		500	2.7	9
thioglycolic acid		500	-29.2	12
ammonium thiocyanate		500	82	4
butyl thioglycolate		100	94.2	3
		1000	92.6	3
sodium thiosulfate		500	45.4	7
thiobarbituric acid		500	1.7	11
2-aminoethanethiol		500	95.3	7
MA:VCap-2-DBAPA		500	18.1	7
		2500	-75.0	6
	thioglycolic acid	500 + 100	92.2	6
	butyl thioglycolate	500 + 100	93.1	4
		2500 + 1000	99.7%	6
	ammonium thiocyanate	500 + 100	96.0	5
	1-butylimidazole	500 + 100	10.2	12
	2-isobutylthiazole	500 + 100	8.2	5
		500	16.3	6
		butyl thioglycolate	500 + 100	93.1
MA:VCap-2-DBAPA-AO		500 + 100	98.7	4
	mercaptoethanol	500 + 100	98.2	6
		2500 + 1000	98.2	6
		500	37.3	13
		butyl thioglycolate	500 + 100	99.3
VP:VCap		500 + 100	98.8	5
	2-aminoethanethiol	500 + 100	98.8	5

^aHighest reading obtained due to overload error.

the most significant molecules tested as synergists. Terpolymers of *N*-vinyl pyrrolidone, cyclohexyl vinyl ether, and alkyl acrylates gave better KHI with added alkylimidazoles.⁶⁵ A recent KHI performance study with *N*-vinyl lactam polymers and alkylimidazoles with 1–3 carbon atom alkyl groups showed that the best synergy was obtained with 2-propylimidazole.⁶⁶

Mercaptoethanol is becoming more widely used in sweet CI formulations.⁶⁷ It does not react with imidazolines and other amines like thioacids. In the gas hydrate rocking cells, mercaptoethanol had no impact on the KHI performance of MA:VCap.DBAPA-AO (Table 4). The lack of impact has been shown previously for KHI polymers, but the polymer structures were not reported.⁶⁸ Mercaptoacetic acid is also

widely used as a sweet corrosion FFCI synergist.^{1,2} We found it had no significant effect on the KHI performance of MA:VCap-DBAPA-AO. In contrast, thioglycolic acid had an antagonistic effect. Probably the best sulfur-based synergist we tested with MA:VCap-DBAPA-AO was 2-aminoethanethiol (cysteamine), which lowered the average T_0 value compared to MA:VCap-DBAPA-AO alone by almost 2 °C. Butyl thioglycolate only lowered this value by about 1 °C. 2-Aminoethanethiol is non-hazardous; it is also used as a medication to treat cystinosis, and it has been claimed as a corrosion inhibitor for sweet gas environments (i.e., no or negligible H_2S), especially in blends with polyaspartates.⁶⁹ Its efficiency was shown to be better than that of thioglycolic acid. 2-Aminoethanethiol also has good corrosion inhibition efficiency for steel in a 0.1 M HCl solution.^{70,71} Reaction products of 2-aminoethanethiol and aldehyde have also been proposed as acidizing corrosion inhibitors.⁷² Cysteamine-modified polyaspartic acid has also been claimed as a new class of green corrosion inhibitor for mild steel in sulfuric acid medium.⁷³

We also investigated some polyethers, such as polypropyleneglycol 400, and polyamines, some of which have been claimed as KHI synergists (Tables 4 and 5).⁵⁵ The polyamine, polylysine, and polyguanidine (polyhexamethylene biguanide) were chosen as we hoped they would also have corrosion inhibition properties. Among the polymers tested, the hyperbranched polyglycerine showed a weak synergistic effect, but none of the other polyethers or polyamines improved the maleic polymer KHI's performance. Therefore, they were not chosen for corrosion inhibition testing. In summary, the best new candidate synergists for CI testing were 1-butylimidazole, butyl thioglycolate, and 2-aminoethanethiol.

