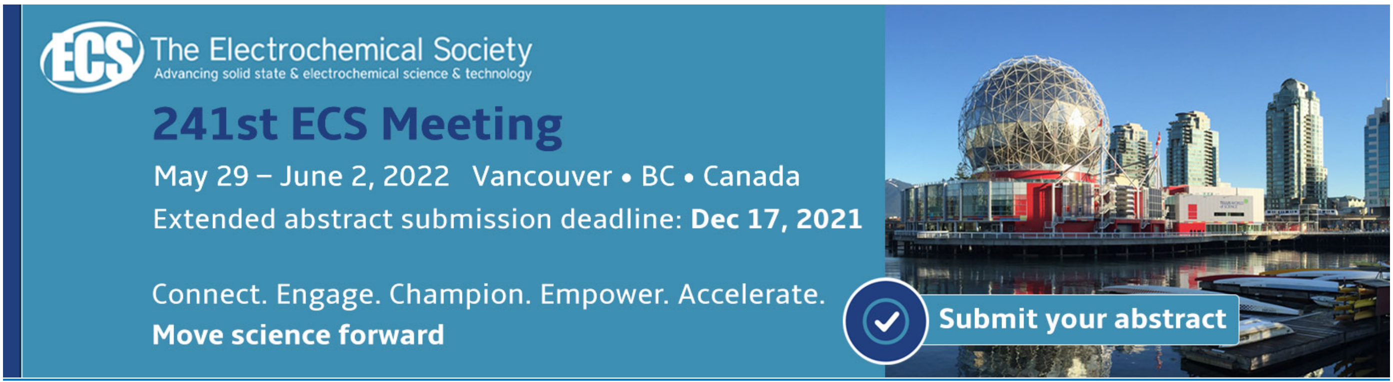
IOP Conference Series: Materials Science and Engineering

Multi-functional oilfield production chemicals: maleic-based polymers for gas hydrate and corrosion inhibition

To cite this article: M A Kelland *et al* 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1201** 012081



Multi-functional oilfield production chemicals: maleic-based polymers for gas hydrate and corrosion inhibition

M A Kelland,*[1] J Pomicpic,[1] R Ghosh,[1] C Undheim,[1] T H Hemmingsen,[1] Q Zhang,[2] M A Varfolomeev,[3] R S Pavelyev,[3] and S S Vinogradova[4]

[1] Department of Chemistry, Bioscience Environmental Engineering, Faculty of Science and Technology, University of Stavanger, N-4036, Norway.
[2] College of Engineering, Peking University, Beijing 100871, China.
[3] Department of Petroleum Engineering, Kazan Federal University, 420008 Kazan, Russian Federation.
[4] Department of Electrochemical Engineering, Kazan National Research Technological University, 420015 Kazan, Russian Federation.

[*] Contact author: malcolm.kelland@uis.no

Abstract. Several chemical problems can occur during the production of oil and gas through flow lines. This includes corrosion, scale deposition and gas hydrate plugging. Three separate chemicals may be needed to treat these issues. Kinetic hydrate inhibitors (KHIs) are used in cold oil or natural gas production flow lines to prevent the formation and plugging of the line with gas hydrates. They are often injected concomitantly with other production chemicals such as corrosion and scale inhibitors. KHIs are specific low molecular weight water-soluble polymers with amphiphilic groups formulated with synergists and solvents. However, many corrosion inhibitors (CIs) are antagonistic to the KHI polymer, severely reducing the KHI performance. It would be preferable and economic if the KHI also could act as a CI. We have explored the use of maleic-based copolymers as KHIs as well as their use as film-forming CIs. KHIs were tested using a natural gas mixture in high pressure rocking cells using the slow constant cooling test method. A terpolymer from reaction of vinyl acetate:maleic anhydride copolymer with cyclohexylamine and 3,3-di-n-butylaminopropylamine (VA:MA-60% cHex-40% DBAPA), gave excellent performance as a KHI, better than the commercially available poly(*N*-vinyl caprolactam) (PVCap). CO_2 corrosion inhibition was measured by Linear Polarization Resistance (LPR) in a 1 litre CO_2 bubble test equipment using C1018 steel coupons. The new terpolymer gave good CO_2 corrosion inhibition in 3.6 wt% brine, significantly better than PVCap, but not as good as a commercial imidazoline-based surfactant corrosion inhibitor. The terpolymer also showed good corrosion inhibition efficiency at high salinity conditions, (density 1.12 g/cm^3). VA:MA-60% cHex-40% DBAPA shifted the open-circuit potential to more positive values and significantly decreased the corrosion rate.

1. Introduction

Production of oil and gas is fraught with various chemical problems that occur in the flow lines. These include corrosion and various “fouling” issues such as scale, wax, gas hydrates and asphaltenes [1-2]. Usually each of these fouling problems requires a different chemical solution, which can cause various incompatibilities. For example, injecting mixtures of chemicals may require more than one liquid phase, the chemicals may react together and can even cause their own fouling [3]. In addition, the inhibition performance of each chemical may be reduced if there are interactions between them. Therefore, the development of dual or multi-functional production chemicals could be of great interest to overcome some of these issues as well as being economically attractive. In this paper we review the technology of kinetic hydrate inhibitors (KHIs) and film-forming corrosion inhibitors (FFCIs) and attempts to design and synthesise polymers with dual functionality. In addition, we report on our first results to make dual-functional KHI-CIs using maleic-based polymer chemistry.

1.1 Low dosage hydrate inhibitors (LDHIs) - Kinetic hydrate inhibitors (KHIs)

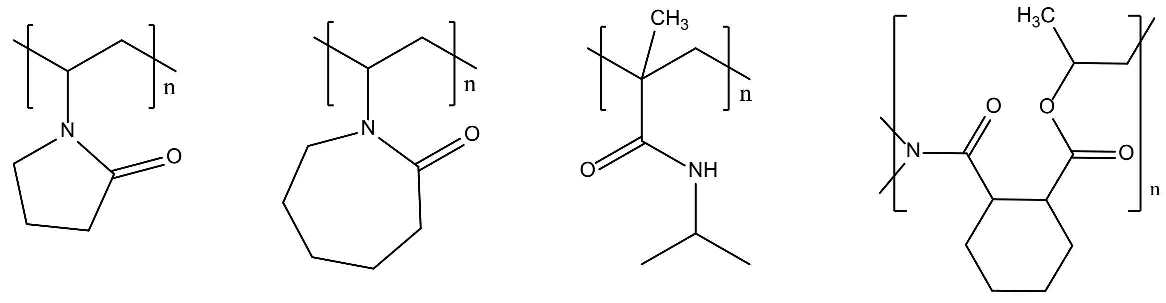
Gas hydrates are clathrate structures, resembling ice to the naked eye. The clathrate is made of a lattice of water cages held together by hydrogen-bonding with small gas molecules within the cages [1-2] Three main gas hydrate structures are known, sI, sII and sH, with the first two structures being known to form in flow lines. sI hydrate is the thermodynamically favoured structure for very methane-rich natural gas and sII is favoured for natural gas with mixtures of small alkanes. However, both structures can be initially formed (kinetically) with all gas mixtures. Blockage of flow lines with gas hydrates, particularly subsea and in deep water is a major flow assurance problem in upstream transportation of unprocessed oil, condensate gas and water mixtures.

Various methods have been developed to prevent gas hydrate blockages of flow lines. [4] These include engineering solutions as well as chemical methods. The use of thermodynamic inhibitors (THIs) is the commonest chemical method. THIs include methanol, ethanol, short-chained glycols and salts. The use of THIs has several disadvantages. Firstly, the operator has to be certain that enough THI is present in the water phase to keep the fluids outside the hydrate phased boundary. Methanol for example partitions also to the gas and liquid hydrocarbon phases and this needs to be calculated for the conditions of the whole flow line. For THIs, high concentrations are needed to move the equilibrium. Perhaps 20-80 wt.% of the water phase needs to be added as THI in some cases. Methanol is the most powerful THI but can follow the propane fraction in the natural gas phase and kill the catalysts used in the refinery. This lowers the economic price of the propane. Methanol is also flammable. Monoethylene glycol (MEG) is more expensive than methanol and less powerful as a THI than methanol and is often regenerated for reuse.

