# Model Compound Study of the Mitigative Effect of Crude Oil on Pipeline Corrosion

*F. Ayello,[*] W. Robbins,[**] S. Richter,[‡,**] and S. Nešić[**]*

## ABSTRACT

*Internal corrosion of crude oil pipelines can lead to spills that can be very costly, both financially and environmentally. The corrosion is controlled mostly by mitigation methods, such as through design or by the use of corrosion inhibitors. However, it has been observed that some, but not all, crude oils can have an inhibitive effect on their own. There are different mechanisms for crude oils to mitigate corrosion, such as inhibition through the water phase by inhibitor-like molecules native to the crude oil, wettability alteration from water wet steel surface to oil wet, thereby limiting the access of the water to the surface, or by lowering the interfacial tension between oil and water and facilitating dispersion of water in oil, which reduces the likelihood of corrosion by keeping the water from being in contact with the steel surface. Model compounds representative of the naturally occurring surface-active compounds commonly found in crude oil were tested for their effect on corrosion inhibition, wettability alteration, and interfacial tension. It was found that the structure of the compound rather than the type of head group had the largest effect on its efficiency, especially for corrosion inhibition, while the type of head group had a larger effect on the surface wettability and interfacial tension.*

*KEY WORDS: contact angles, corrosion inhibition, crude oil, interfacial tension, multiphase flow, surface-active compounds, wettability*

## INTRODUCTION

Pipelines carrying crude oil can corrode internally as a result of the presence of water in the produced fluid. The corrosion can be mitigated with corrosion inhibitors, but, in some cases, uninhibited lines are protected from corrosion because of the crude oil itself. However, this is not the case for every crude oil; although some crude oils can lower the corrosion rate even when the water cut,[1] which is the volumetric ratio of water in the liquid phase, is 99%. There are also crude oil pipelines that corrode at water cuts as low as 2%.[2]

Efird and Jansinski[3] found that the degree of corrosion inhibition of crude oils varies and suggested that it was from the chemical composition of the oil. Later, Efird, et al.,[4] took the steel wettability into an account as well, i.e., whether oil or water wetted the steel surface by measuring the corrosion rate at a range of water cuts. Smart[5] suggested that oxygen-, sulfur-, and nitrogen-containing compounds to be the crude oil compounds responsible for wettability alteration along with other polar surface-active compounds such as amines and asphaltenes, but until now no systematic study has been performed to confirm this.

It has long been established that surface-active compounds, such as inhibitors, adsorb on the metal surface[6] to form an organic protective film leading to corrosion inhibition.[7] It also has been shown that sur-

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face-active compounds can induce a wettability alteration (from water wet to oil wet) on iron carbonate[8] and pipeline steel[9] substrates. By promoting wettability alteration from water wet to oil wet, crude oils can promote protection from corrosion by hindering water from coming into direct contact with the steel to initiate the corrosion process.

Vera and Hernandez[10] pointed out that oil-water flow patterns can depend on the properties of the crude oil. There are two dominant flow patterns in oil-water pipeline flow, stratified and dispersed. For oil, continuous flow corrosion is more prevalent in stratified flow since the water flows freely at the bottom of the pipe, while in dispersed flow the water is entrained in the flowing oil phase. The transition between stratified and dispersed flow depends on the force balance between the turbulence in the flow, which acts to break up the water phase into smaller droplets, and the interfacial tension, which opposes the break-up process.[11] The surface-active compounds can accumulate at the oil-water interface, lowering the oil-water interfacial tension[12] and promote dispersion[13] by facilitating the break-up process, and, in some cases, can even stabilize emulsion.[14]

Efforts have been made to decipher which components from crude oils promote corrosion inhibition. The task is made more complicated by the fact that crude oils can differ substantially in their composition or characterization. For instance, crude oils classified as paraffinic did not seem to contribute to the corrosion inhibition in the same way as asphaltenic crude oils,[15] although in both cases, resins, asphaltenes, and the presence of sulfur and nitrogen compounds were implicated as being corrosion-inhibitive. A later study identified nitrogen- and oxygen-containing compounds as inhibitive species capable of partitioning to the water phase.[16] Stroe, et al.,[17] found that mainly nitrogen-containing "inhibitor-like" compounds passed from the oil to the water phase, and although increased partitioning correlated with increased corrosion inhibition, it was not possible to relate the corrosion inhibition to the total nitrogen content of the crude oil.