Corrosion Inhibition Experimental Results. Table 6 summarizes the CO_2 corrosion test results. This includes results for a range of additives, nearly all of which were tested as KHI synergists, either by themselves or in combination with MA:VCap-DBAPA and its amine oxide derivative MA:VCap-DBAPA-AO. We point out that this is the first stage of exploring potential synergists for the maleic polymers such that concentrations and ratios have not been optimized for best performance. Some work on maleic polymers for oxygen corrosion inhibition has been reported.³⁵

For comparison, the commercial CI, fatty imidazoline, was tested. This inhibitor is commonly blended with other surfactants to improve the performance.^{1,2} This imidazoline showed good performance at 100 and 500 ppm, giving inhibition efficiencies of 76.5 and 85.4%, respectively. Sulfur-based additives in corrosion inhibitor packages have been used to boost the CI surfactant's performance. However, test data have to be interpreted with caution. Laboratory results with thio-based (S or -SH) species can sometimes look very good but can mask problems and perform worse in the field.⁷⁴ Thus, some sulfur-based synergists (thiosulfate, thioglycolic acid, and thioethanol) perform better in benchtop laboratory bubble tests with limited stirring, shearing, and abrasive conditions compared to the field. In fact, the H_2S in sour gas systems will initially cause reduced corrosion in the laboratory by forming a protective FeS film on the steel surface.⁶⁵ The addition use of the sulfur-based product, thioglycolic acid (mercaptoacetic acid), or acetic acid did not improve the performance of the imidazoline. This may be due to the protonation of the imidazoline groups (on top of the effect of carbonic acid) changing the water solubility. The protonation causes the lone

pair on the nitrogen atom to be used, making the surfactant less likely to chemisorb via the Lewis acid–base reaction to the steel surface. The addition of LAWS (1:4 blend of toluene and decane) lowered the imidazoline CI performance a little, probably due to being partial partitioning to the hydrocarbon phase. Partitioning is a key issue in designing optimal hydrophilic-lipophilic balances in oilfield CI structures and formulations.

Other N- and S-based molecules tested, such as those tested as KHI synergists, were tested by themselves for corrosion inhibition (Table 6). Surprisingly, there was a vast difference in the results. Some of the sulfur-based molecules gave good inhibition by themselves. For example, thioglycolic acid caused corrosion promotion, whereas its butyl ester, butyl thioglycolate, was one of the best inhibitors, giving 94.2% inhibition when added at 100 ppm. The result was slightly worse at 1000 ppm, giving 92.6%. Sodium thiosulfate gave some corrosion inhibition by itself, lowering the corrosion rate by 45.4%. The best sulfur-based product tested by itself was 2-aminoethanethiol, giving 95.3% inhibition. We speculate that the presence of both the thiol and amine groups give a stronger interaction with the metal surface. We also tested polyethyleneglycol (PEG 400), a KHI synergist, but this showed negligible effect by itself, and therefore we did no further tests on oxygenated polymers such as polyglycerine, which showed some KHI synergy with MA:VCap-DBAPA.

We then tested the maleic polymers MA:VCap-DBAPA and MA:VCap-DBAPA-AO for corrosion inhibition by themselves and with various synergists. By themselves, at 500 ppm, these two polymers both showed weak inhibition abilities. At 2500 ppm, a typical KHI concentration, MA:VCap-2-DBAPA promoted corrosion quite badly, with a negative efficiency of -75.0%. However, the addition of several S-based additives dramatically changed the result to 92+% corrosion inhibition efficiency. These included ammonium thiocyanate, butyl thioglycolate, thioglycolic acid, 2-aminoethanethiol, and thiobarbituric acid. Butyl thioglycolate was the most promising candidate since it also gave some KHI synergy with the maleic polymers. Therefore, we also increased the test concentration of MA:VCap-DBAPA-AO to a typical KHI dosage of 2500 ppm with added 1000 ppm butyl thioglycolate. The corrosion inhibition efficiency was now 99.7%, possibly higher as the resistance to iron oxidation was now so high that it caused an overload during the test. It should be noted that sulfur synergists are added to CI surfactant blends only for sweet corrosion, but not needed for sour corrosion as it already has H_2S .^{1,2} Therefore, it is possible that our maleic-based KHI polymers will function even better in sour gas as CIs than in sweet gas.⁷⁵

KHI Performance Tests with the Best Corrosion Inhibition Enhancers and Commercial KHI Polymers.

Due to the good CI performance of 2-aminoethanethiol and butyl thioglycolate with the maleic copolymers, we also tested these synergists in blends with the classic KHI homopolymer PVCap and the copolymer VP:VCap using 500 and 100 ppm, respectively (Table 7). Only blends with VP:VCap were tested for CI efficiency but both polymers were used for KHI tests. The CI efficiency of VP:VCap increased greatly from 37.3% for the polymer alone, with the best result being 99.3% for butyl glycolate.