About 30 years ago, low dosage hydrate inhibitors (LDHIs) began to be developed [3, 5]. They were especially needed for long cold flow lines where the use of large amounts of THIs would be prohibitively expensive. LDHIs were designed to be used at much lower concentrations than THIs, usually 0.1-3.0 wt.% based on the produced water to save both storage and pumping costs as well saving platform space for new fields designed for LDHI deployment. Two main types of LDHIs were envisaged, kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). Both types are now commercially in use, KHIs being first used about 1995 in offshore gas fields UK, and AAs first used around the turn of the millenium in the Gulf of Mexico.

AAs are surfactants and have some control over the hydrate crystallization process causing a transportable dispersion of hydrate particles to be formed. Since they do not have to completely stop hydrate formation they can theoretically be used at very high driving forces. Many of the commercial AAs are cationic quaternary ammonium surfactants with butyl groups in the polar head which can interact with the cages on the surface of hydrate particles. The term “hydrate-philic” has been coined to describe this interaction.

KHIs are formulations containing one or more water-soluble polymers with solvents and synergists to enhance the performance. [6-13] KHIs delay hydrate formation by inhibiting the growth of hydrate particles (both nuclei and crystals). They do not work at such high driving forces as AAs. Some of the best KHIs available today can give over 48h delay times at ca. 13-14 °C subcooling with a 1-2 wt.% dosage rate but this depends on many factors including the pressure, gas composition, water cut, salinity and the presence of other production chemicals. Examples of monomers used in KHI polymers include *N*-vinyl pyrrolidone (VP), *N*-vinyl caprolactam (VCap), *N*-isopropylacrylamide and amides and/or ester linkages to hexahydrophthalic acid (HPEA) (Figure 1).



PVP PVCap PNIPMAm HPEA

Figure 1. Common monomer units in commercial KHI polymers.

1.2 Corrosion Inhibitors (CIs) and compatibility issues with KHIs

Corrosion inhibitors in one form or another are nearly always needed in upstream flow lines due to the presence of water, CO_2 and sometimes H_2S [3, 14-16]. However, many of the classic flow line film-forming corrosion inhibitors (CIs) (e.g. amidoamine, quaternary ammonium salts, imidazoline and phosphate ester surfactants) are antagonistic to the KHI polymer, severely reducing the KHI performance (Figure 2). Conversely, KHIs can also negatively influence the performance of CIs. [17] These effects may be due to preferential adsorption of KHIs on the walls of the pipe or to CI–KHI surfactant–polymer interactions. Many surfactants (nonionic, cationic, and amphoteric) can accelerate hydrate formation if they have good foaming or emulsifying properties giving better contact of the gas (or gas in oil) with the water phase [18].

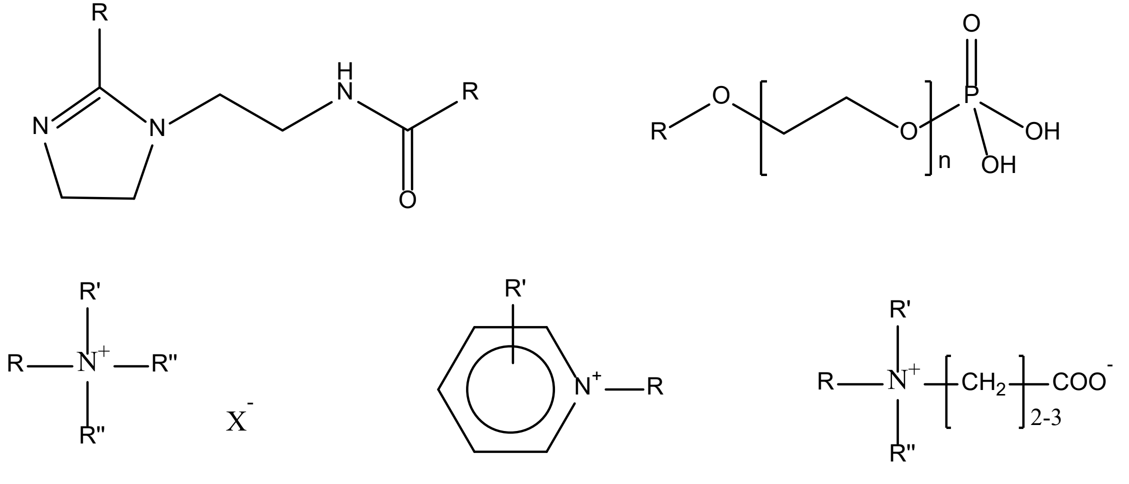


Figure 2. Common surfactants used as film-forming corrosion inhibitors. R is usually an alkyl group in the range C12-18.

The chemical suppliers and service companies have found some CIs that do not affect the KHI performance but rarely with the efficacy level of the best CIs [19-21]. It has been claimed that the incompatibility was due to the absorption of CI onto the polymer structure of the KHI, PVCap. LC/MS measurement suggested that the structure of PVCap was altered in the presence of a phosphate ester surfactant, which lowered the performance of the PVCap with a 25% pass rate (a compatible CI showed 100% pass rate). Other well-known CIs, such as imidazoline surfactants, were partially associated with the PVCap structure and resulted in a lowering of the PVCap performance with 50% pass rate [22]. Some KHI-compatible CIs have now been reported but rarely is the chemistry described for proprietary reasons [23-31]. Therefore, it would be preferable and economic if the KHI polymer could also act as a CI. Polymers possess multi-functionality and better film-forming capabilities, which could significantly improve protective barrier properties [32].

1.3 Polymeric corrosion inhibitors

Polymers can have corrosion inhibition properties, but the industry is still dominated by simple non-polymeric surfactants. Several new classes of polymeric FFCIs have been developed for use in flow lines and some have been commercialised. For example, polyamine and polyquats with ester linkages have been reported. The ester groups give improved biodegradation [33-35]. Polyepoxysuccinic esters have also been claimed as CIs [36-38]. Vinyl-based polymers have also been reported [39]. These vinyl polymers can contain a wide variety of functional groups in the side chains designed for different applications. Examples of groups include esters, alkanolamino or alkylamino ethoxylate groups, quaternary ammonium groups and heterocyclic rings such as imidazolines. Other vinyl-based polymers include tertiary amine methacrylate-based polymers. [40] Sulphur chemistry is often used in FFCI formulations. Some sulphur-based polymers have been reported such as coatings of poly(2-aminothiazole) [41].

1.4 Polymeric scale inhibitors as corrosion inhibitors

Polymeric oilfield scale inhibitors, for treating barite or calcite scale mainly, have multiple carboxylate and/or sulphonate groups. Some phosphinate or phosphonate groups may also be included in the polymer. [1-2] Typical vinylic polycarboxylates include polyacrylates and polymaleates and copolymers thereof. Sulphonated monomers that can be used include vinyl sulfonic acid, acrylamide-propanesulphonic acid and styrene sulphonic acid. More biodegradable polycarboxylates include polyaspartates and carboxymethylinulin although these are generally less thermally stable than the vinylic polymers. Scale inhibitors in general are not detrimental to the performance of neutral KHIs and can in fact enhance the performance in some cases [42-43].

Polyaspartate salts are known to have CI properties besides its more common use as a scale inhibitor. However, other polycarboxylate scale inhibitors such as polyacrylates are poor CIs for CO_2 and H_2S under flow line conditions [44]. This is probably due to additional nitrogen atoms in the polyaspartates which are polyaminoacids. Used alone, polyaspartates showed best potential as a CI in low-chloride, low-pH conditions, which are relatively rare in petroleum production [45-47]. Blends of polyaspartates with known FFCIs or alkylpolyglucosides show synergetic effects. Some blends have been used offshore [48-50]. Improvements to polyaspartates have been reported by adding theonine, amino thiol or amino disulphide compounds [51-53]. Other variations on polyaspartate reverting from the precursor polysuccinimide or related polyimides have been reported [54-56].