A different approach than testing whole crude oils is to select model compounds that are representative of crude oil compounds. Although this approach makes use of a much simplified system compared to testing whole crudes, it provides information about the contribution of specific groups of chemicals. Previously, the corrosion inhibition and wettability effect of asphaltenes was studied[18] using this methodology; in this paper, results from other surface-active compounds are presented. Model compounds of surface-active compounds were selected to represent oxygen-, sulfur-, and nitrogen-containing compounds, and they were tested for corrosion inhibition, wettability, and dispersion of water in oil.

**TABLE 1**

*Elemental Composition of the Mild Steel (C1018) Sample Used as a Rotating Cylinder Electrode for the Electrochemical Corrosion Measurements*

| Element | Weight (%) |
|---|---|
| Mn | 0.83 |
| Si | 0.22 |
| C | 0.19 |
| Cu | 0.16 |
| Ni | 0.16 |
| Cr | 0.13 |
| V | 0.058 |
| Mo | 0.042 |
| Sn | 0.021 |
| Pb | 0.017 |
| P | 0.015 |
| Sb | 0.015 |
| S | 0.013 |
| As | 0.01 |
| Co | 0.007 |
| Al | 0.004 |
| Nb | 0.003 |
| Ca | 0.002 |
| Zr | 0.002 |
| B | 0.0002 |
| Ta | <0.001 |
| Ti | <0.001 |
| Fe | Balance |

## EXPERIMENTAL PROCEDURES

### Materials

The water phase was 1 wt% sodium chloride (NaCl) deionized (DI) water, purged with carbon dioxide ($CO_2$) and adjusted to pH 5 for each test, and the model oil phase was a clear paraffinic, light distillate (LVT200[†]). The steel used for corrosion tests was C1018 (UNS G10180)(1) carbon steel with a chemical composition outlined in Table 1, and the steel used for contact angle tests was API(2) 5L X65 carbon steel.

As a result of the large number of chemical compounds found in crude oil, it is not possible to test every single one of them. However, it is possible to choose model compounds that represent different classes of surface-active compounds found in crude oil: aromatics, and oxygen-, sulfur-, and nitrogen containing compounds. These classes are listed in Table 2 along with their subclasses and the chemical compound chosen to represent each subclass.

Aromatic compounds adsorb onto the steel surface by sharing π-electron density from the aromatic ring with the metal surface.[19] The aromatic chosen for this study is 1,2,3,4-tetrahydronaphthalene, which also is used to dissolve the nitrogen-containing compounds in the model oil.

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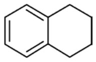
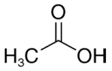
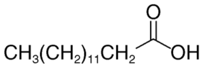
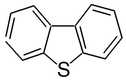
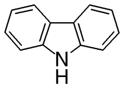
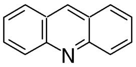
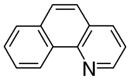
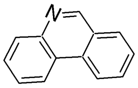
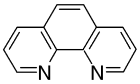
[†] Trade name.

(1) UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

(2) American Petroleum Institute (API), 1220 L Street NW, Washington, DC 2000.

**TABLE 2**

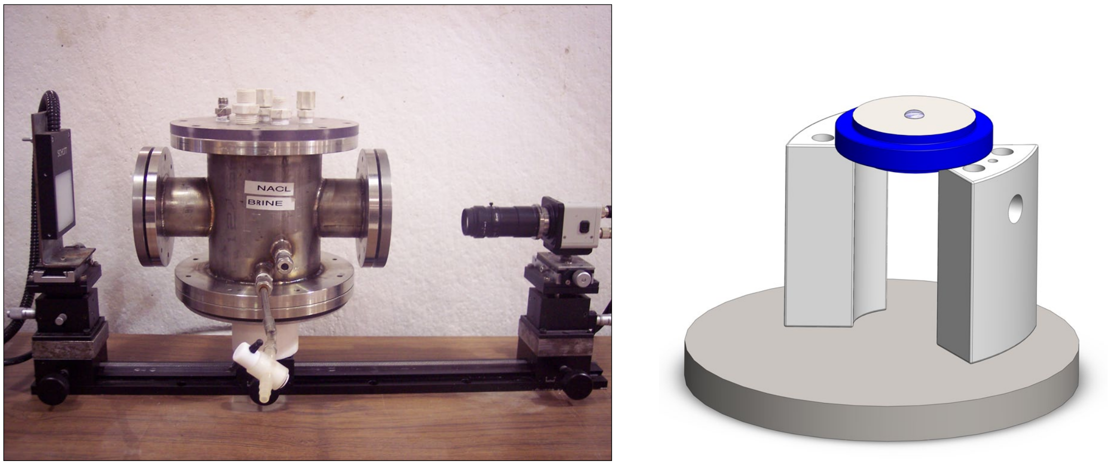
*List of the Surface-Active Compounds Used in the Present Research*