Next, blends of 2-aminoethanethiol and butyl thioglycolate with the KHI polymers were investigated for KHI performance using the SCC screening method in steel rocking cells. 2500

Table 7. KHI Tests with 2500 ppm VCap-Based Polymers with Synergists

synergist	T_o (av.) [°C]	St. Dev. [°C]	T_a (av.) [°C]
no additive	17.1	0.5	16.9
PVCap	9.7	0.3	8.4
PVCap + fatty acid imidazoline 1000 ppm	11.9	0.4	9.0
PVCap + BGE 1000 ppm	8.7	0.4	8.2
PVCap + butyl thioglycolate 1000 ppm	7.2	0.4	6.8
PVCap + 2-aminoethanethiol 1000 ppm	9.7	0.5	8.4
VP:VCap	8.0	0.5	6.4
VP:VCap + fatty acid imidazoline 1000 ppm	10.4	0.3	8.3
VP:VCap + BGE 1000 ppm	7.9	0.6	6.0
VP:VCap + butyl thioglycolate 1000 ppm	8.3	0.4	5.7
VP:VCap + 2-aminoethanethiol 1000 ppm	8.3	0.7	6.5

ppm polymer and 1000 ppm synergist were used in the KHI tests. The synergist concentration is probably higher than necessary for optimal corrosion inhibition, but we wanted to enhance and negative effects on the KHI polymer by using 1000 ppm. Table 7 summarizes the test results as well as the results with the addition of fatty imidazoline CI and with BGE. The antagonistic effect of this corrosion inhibitor with PVCap was given earlier in Table 2. With VP:VCap, addition of the fatty imidazoline gave an average T_o value of 10.4 °C, on average 2.4 °C higher than with VP:VCap alone, indicating a similar level of antagonism as seen with PVCap. The two small molecules, aminoethanethiol and butyl thioglycolate, did not cause significant antagonism with the KHI polymers. In fact, butyl thioglycolate gave some synergy with PVCap, lowering the average T_o value from 9.4 to 7.2 °C. This was a stronger synergetic effect than adding 1000 ppm BGE to PVCap. In conclusion, both aminoethanethiol and butyl thioglycolate greatly increase the CI effect of VCap-based polymers without reducing the KHI performance, as seen with the fatty acid imidazoline. In addition, imidazoline-based corrosion inhibitors are often quite toxic due to their strong surface-active properties. Butyl thioglycolate and aminoethanethiol would be expected to be less toxic due to their much shorter alkyl chain. Further, mercaptocarboxylic acids and their esters, such as butyl thioglycolate, were found to be readily biodegradable or at worst showed good biodegradability in the OECD301D and OECD301F tests.⁷⁶

CONCLUSIONS

The copolymer MA:VCap-DBAPA and its amine oxide derivative MA:VCap-DBAPA-AO, which are known to exhibit good KHI performance, were shown to have limited sweet corrosion inhibition properties, insufficient for corrosion protection in the field when used alone. Blends of these polymers with a variety of small molecules were investigated as additives to boost the corrosion inhibition. These included oxygenated molecules and polymers, as well as sulfur- and nitrogen-based additives. Several sulfur-based additives strongly improved the CI efficiency of the maleic polymers without having a negative effect on the KHI performance. Blends of the best additives with MA:VCap-DBAPA and MA:VCap-DBAPA-AO were investigated for KHI perform-

ance. Two additives, 2-aminoethanethiol and butyl thioglycolate, showed significant KHI synergy. For example, 2500 ppm MA:VCap-DBAPA plus 1000 ppm butyl thioglycolate gave an average hydrate onset temperature (T_o) of 4.4 °C (12.7 °C below the T_o result for no additive) while also giving a 99.7% CI efficiency. Butyl thioglycolate and 2-aminoethanethiol were also found to greatly enhance the CI efficiency of the industrial KHIs, PVCap homopolymer, and VP:VCap copolymer. Butyl thioglycolate also boosted the KHI performance of PVCap.

There are a large number of other blends that could be investigated, but the main point of the study was achieved, which was to show that MA:VCap-DBAPA(-AO) copolymers can function well as KHIs and also as CIs, in this case when the correct sulfur-based synergist is added. As a note of caution, we stress that sulfur-based molecules should be tested carefully for corrosion inhibition. The tests we have carried out are not at high shear, and field and laboratory results are not always the same. Gas-phase corrosion inhibition testing would also be useful to determine top-of-the-line corrosion (TLC) in subsea flow lines. We will report on our attempts to use other methods of designing dual-function KHI-CIs using maleic-based polymers in later publications. Future work will investigate butyl thioglycolate and 2-aminoethanethiol as new KHI and CI synergists, as well as tuning the maleic polymer structures for triple KHI-CI-SI functionality.

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Notes

The authors declare no competing financial interest.

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