1.5 Kinetic hydrate inhibitors (KHIs) as corrosion inhibitors (CIs)

Some researchers have taken the concept of polymeric CIs further to introduce KHI properties to the polymer. These include some of the classic vinylic amide monomers such as N-vinyl caprolactam (VCap) copolymerised with other vinyl monomers with acid or hydroxyl moieties [57-58]. Others have copolymerised vinylic amide monomers such as VCap with vinyl monomers containing functional groups well known in corrosion inhibitor surfactants. (Figure 3) For example, the use of quaternary ammonium monomers or vinyl imidazole gave copolymers with KHI performance only a little worse than a commercial VP:VCap copolymer and good corrosion inhibition in 2M aqueous HCl. Inclusion of a percentage of more hydrophobic monomers such as N-dodecylacrylamide improved the corrosion inhibition further [59-60].

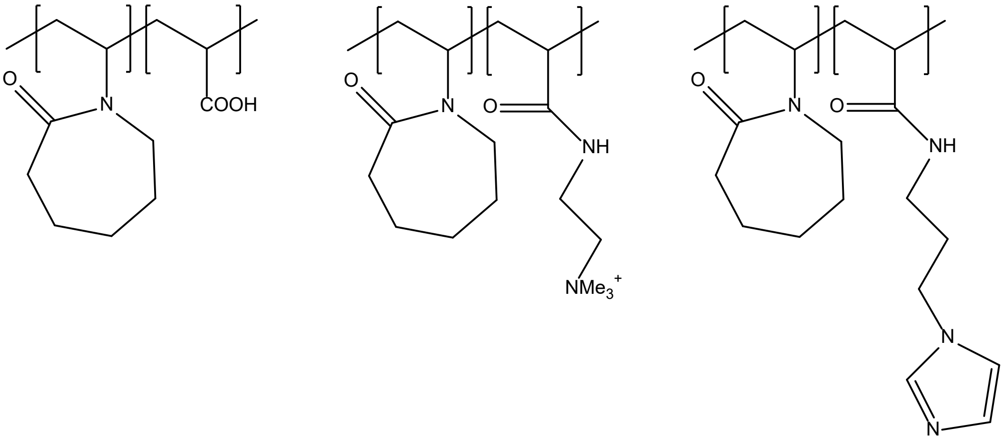


Figure 3. Structures of PVCap-based KHIs: (from left) PVCap-co-AA, PVCap-co-ATCH, and PVCap-co-APIM.

Polyurethane have also been investigated as dual KHs and CIs. Polyurethane has several components that react together, giving the method great flexibility to tailor the polymer for multi-purpose use. [61-62] Incorporation of butyl groups to polyurethanes via the use of butylamines gave polymers with both good CI and KHI efficacy. (Figure 4).

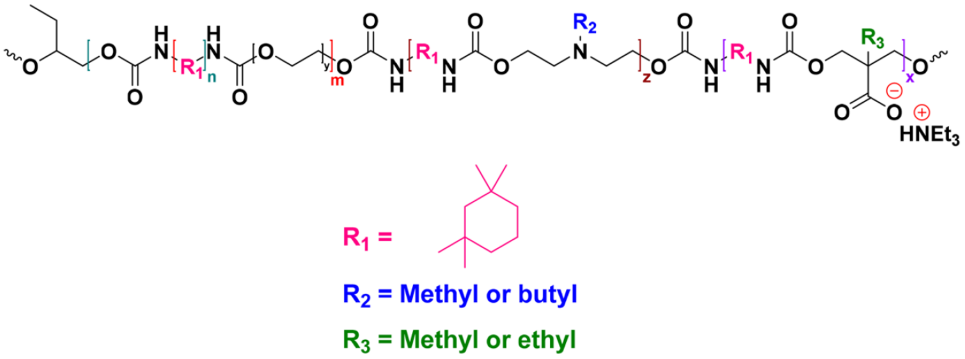


Figure 4. Structure of polyurethanes with KHI and CI properties.

Polyacrylamides with cycloamino hydrophobic groups have been claimed as superior CIs to a range of commercial CIs (structures not given) by reacting the acrylamido monomers with a sulphur-containing species such as a thioacid or thiol. An example is poly(*N*-pyrrolidine acrylamide-co-*N*-piperidine acrylamide) with end-caps of thioglycolic acid [63]. These polymers without the sulphur chemistry have previously been claimed as KHIs for sour gas applications [64]. However, it is not clear if there is free thioglycolic acid in the polymer sample since more was added than is needed for end-capping, and this acid can act as a good CI synergist with the polymer.

2. Maleic-based polymers as KHIs and CIs

Recently, we began exploring maleic-based polymers as KHIs. The beauty of using maleic chemistry is that the maleic anhydride monomer unit can be reacted and ring-opened with all manner of molecules to add the functional groups required for hydrate, corrosion or scale inhibition. It does not require the synthesis of a new monomer which would be the case with acrylate or acrylamide chemistry. Maleic polymers have been known for about 25 years as potential KHIs but have not been commercialised. The low cost of maleic anhydride (made from oxidation of benzene) is one of the driving forces for developing maleic-based KHIs. Maleic anhydride does not polymerise easily by itself, but low molecular weight oligomers can be accessed. Copolymers with a variety of comonomers are known and much higher molecular weights can be obtained. Polymaleic anhydride can then be derivatized by reaction with alcohols or amines to form polyester or polyamides or mixtures of both functional groups (Figure 5). The first maleic-based KHIs were made in the 1990's by reacting copolymers such as maleic anhydride:vinyl acetate copolymer with small amines such as isobutylamine but they showed limited performance [65].

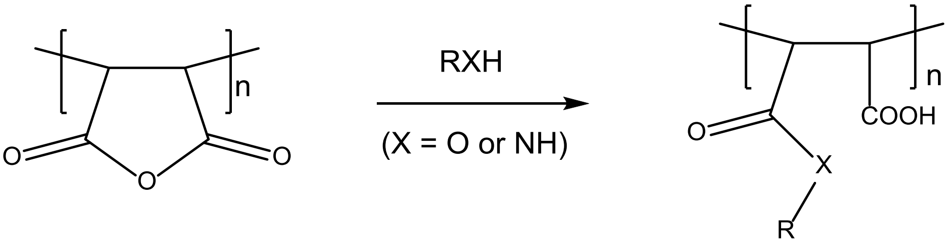


Figure 5. Polyamide and polyester products from the reaction of polymaleic anhydride with alcohols and amines.

Over the last 20 years, our understanding of the structural features that make high-performing KHI polymers has expanded and improved. This led to a recent study involving improvements to maleic:vinyl acetate 1:1 copolymers.[66] Reaction of the maleic anhydride units with a 60:40 molar mixture of cyclohexylamine and 3,3-di-n-butylaminopropylamine gave a terpolymer (VA:MA-60%-cHex-40% DBAPA) with a better KHI performance than copolymers made using isobutylamine (Figure 6) or the well-known KHI polymer, PVCap. The maleic-based terpolymer has a molecular weight 11200 g/mol. Polymer molecular weight analysis was carried out by GPC/SEC using DMF solvent at 0.6mL/min, 40 °C using polystyrene standards.

2.1 KHI Performance tests

KHI tests were carried out in rocking cells using a synthetic natural gas (Table 1) that forms sII hydrate as the preferred thermodynamically stable phase [66]. The 40ml steel cells were filled with 20ml of test solution containing 2500ppm polymer. The slow constant cooling test method was used. The cells were flushed and pumped to remove air, and then pressurized with the natural gas blend to 76 bar before cooling from 20.5 °C to 2 °C at a rate of 1 °C/h with rocking of the cells. The first sign of pressure drop not due to the temperature drop was taken as the onset of hydrate formation. The temperature when this occurred is denoted as To. The temperature when hydrate formation was at its most rapid was taken as Ta. The value To-Ta can give some indication of the ability of the polymer to inhibit hydrate crystal growth. Results are given in Table 2. Each test was repeated 5-10 times. Individual To and Ta values varied by maximum 10-15% of the average but sufficient tests were carried out to obtain statistically significant performance comparisons and a rough ranking order for a series of additives.