| Description | Chemical Class | Name | Formula | Molecular Structure | Molecular Weight (g/mol) |
|---|---|---|---|---|---|
| Aromatic | Naphthalene | 1,2,3,4-Tetrahydronaphthalene | $C_{10}H_{12}$ |  | 132.2 |
| Oxygen-containing compounds | Short-chain carboxylic acid | Acetic acid | $CH_3COOH$ |  | 60.05 |
| | Long-chain carboxylic acid | Myristic acid | $CH_3(CH_2)_{12}COOH$ |  | 228.37 |
| | Naphthenic acid | Mixture | $(CH_2)_n$–R–COOH<br>R=cyclopentane or cyclohexane, n>12 | Saturated ring structure | ~214 |
| Sulfur-containing compounds | Thiophene | Dibenzothiophene | $C_{12}H_8S$ |  | 184.26 |
| | Sulfides | Dioctyl sulfide | $C_{16}H_{34}S$ | $(CH_2)_7CH_3$–S–$(CH_2)_7CH_3$ | 258.51 |
| | Mercaptans | 1-Tetradecanethiol | $CH_3(CH_2)_{13}SH$ | $(CH_2)_{13}CH_3$–SH | 230.45 |
| Nitrogen-containing compounds | Pyrrolic | Carbazole | $C_{12}H_9N$ |  | 167.2 |
| | Pyridinic | Acridine | $C_{13}H_9N$ |  | 179.2 |
| | | Benzo(h)quinoline | $C_{13}H_9N$ |  | 179.2 |
| | | Benzo(c)quinoline | $C_{13}H_9N$ |  | 179.2 |
| | | Phenanthroline | $C_{12}H_8N_2$ |  | 180.2 |

Carboxylic acids are the type of oxygen-containing compounds with the highest potential for adsorption in crude oil. They adsorb onto the steel surface by the interaction of electron density, as manifested by unshared electron pairs on the oxygen within the molecule, with the metallic surface,[20] blocking the metal's active site and therefore decreasing the corrosion rate. However, not all carboxylic acids are protective and small-chain organic acids are known to increase the corrosion rate,[21] while long-chain organic acids, or naphthenic acids, can induce corrosion protection. Acetic acid ($CH_3COOH$) was used as representative of small molecule organic acids, and myristic acid ($CH_3[CH_2]_{12}COOH$) was chosen to represent long-chain organic acids. The molecular formula used for the naphthenic acids was R–$(CH_2)_n$–COOH, where R represents saturated 5- and 6-membered ring structures, n = 1 to 2, and total C# is >1. In this study, a commercially available mixture of naphthenic acids extracted from diesel distilling cut was tested. Mass spectrometry study of the mixture suggests that 1 to 3 ring structures are prevalent for the naphthenic acid molecules.[22]

Sulfur-containing compounds can adsorb in an analogous fashion as oxygen-containing compounds using unshared electrons. Sulfur-containing compounds are subdivided into two categories: non-polar (sulfide, thiophenes) and polar forms (thiols commonly known as mercaptans).[23] The thiols are more reactive than sulfides because of their polarity and active hydrogen. In sulfur heterocycles (such as the thiophenes), the sulfur atom has only one bond to absorb at the metal surface. Therefore, sulfur heterocycles are less surface-active than sulfides. Dioctyl sulfide, dibenzothiophene, and tetradecanethiol were tested to represent sulfides, thiophenes, and mercaptans, respectively (Table 2).