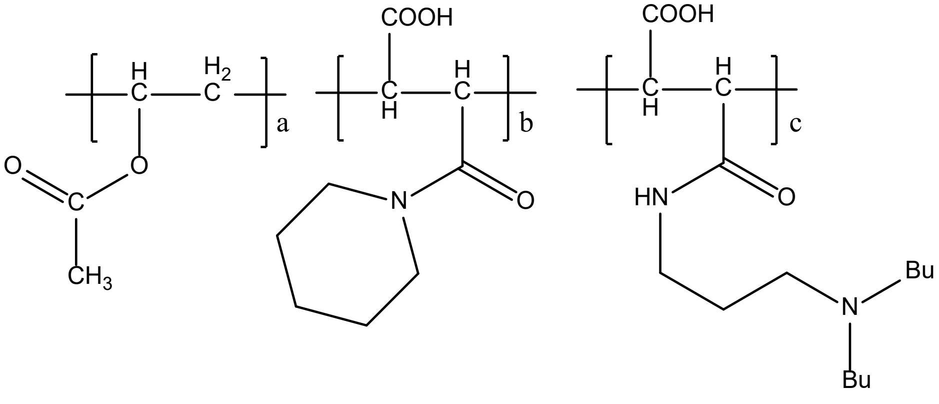


Figure 6. Structure of VA:MA-60% cHex-40% DBAPA, a terpolymer from reaction of vinyl acetate:maleic anhydride copolymer with cyclohexylamine and 3,3-di-n-butylaminopropylamine.

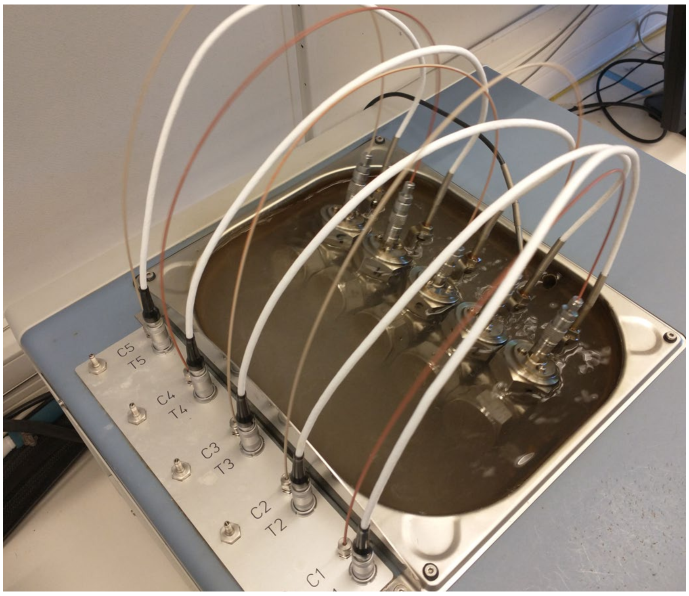


Figure 7. High-pressure rocking cell equipment showing the five steel cells at maximum rock position in the temperature-controlled bath.

Table 1. Composition of the synthetic natural gas (SNG) mixture.

Component	Mol %
N2	0.11
CO_2	1.82
n-butane	0.72
iso-butane	1.65
propane	5.00
ethane	10.30
methane	80.40

With no additive the average onset temperature (Av. To) was 17.1 ºC which is about 3.4 ºC below the equilibrium value for sII hydrate formation. This is a typical result due to the stochasticism of hydrate formation. With the commercial PVCap the To value dropped to 9.7 ºC on average. But when 500ppm of the imidazoline corrosion inhibitor was added to the PVCap the average To value rose to 11.9 indicating an adverse effect of the imidazoline surfactant on the KHI performance (Table 1). By itself 2500ppm imidazoline has negligible KHI effect.

Table 2. Slow constant cooling KHI test results with 2500ppm polymer unless otherwise stated.

Additive	Av. To / ºC	Av Ta / ºC
No additive	17.1	16.9
PVCap	9.7	9.4
Imidazoline	17.6	17.5
PVCap + 500ppm imidazoline	11.9	9.0
VA-MA-iBu	10.2	9.9
VA:MA-40% cHex-60% DBAPA	6.2	5.5

Knowing the types of functional groups that are used in film-forming CIs, we were interested to test the corrosion inhibition performance of the copolymer VA:MA-40% cHex-60% DBAPA and compare it to commercial CIs. To do this we carried out corrosion tests under two sets of conditions.

3. Corrosion inhibitor testing equipment and procedures under mild conditions

3.1 Equipment

The bubble testing equipment provided by Gamry Instruments consists of a 1 litre glass kettle, a three-electrode system, and an external computer containing a potentiostat to perform and record the Linear Polarization Resistance (LPR) measurement of the corrosion process. The system is schematically illustrated in Figure 8. The three-electrode system consists of a working electrode, that holds the 5cm^2 C1018 mild steel metal sample that is being analysed, a counter electrode, and reference electrode. The working electrode is a cylindrical assembled mechanism that consists of a threaded stainless-steel rod in the centre, which is inserted into a Pyrex glass tube and sealed off with Teflon gaskets and rubber seals. The metal sample is screwed onto the tip-end of the stainless-steel rod and the electrode from the potentiostat is connected to the opposite end. The reference electrode is a liquid junction Ag/AgCl electrode saturated with KCl with a potential of 199mV vs. NHE. The counter electrode is a cylindrical spectroscopic graphite rod with an area of 120 cm^2 counter electrode, and reference electrode, where the working electrode holds the C1018 mild steel metal sample that is being analysed.

3.2 Test procedure

The glass container was filled with 800 ml 3.6 % NaCl brine solution and saturated with 99.9% vol. CO_2-gas by introducing it through a gas dispersion tube directly into the solution at a high gas flow rate. (The O_2 content is < 0.1 ppm according to the supplier which may cause some interference from O_2 corrosion). This was accompanied by stirring at approximately 250-300rpm for at least 30 min before testing. To ensure a proper CO_2-gas saturation the pH of the test solution was checked and maintained at pH = 4-5 due to the production of carbonic acid. When this is achieved, the stirring rate is lowered to 200 rpm, and electrodes inserted. The corrosion inhibitor solution was inserted with a syringe, and the LPR measurement initiated approximately 5min after inserting the inhibitor. A photo of the complete bubble testing equipment is given in Figure 9.

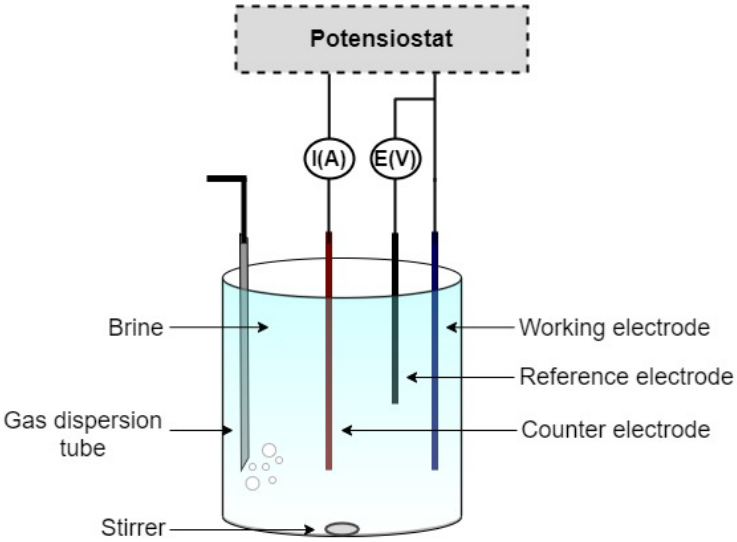


Figure 8. Schematic illustration of the bubble testing equipment.

The LPR measurement was carried by introducing a potential to the metal sample of ±20 mV relative to the metal sample's open circuit potential (E_{OC}). This induced a current to flow through the metal sample surface due to the change in potential to the overall system. A positive current would indicate an oxidation reaction and a negative current would indicate a reduction [67].

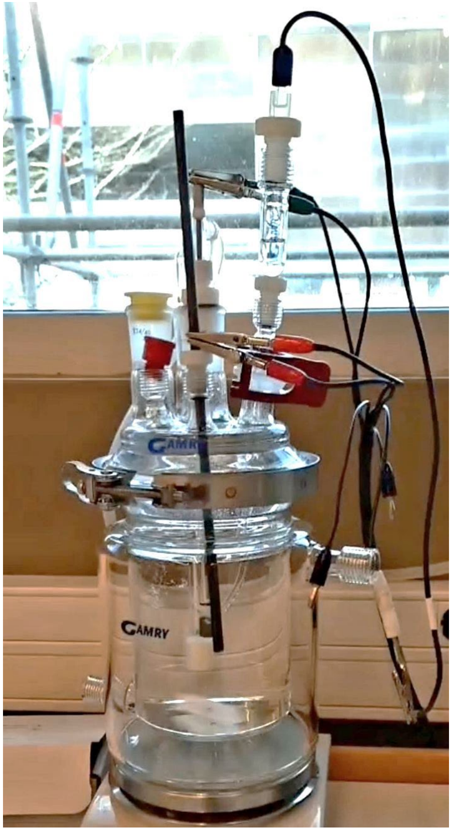


Figure 9. The assembled electrochemical bubble test cell for CO_2 corrosion inhibitor testing.

The applied potential and responding current were continuously controlled and sampled by the potentiostat, which can be represented as a current (I) versus voltage (V) graph. The final graph illustrates the overall corrosion behaviour of the metal with the amount of current generated corresponding to the metal sample's resistance towards corrosion when the introduced potential changes [70]. By using the Stern-Geary equation (1) a more simplified relationship (2) is implied. The relationship states that the applied potential (ΔE) corresponds to the current generated (ΔI). This can then be used to estimate the polarization resistance (R_P) and approximate the corrosion rate of the metal sample to the given environment to which it is exposed [67-68].

$$(1)\ R_P = \frac{\beta_a * \beta_c}{2{,}303 * I_{corr} * (\beta_a + \beta_c)}$$

$$(2)\ R_P = \frac{\Delta E}{\Delta I}$$

When the test is completed and the graph is created, the data are analysed linearly with a voltage range of ±5 mV over the metal samples E_{OC}, which corresponds to the metal samples' corrosion potential (E_{corr}) as illustrated in Figure 10.

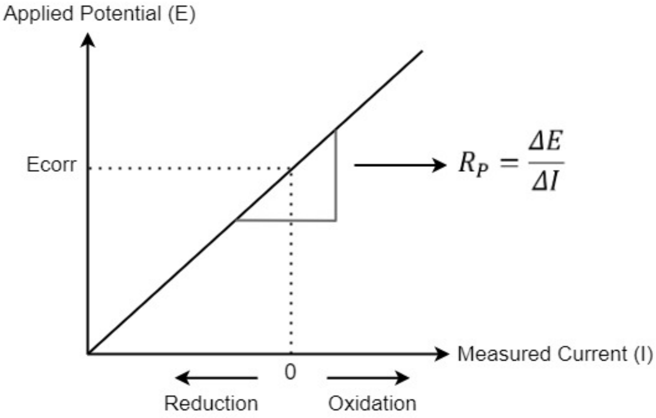


Figure 10. Illustration of LPR measurement curve.

A minimum of 5 LPR measurements was manually repeated in a 30min time-interval to get a consistent measurement sequence of the given system. The measuring sequence on the given system was repeated in replicated environmental conditions to ensure that the collected data was close to constant. Since the metal sample surface morphology alternates to some extend during each LPR measurement, this procedure was observed to provide with smoother alternation of the collected data readings and made it easier to detect sudden anomalous readings if it were to occur.

3.3 Analysis of corrosion data results

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. Since this could make the estimated corrosion rate measurement to be inaccurate, any anomalous measurements were excluded from the overall corrosion rate analysis. The estimated corrosion rate of minimum 15 measurements was used to make a test number versus corrosion rate graph for a visual representation of how the corrosion behaviour present itself. This graph was constructed individually in both the absence and presence of CI, making it possible to perform a visual comparison of the CI performance to a blank baseline. The degree of deviation in each constructed graph is evaluated by using the R^2 value.

To perform more quantitative analysis, the percent CI efficiency (%η) was calculated through the mathematical equation:

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

where $X_0 = 2.743$ mm/year was the worst-case corrosion rate without added CI, and the X_1 the corrosion rate with the CI added. This gives an indication of how well the additive inhibits the corrosion process, meaning that a high %η indicates a good inhibition performance [69-70].

3.4 Discussion of corrosion test results

Three products were tested for corrosion inhibition in this study, a commercial KHI, PVCap, a commercial imidazoline surfactant corrosion inhibitor and the maleic terpolymer that showed excellent KHI performance, VA:MA-40% cHex-60% DBAPA (Figure 11).

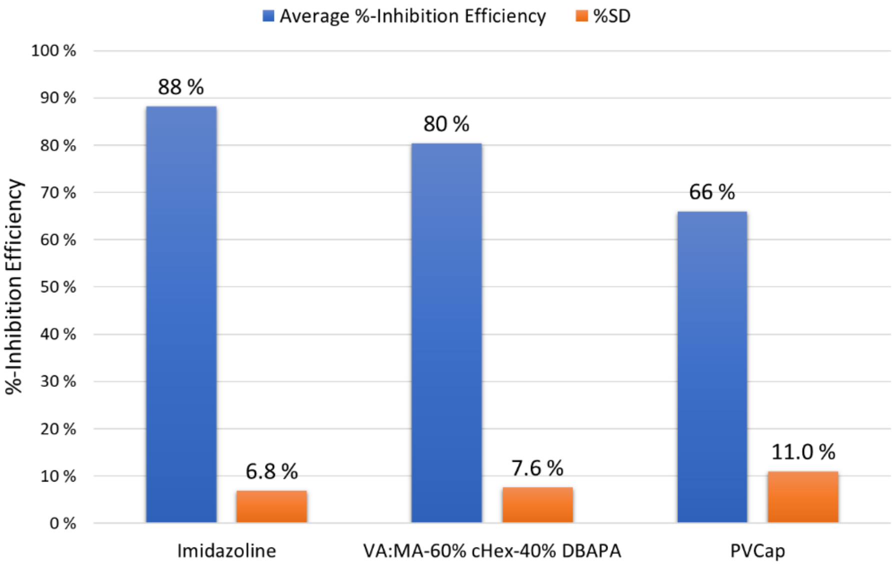


Figure 11. Corrosion inhibition efficiency and standard deviation (SD) for chemicals tested in this study.

4. Corrosion inhibitor testing equipment and procedures under high salinity conditions

The next step of our work was corrosion studies using carbon steel AISI 1023 coupons at high salinity conditions for the commercial inhibitor and synthesized copolymer VA:MA-40% cHex-60% DBAPA.

4.1 Equipment

Electrochemical measurements were carried out using the ZIVE SP2 workstation. The cell was a glass vessel with a volume of 500 ml with a Teflon lid. A working electrode, a reference electrode, an auxiliary electrode, and a glass tube for supplying carbon dioxide were introduced into the cell through the lid. The surface area of the working electrode was 10 cm^2, the waterline was isolated by varnish. The reference electrode was a silver chloride electrode of EVL-IM3 type. The auxiliary electrode was platinum electrode.

4.2 Test procedure

The bubble test method was used for the measurements. Carbon dioxide was passed through the solution. First, the cell was closed with a lid and CO_2 was purged for 10-15 minutes at a volumetric flow rate of 30 ml/min in each experiment. Then the solution was poured into the cell and injection of CO_2 was continued with the same volumetric flow rate for 20-30 min. After that, the volumetric rate of CO_2 was reduced to 8 ml/min, and electrodes were inserted for making measurements at a room temperature (25 ± 2) ºC.

The values of open-circuit potential (E_{OCP}) were recorded at least for one hour after immersion of inhibitor samples in the solution. E_{OCP} value at the end of immersion was taken for the analysis, if the variation did not exceed 30 mV for last 0.5 hour. Potentiodynamic polarization experiments were carried out by sweeping the working electrode potential ±250 mV away from the E_{OCP} at 1 mV/s scan rate. Anodic and cathodic polarization curves were recorded, that shows the correlation between potential of studied electrode and current density under polarization from external supply source of direct current. From these experiments the kinetic parameters of reaction were determined: corrosion potential and corrosion current, the values of Tafel equation parameters (Tafel slopes). To compensate for the ohmic resistance potential in the solution, a Luggin capillary was used.