Nitrogen-containing compounds adsorb in an analogous fashion as both oxygen- and sulfur-containing compounds. They are subdivided into two cat-



(a) (b)

**FIGURE 1.** *(a) Image of the goniometer used for the measurements, including a stainless steel vessel, a camera, and a backlight. (b) A polytetrafluoroethylene (PTFE) holder sits inside the vessel of the goniometer and serves to hold the carbon steel sample, which is used as a substrate for the contact angle measurement.*[24]

egories: pyridinic forms (known as basic nitrogen), which accounts for about a third of the nitrogen compounds found in the crude oil, and pyrrolic forms (known as neutral nitrogen), which accounts for two-thirds of the nitrogen compounds.[23] Acridine was originally chosen to represent pyridinic compounds and carbazole to represent pyrrolic compounds (Table 2). Additional pyridinic compounds were tested after the preliminary results for acridine showed exceptional corrosion inhibition; these were benzo(h)quinoline, benzo(c)quinoline, and phenanthroline.

## *Corrosion Measurements*

A 2 L glass cell apparatus mounted with a rotating cylinder electrode (RCE), with a surface area of 5.3 cm$^2$, was used for the corrosion measurements. The experimental setup has been described in detail in a previous publication[18] and consists of a three-electrode system, including a 15 mm diameter carbon steel rotating cylinder working electrode, a silver/silver chloride (Ag/AgCl) reference electrode, and a platinum counter electrode.

At the beginning of each test, 1.8 L of the water phase (1 wt% NaCl in DI water purged with 1 bar $CO_2$ and adjusted to pH 5.0) with deareated sodium bicarbonate ($NaHCO_3$) was prepared, and the C1018 carbon steel working electrode with the chemical composition listed in Table 1 was polished with 400 grit and 600 grit sandpaper and cleaned with acetone ($CH_3COCH_3$) and isopropanol ($C_3H_8O$) in an ultrasonic bath. During testing, the working electrode was rotated (2,000 rpm) in the glass cell.

The surface-active compounds (Table 2) were introduced in the glass cell by adding them to 200 mL of the model oil, which was placed on top of the water phase. The concentration of the compounds is measured in weight percentages, where 0.1 wt% equals 1,000 ppm concentration, to be in a similar range of concentration as commonly found in the native crude oil. The exception is the acetic acid, which was dissolved in the water phase, and the nitrogen-containing compounds, which were dissolved in a 40% tetrahydronaphthalene-model oil mixture. The rotating working electrode was moved subsequently up into the oil phase for 20 min to allow for the adsorption of the surface-active compounds on the metal surface after which the working electrode was moved down into the water phase and the corrosion rate was measured every 5 min using linear polarization resistance (LPR). Baseline tests were conducted by exposing the working electrode to the pure model oil phase as well as the 40% tetrahydronaphthalene-model oil mixture.

The corrosion inhibition (CI [%]) is calculated using the inhibited ($CR_{inh}$ [mm/y]) and the uninhibited ($CR_{uninh}$ [mm/y]) corrosion rates with the following formula:

$$CI = (CR_{uninh} - CR_{inh})/CR_{uninh} \times 100 \qquad (1)$$

## *Contact Angle Measurements*

The contact angle measurements were conducted in a goniometer such as shown in Figure 1(a).[24] The setup includes a stainless steel vessel with windows on either side. A back light lights up the inside of the vessel through a glass window protruding from each side of the vessel allowing the camera to record the evolution of the droplet with time. The vessel is mounted on an adjustable slider to allow for optimal distance for the video camera to capture the image of the droplet. There is a polytetrafluoroethylene (PTFE) holder positioned inside the vessel of the goniometer and the steel sample is mounted on top of the holder (Figure 1[b]). It is possible to measure either