A commercial corrosion inhibitor of the amine type Armohib CI-28 (AkzoNobel, Amsterdam, Netherlands) was used for comparison. Corrosion studies were made using carbon steel AISI 1023.

Before experiments the working surface of the electrode was polished by emery paper and washed with distilled water, then with ethanol. [61] The solution was a model of high salinity water with a density of 1.12 g/cm^3 according to the standard GOST 9.506-87. It has the next composition, g/dm^3: $CaCl_2*6H_2O$ - 34.00; $MgCl_2*6H_2O$ - 17.00; NaCl - 163.00; $CaSO_4*2H_2O$ - 0.14. The overall salinity was more than 18 %.

4.3 Corrosion test results at high salinity conditions

Obtained corrosion results are presented in Table 3. According to the experimental data the usage of both reagents causes a decrease in the rates of oxidation and reduction reactions. Increase of concentration of VA:MA-60% cHex-40% DBAPA induces the shift of E_{OCP} to the more positive values from -0.622 V for the 50 ppm solution to -0.532 V for 1000 ppm solution. The similar behavior was observed for the commercial inhibitor Armohib CI-28 as can be seen from Table 3. These results indicate that molecules of both inhibitors are adsorbed on the electrode surface, and the inhibitory effect is caused by an increase in the overvoltage of electrode reactions. For the VA:MA-60% cHex-40% DBAPA, the overvoltage of the electrode reactions was 0.133V, and for the commercial inhibitor Armohib CI-28 it was 0.123V. The corrosion rate is also decreased with the addition of reagents and growth of their concentration. According to the experimental data the minimum corrosion current was observed for the 1000 ppm solution of VA:MA-60% cHex-40% DBAPA (Table 3). The inhibition efficiency of VA:MA-60% cHex-40% DBAPA at this concentration is equal to 96.3% which is significantly higher than for Armohib CI-28 (77.5%). However, after standing in the high salinity water solution for several days (more than 3 days) the anti-corrosion activity of VA:MA-60% cHex-40% DBAPA drops dramatically due to precipitation. This fact requires additional studies which will be done in future.

Table 3. Open-circuit potential (Eocp), Tafel equation parameters (βa, βc) and corrosion current (icorr) values in the presence of commercial inhibitor Armohib CI-28 and maleic terpolymer VA:MA-60% cHex-40% DBAPA of various concentrations.

Inhibitor	Eocp [mV SCE]	βa [V/div]	βc [V/div]	icorr [mA* cm^{-2}]
		1000 ppm		
Armohib CI-28	-542.4	0.046	0.067	0.0018
VA:MA-60% cHex-40% DBAPA	-532	0.061	0.111	0.0003
		500 ppm		
Armohib CI-28	-566.4	0.059	0.186	0.0029
VA:MA-60% cHex-40% DBAPA	-591	0.052	0.059	0.00033
		50 ppm		
Armohib CI-28	-585.9	0.068	0.192	0.0032
VA:MA-60% cHex-40% DBAPA	-622	0.059	0.143	0.00043
		Blank		
	-665	0.062	0.257	0.008

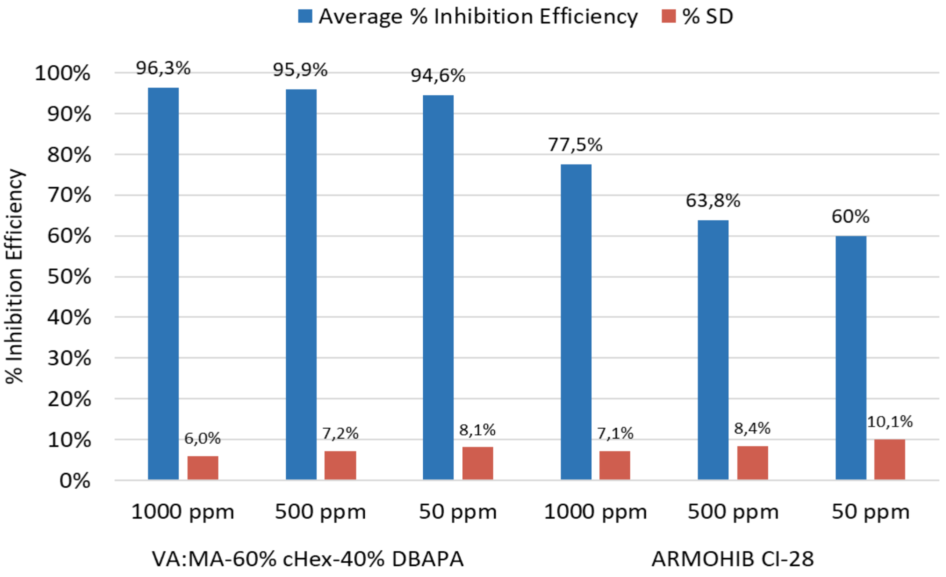


Figure 12. Corrosion inhibition efficiency with standard deviation (SD) for synthesized terpolymer VA:MA-60% cHex-40% DBAPA and commercial inhibitor Armohib CI-28 at different concentrations (50, 500, 1000 ppm) under high salinity conditions.

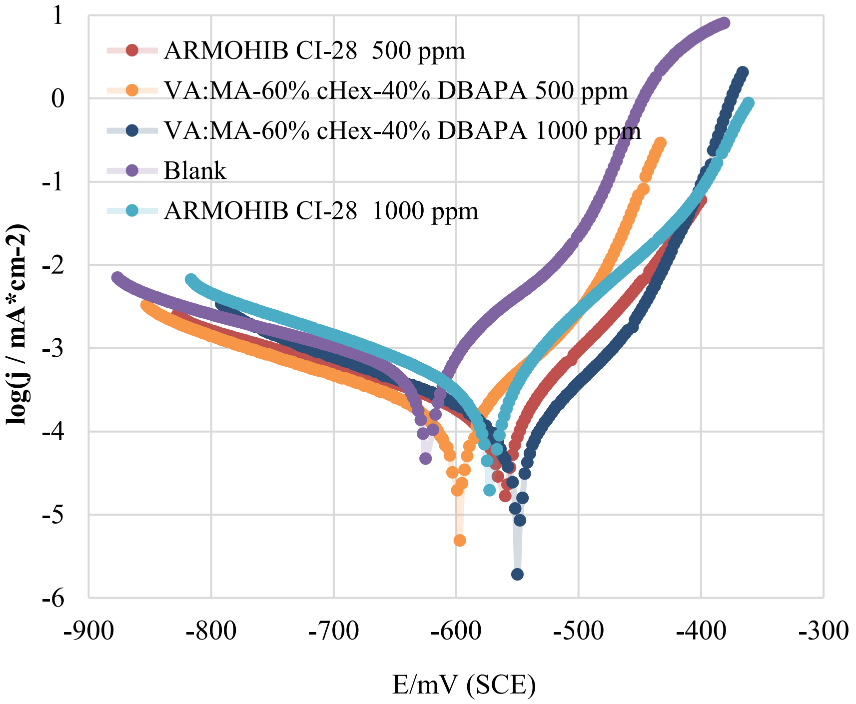


Figure 13. Potentiodynamic polarization curves (Tafel curves) in solutions of synthesized terpolymer VA:MA-60% cHex-40% DBAPA and the commercial inhibitor Armohib CI-28 at different concentrations (500 and 1000 ppm) under high salinity conditions.

The introduction of inhibitors also can affect the limiting stages of electrochemical reactions (dissolution of anodic carbon steel and cathodic reactions of hydrogen evolution), which manifests in a change in the slopes of the Tafel curves (Figure 13). The change in the slopes of the curves in the region of cathodic and anodic polarization is insignificant, which indicates that these compounds can be classified as mixed-type inhibitors.

5. Conclusion

Multi-functional chemicals to treat corrosion, and prevent scale deposition and gas hydrate formation kinetically have been reviewed. No single product to treat all three issues for a wide range of field conditions is currently available. We have synthesized a range of maleic-based copolymers and tested their performance as KHIs as well as their use as film-forming CIs. In slow constant cooling tests, a terpolymer from reaction of vinyl acetate:maleic anhydride copolymer with cyclohexylamine and 3,3-di-n-butylaminopropylamine (VA:MA-60% cHex-40% DBAPA), gave excellent performance as a KHI, better than commercial PVCap. The same terpolymer also gave good CO_2 corrosion inhibition on C1018 steel when measured using bubble test equipment. The performance was significantly better than PVCap but not as good as a commercial imidazoline-based surfactant corrosion inhibitor. At high salinity conditions (more than 18 % salts) the performance of VA:MA-60% cHex-40% DBAPA as CO_2 corrosion inhibitor was better than for commercial inhibitor Armohib CI-28 using carbon steel AISI 1023 coupons. Inhibition efficiency of the new terpolymer was over 90 %. However, it decreased after several days due to reagent precipitation in high salinity water.

We are currently optimizing the polymer to improve its KHI and CI performance as well as building scale inhibition properties into the structure. We will report on these findings in future publications.

Funding

The reported study was funded by The Research Council of Norway and RFBR according to the research project № 20-55-20010.

References

[1] Kelland M A 2014 *Production Chemicals for the Oil and Gas Industry*, 2nd ed.; CRC press: Boca Raton, FL, 2014.

[2] Frenier W F and Ziauddin M, 2014, *Chemistry for Enhancing the Production of Oil and Gas* (SPE Books).

[3] Swanson T A, Petrie M and Sifferman, T R, 2005, The Successful Use of Both Kinetic Hydrate and Paraffin Inhibitors Together in a Deepwater Pipeline with a High Water Cut in the Gulf of Mexico," SPE 93158, *Proceedings of the SPE International Symposium on Oilfield Chemistry*, Houston, TX, February 2–4.

[4] Sloan E D and Koh, C A, 2008, *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL.

[5] Kelland M A, 2006, *History of the development of low dosage hydrate inhibitors*. Energy Fuels **20**, 825−847.

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

[7] Perrin A, Musa O M and Steed J W, 2013, The chemistry of low dosage clathrate hydrate inhibitors. *Chem. Soc. Rev*. **42**, 1996−2015.

[8] Zhukov A Y, Stolov M A, and Varfolomeev M A, 2017 Use of Kinetic Inhibitors of Gas Hydrate Formation in Oil and Gas Production Processes: Current State and Prospects of Development. *Chem. Technol. Fuels Oils* **53**, 377−381.

[9] Shahnazar S, Bagheri S, TermehYousefi A, Mehrmashhadi J, Karim M S A, and Kadri N A, 2018, Structure, mechanism, and performance evaluation of natural gas hydrate kinetic inhibitors. *Rev. Inorg. Chem*. **38**, 1−19.

[10] Kamal, M S, Hussein, I A, Sultan, A S, and von Solms, N, 2016, Application of various water

soluble polymers in gas hydrate inhibition, *Renewable and Sustainable Energy Reviews* 60, 206–225.

[11] Wang, Y, Fan, S and Lang, X, 2019, Reviews of gas hydrate inhibitors in gas-dominant pipelines and application of kinetic hydrate inhibitors in China, *Chinese Journal of Chemical Engineering* **27**, 2118–2132.

[12] Chin Y D, Srivastava, A, 2018, Advances in LDHIs and Applications, OTC-28905, *Offshore Technology Conference*, 30 April - 3 May, Houston, Texas, USA.

[13] Makogon, T Y, 2019, *Handbook of Multiphase Flow Assurance*, Elsevier Science & Technology.

[14] Saji V S and Umoren, S A, Eds., 2018, *Corrosion Inhibitors in the Oil and Gas Industry*, Wiley-VCH.

[15] Olajire A A, 2017, Corrosion inhibition of offshore oil and gas production facilities using organic compound inhibitors - A review. *J. Molecular Liquids* **248**, 775-808.

[16] Heidersbach R, 2018, *Metallurgy and Corrosion Control in Oil and Gas Production* (Wiley Series in Corrosion) 2nd Edition, Wiley, New Jersey.

[17] Woie K, 2011, *A study of the interaction between a kinetic hydrate inhibitor and selected corrosion inhibitors*, Master Thesis, University of Stavanger, Norway.

[18] Pakulski M, 2007, Accelerating Effect of Surfactants on Gas Hydrates Formation, SPE 106166, *International Symposium on Oilfield Chemistry*, Houston, TX, February 28-March 2.

[19] Menendez C M, Jardine J, Mok W Y, Ramachandran S, Jovancicevic V, Bhattacharya A, 2014, New Sour Gas Corrosion Inhibitor Compatible with Kinetic Hydrate Inhibitor. *International Petroleum Technology Conference*, Doha, Qatar, Jan 19−22, IPTC: Kuala Lumpur, Malaysia.

[20] Moloney J, Mok W Y, Gamble C G, 2009, Compatible Corrosion and Kinetic Hydrate Inhibitors for Wet Sour Gas Transmission Lines. In *CORROSION 2009*, Atlanta, GA, March 22−26, 2009; NACE International, Document no. NACE-09350.

[21] Obanijesu E O, Gubner R, Barifcani A, Pareek V, Tade M O, 2014, The influence of corrosion inhibitors on hydrate formation temperature along the subsea natural gas pipelines. *J. Pet. Sci. Eng.* **120**, 239−252.

[22] Moore J A, 2009. Understanding Kinetic Hydrate Inhibitor and Corrosion Inhibitor Interactions. *Proceedings of the Offshore Technology Conference*, Houston, TX, May 4−7, OTC, Richardson, TX.

[23] Anderson J and Clark, L W, 2006 Development of Effective Combined Kinetic Hydrate Inhibitor/Corrosion Inhibitor (KHI/CI) Products, *Proceedings of the 5th International Conference on Gas Hydrates,* Trondheim, Norway, June 12–16.

[24] Fu, B, 2007, Development of Non-interfering Corrosion Inhibitors for Sour Gas Pipelines with Co-injection of Kinetic Hydrate Inhibitors, Paper 07666, NACE CORROSION Conference, Nashville, TN, March 11–15.

[25] MacDonald A W R, Petrie, M, Wylde J J, Chalmers A J and Arjmandi, M, 2006, Clariant Oil Services, Field Application of Combined Kinetic Hydrate and Corrosion Inhibitors in the Southern North Sea: Case Studies, SPE 99388, *SPE Gas Technology Symposium*, Calgary, Alberta, Canada, May 15–17.

[26] Moloney J, Mok W, Gamble C, 2008, Corrosion and Hydrate Control in Wet Sour Gas Transmission Systems, SPE 115074, *SPE Asia Pacific Oil and Gas Conference and Exhibition*, Perth, Australia, October 20–22.

[27] Moore, J A, Ver Vers L, and Conrad, P, 2009, Understanding Kinetic Hydrate Inhibitor and Corrosion Inhibitor Interactions, SPE 19869, *Offshore Technology Conference*, Houston, TX, May 4–7.

[28] Garming, J F, Anthony J, de Vries G J, Morales N L, Webber, P A and Trompert, R A, 2013, A Mature Southern North Sea Asset Considers Conversion to Wet Gas Operation which Requires the Development of Compatible and Novel Chemistries for Flow-Assurance and Asset Integrity, 24092, *Offshore Technology Conference*, Houston, TX, May 6–9.