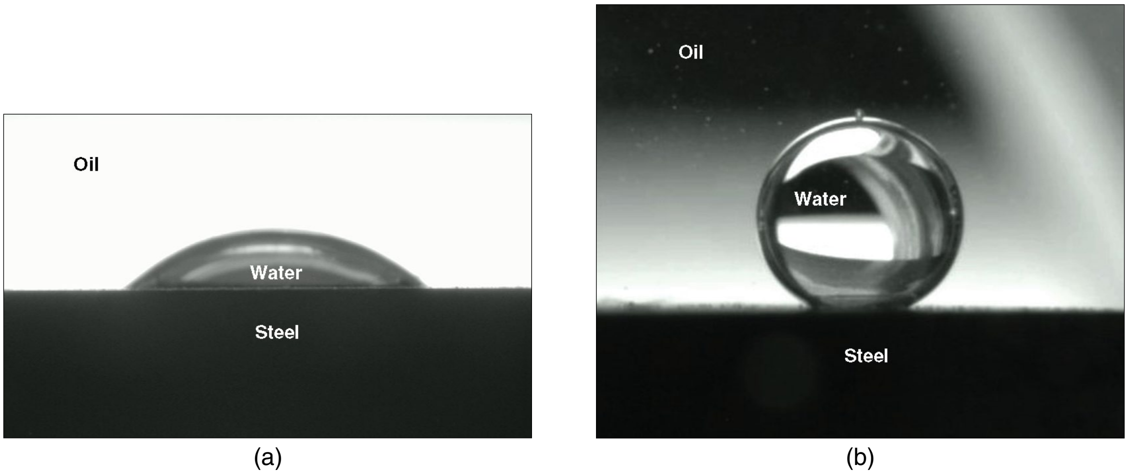


**FIGURE 2.** *Example of a water-in-oil contact angle of (a) hydrophilic (low contact angle) and (b) hydrophobic (high contact angle) surface.*

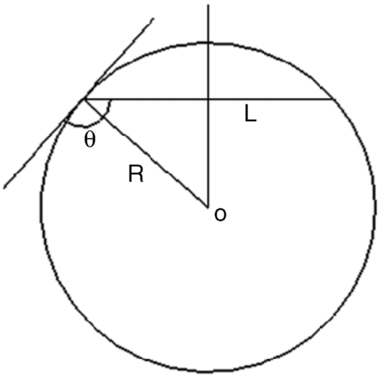


**FIGURE 3.** *Geometric correlation needed to calculate the contact angle. The image shows the oil-in-water configuration of the droplet.*

the water-in-oil contact angle of a water droplet surrounded by the oil phase (Figure 2) or an oil-in-water contact angle of an oil droplet surrounded by the water phase. This has been described in detail in a previous publication.[18]

For a water-in-oil contact angle measurement, the substrate is hydrophilic (Figure 2[a]) if a droplet of water is able to spread out and forms a contact angle less than 90°. The substrate is hydrophobic (Figure 2[b]) if a water droplet has little or no tendency to spread out and forms a contact angle greater than 90°. The contact angle is always measured from the water phase.

The current work was done using water-in-oil contact angles. The preparation of the oil and the water phase was as follows: 1% by weight of surface-active compound was added to 1 L of model oil. The oil phase (model oil, 800 mL) and water phase (1% NaCl, pH 5, 1 bar $CO_2$, 200 mL) were mixed in a beaker for 1 h, then left to settle overnight to equilibrate. A flat carbon steel (X65) sample was cleaned with acetone and polished sequentially with 400 grit and 600 grit sandpaper, then further cleaned with isopropanol in an ultrasonic bath for 2 min. The sample was then dried and immersed in the vessel of the goniometer, which previously had been filled with model oil and purged with $CO_2$. A droplet of water then was added on the top of the sample (Figure 1[b]), and the evolution of the droplet at the metal surface was recorded for 2 h. Baseline tests were conducted by using a pure model oil as well as a 40% tetrahydronaphthalene-model oil mixture.

The contact angle, θ, was calculated using Equation (2) using an imaging analysis software to measure L and R, with R being the radius of the droplet and L the length of the wetted area as shown in Figure 3. Since only the ratio of L and R is important, the unit of measurement is pixels:

$$\theta = 180° - \arcsin\left(\frac{L}{2R}\right) \qquad (2)$$

### *Interfacial Tension Measurements*

The interfacial oil-water tension was measured with a tensiometer using the Du Noüy ring method with a platinum ring. The preparation of the liquid solutions was the same as outlined for the contact angle measurements. The glassware and the platinum ring were rinsed with acetone and isopropanol. The glassware was dried in air while the platinum ring was heated with a flame (holding the ring ca. 1 cm from the flame). The pre-partitioned water phase was poured into the glassware, and the oil phase was carefully poured on top of the water phase. The platinum ring was inserted into the water phase after the oil phase had been placed on top. This helped with the reproducibility of the results without changing the results compared to placing the platinum ring in the water phase before pouring the oil phase on top. The ring was pulled up through the oil-water interface and the tension [mN/m] at which the interface broke was read of the dial on the tensiometer.

## RESULTS AND DISCUSSION

### Corrosion Inhibition Measurements

In this study, carboxylic acids represent the oxygen-containing compounds found in crude oil. While the addition of short-chain acetic acid increased the corrosion rate when added to the water phase (Table 3), the exposure of the steel to the long-chain myristic acid or naphthenic acids dissolved in the oil phase-promoted inhibition (Figure 4).