[29] Alapati R, Sanford E, Kiihne E, Vita E, 2010, Proper Selection of LDHI for Gas Condensate

Systems, in the Presence of Corrosion Inhibitors. OTC 20896. *Offshore Technology Conference*, Houston, Texas, May 3-6.
[30] Tian, J, Bailey, C, Fontenot J F and Nicholson, M, 2011, Low Dosage Hydrate Inhibitors (LDHI): Advances and Developments in Flow Assurance Technology for Offshore Oil and Gas Productions, OTC 21442, *Offshore Technology Conference*, Houston, TX, May 2–5.
[31] Abla M. I, Breshears J D, Hoots J E, Moloney J, Scott A, Webber P A, 2020, U.S. Patent Application, 20200166458.
[32] Tiu B D B, Advincula R C, 2015, Polymeric corrosion inhibitors for the oil and gas industry: Design principles and mechanism, *Reactive and Functional Polymers* **95**, 25–45.
[33] Hellberg, P-E, Gorochovceva N, 2011, Polymeric Corrosion Inhibitors, International Patent Application WO/2011/000895.
[34] Hellberg P-E, Gorochovceva N, 2012, Polymeric Corrosion Inhibitors, International Patent Application WO/2012/028542.
[35] Hellberg P, 2011, Environmentally Acceptable Polymeric Corrosion Inhibitors, SPE 140780, SPE International Symposium on Oilfield Chemistry, 11-13 April, The Woodlands, Texas, USA.
[36] Carter C G and Jovancicevic V, 1992, U.S. Patent 5135681.
[37] Carter C G, Jovancicevic V, Hartman J A and R. P. Kreh, 1992, U.S. Patent 5183590.
[38] Carter C G, Fan, L-D G, Fan, J C, Kreh R P and Jovancicevic V, 1994 U.S. Patent 5344590.
[39] Becker H L, 2012, US Patent Application 20100105580. H. L. Becker, U.S. Patent 8114819.
[40] Buyuksagis A, Cicek, H Y, Butun V, 2019, Tertiary Amine Methacrylate based Polymers as Corrosion Inhibitors in Double Distilled Water. Part I *Protect. Met. Phys. Chem Surf.* **55** (5), 951-962.
[41] Qiu S, Zhao H and Wang L, 2018, Facile preparation of soluble poly(2-aminothiazole)-based composite coating for enhanced corrosion protection in 3.5% NaCl solution, *Surface Topography: Metrology and Properties,* **6**, 3.
[42] Masoudi R and Tohidi, B, 2006, Experimental Investigation on the Effect of Commercial Oilfield Scale Inhibitors on the Performance of Low Dosage Hydrate Inhibitors (LDHI), Proceedings of the 5th International Conference on Gas Hydrates, Trondheim, Norway, June 12–16.
[43] Magnusson C D, Kelland M A, 2015, Nonpolymeric Kinetic Hydrate Inhibitors: Alkylated Ethyleneamine Oxides. *Energy Fuels* **29**, 6347−6354.
[44] Macedo R G M D, Marques N D, Tonholo J, Balaban R D, 2018, Water-soluble carboxymethylchitosan used as corrosion inhibitor for carbon steel in saline medium, Carbohydrate Polymers, **205**, 371-376.
[45] McMahon J and Harrop D, 1995, Green corrosion inhibitors – An oil company perspective, Paper 32, *NACE CORROSION Conference*, Orlando.
[46] Bain, D I, Fan, G, Fan J and Ross, R J, 1999, Scale and Corrosion Inhibition by Thermal Polyaspartates, Paper 120, *NACE CORROSION Conference*.
[47] Benton W J and Koskan, L P, 1997, U.S. Patent 5607623.
[48] Craddock H A, Caird S, Wilkinson H and Guzmann, 2006, A New Class of 'Green' Corrosion Inhibitors: Development and Application, SPE 104241, *SPE International Oilfield Corrosion Symposium,* Aberdeen, UK, May 30.
[49] Guzmann, M, Ossmer H and Craddock H. 2007, International Patent Application WO/2007/063069.
[50] Obeyesekre, N, Naraghi A and McMurray, J S, 2001, Synthesis and Evaluation of Biopolymers as Low Toxicity Corrosion Inhibitors for North Sea Oil Fields, Paper 1049, *NACE CORROSION Conference*, Houston, TX, USA.
[51] Fan, J C, Fan L-D G and Mazo, J, 2000, International Patent Application WO/2000/075399.
[52] Wang C, Chen, J H, Han J, Wang C B, Hu B S, 2019, Enhanced corrosion inhibition performance of novel modified polyaspartic acid on carbon steel in HCl solution, *J. Alloys and Compounds*, **771**, 736-746.
[53] Chen J X, Wang C, Han J, Hu B S, Wang C B, Zhong Y L, Xu H, 2019, Corrosion inhibition

performance of threonine-modified polyaspartic acid for carbon steel in simulated cooling water. *J. Appl. Polym. Sci.* **136**, 15.

[54] Schmitt G and Saleh, A O, 2000, Evaluation of Environmentally Friendly Corrosion Inhibitors for Sour Service, Paper 335, *NACE CORROSION Conference*, Orlando, FL, USA.

[55] Tang J, Cunningham R T and Yang B, 1998, U.S. Patent 5750070.

[56] Tang J, Fu S-L and Emmons D H, 2000, U.S. Patent 6022401.

[57] Musa O M and Lei C C, 2013, Polymers having acid and amide moieties, and uses thereof, U.S. Patent Application US20130123147 A1.

[58] Musa O M and Lei C C, 2012, Polymers having N-vinyl amide and hydroxyl moieties, their compositions and the uses thereof, U.S. Patent Application US20120077717 A1.

[59] Sheng Q, da Silveira K C, Tian W, Fong C, Maeda N, Gubner R, Wood C D, 2017, Simultaneous hydrate and corrosion inhibition with modified Poly(vinyl caprolactam) polymers. *Energy Fuels* **31**, 6724−6731.

[60] Park J, Kim H, Sheng Q, Wood C D, Seo Y, 2017, Kinetic Hydrate Inhibition Performance of Poly(vinyl caprolactam) Modified with Corrosion Inhibitor Groups, *Energy Fuels* **31**, 9363−9373.

[61] Pavelyev R S, Zaripova Y F, Yarkovoi V V, Vinogradova S S, Razhabov S, Khayarov K R, Nazarychev S A, Stoporev A S, Mendgaziev R I, Semenov A P, Valiullin L R, Varfolomeev M A, Kelland M A, 2020, Performance of Waterborne Polyurethanes in Inhibition of Gas Hydrate Formation and Corrosion: Influence of Hydrophobic Fragments. *Molecules* **25** (23), 5664.

[62] Farhadian A, Varfolomeev M A, Rahimi A, Mendgaziev R A, Semenov A P, Stoporev A S, Vinogradova S S, Karwt R, Kelland M A, 2021, Gas Hydrate and Corrosion Inhibition Performance of the Newly Synthesized Polyurethanes: Potential Dual Function Inhibitors. *Energy Fuels* **35**, 6113−6124.

[63] Ul-Haq I, Abdullah A, Al-Eid M, Al-Ajwad H A, 2021, Acryloyl based polymers with active end cap as corrosion inhibitors, International Patent Application WO2021119114.

[64] Ulhaq, M I, Al-Eid, M, Al-Malki A, Elanany, M, Ali S A, Ajwad, H A, Saleem, Q, Panda, S K, Alawan, N A, 2020, Synthesis and Evaluation of a New Acryloyl-Based Copolymer as Kinetic Hydrate Inhibitor for Sour Gas Environments. *Energy Fuels* **34**, 11, 13580–13587.

[65] Kelland M A, Klug P, 1998, Additives for inhibiting gas hydrate formation, International Patent Application 98/23843.

[66] Zhang Q, Kelland M A, 2021, A new investigation of polymaleamides as kinetic hydrate inhibitors – Improved performance and compatibility with high salinity brines. *Chem. Eng. Sci*. **241**, 116719.

[67] Tait, W S, 1994, *An introduction to electrochemical corrosion testing for practicing engineers and scientists*. Racine, Wisc: PairODocs Publ.

[68] Durrani F, Wesley R, Srikandarajah V, Eftekhari M, Munn S, 2020, Predicting Corrosion rate in Chilled HVAC Pipe Network: Coupon vs Linear Polarisation Resistance Method, *Engineering Failure Analysis* **109**, 104261.

[69] Abbasov, V M, Abd El-Lateef H M, Aliyeva L I, Qasimov E E, Ismayilov I T, Khalaf, M M, 2013, A study of the corrosion inhibition of mild steel C1018 in CO2-saturated brine using some novel surfactants based on corn oil, *Egyptian Journal of Petroleum* **22** (4), 451–470.

[70] Kousar M, Walczak M S, Ljungdahl T, Wetzel A, Oskarsson H, Restuccia P, Ahmad E A, Harrison N M, Lindsay R, 2021, Corrosion inhibition of carbon steel in hydrochloric acid: Elucidating the performance of an imidazoline-based surfactant, *Corrosion Science* 1**80**, 109195.