The baseline values are recorded in a separate test, where the carbon steel working electrode is exposed to the pure model oil phase, before the corrosion rate (Figure 4) is measured in the water phase, producing an average baseline corrosion rate of 0.84 mm/y. This baseline is comparable to the baseline corrosion rate without exposure to model oil, which was recorded at 0.83 mm/y (Table 3). Therefore, it is possible to conclude that the model oil has no effect on the corrosion rate.

The corrosion inhibition of both long-chain myristic acid and naphthenic acid is around 40% at 0.1 wt% concentration as can be seen in Figure 4 and is shown with white markers, but at 1 wt% concentration (black markers) the corrosion inhibition of myristic acid surpassed that of the naphthenic acids, and is 87% compared to 72% for the naphthenic acids. The concentration of naphthenic acids needs to be increased to 10% to produce comparable corrosion inhibition to the myristic acid.

Figure 5 shows the results obtained with the sulfur-containing compounds dibenzothiophene, dioctyl sulfide, and 1-tetradecanethiol for concentrations of 0.1 wt% (shown with white markers) and 1 wt% (shown with black markers). At 0.1 wt% concentration (100 ppm), dibenzothiophene and dioctyl-sulfide are not significantly different from the baseline corrosion. Even at 1 wt% (1,000 ppm) concentration the corrosion inhibition is less than 20%. However, with the addition of 1-tetradecanethiol (a mercaptan), the corrosion rate decreases significantly. Even at 0.1 wt% concentration, 1-tetradecanethiol produces a 40% corrosion inhibition; at 1 wt% concentration, the corrosion inhibition is 82%.

The baseline for the nitrogen-containing compounds is measured after exposure to 40 wt% tetrahydronaphthalene, which is an aromatic used to dissolve both carbazole and acridine in the model oil. The average baseline corrosion rate of the aromatic and model oil mixture is 0.80 mm/y, which is comparable to the 0.84 mm/y baseline after exposure to pure model oil (Figures 4 and 5), showing that the aromatic (tetrahydronaphthalene) has no effect on corrosion. For 0.01 wt% (100 ppm) and 0.1 wt% (1,000 ppm) concentrations of carbazole, there is no corrosion inhibition (Figure 6), while for acridine, there is 80% corrosion inhibition at only 0.01 wt% concentration and more than 99% corrosion inhibition at 0.1 wt% concentration, in which case the LPR polarization resistance, $P_R$, is 40 kΩ.

It is questionable whether the impressive corrosion inhibition obtained with acridine is a characteristic of all pyridinic compounds. Therefore, other pyridinic compounds, namely, benzo(h)quinoline, benzo(c)quinoline, and phenanthroline (Table 2), were

**TABLE 3**

*Corrosion Rate for Acetic Acid Added to the Water Phase (0.1 wt% = 1,000 ppm)*

| Acetic Acid (wt%) | Corrosion Rate (mm/y) |
|---|---|
| 0 | 0.83 |
| 0.001 | 0.90 |
| 0.01 | 1.17 |
| 0.1 | 2.21 |

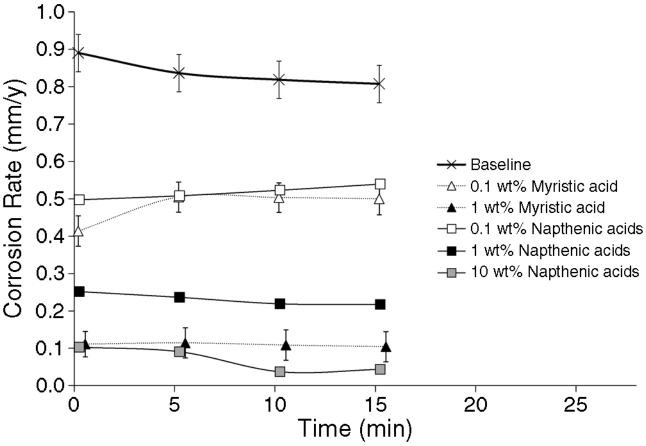


**FIGURE 4.** *Corrosion rate measured with LPR after the steel surface has been exposed to oxygen-containing compounds representative of different forms of carboxylic acids dissolved in model oil.*

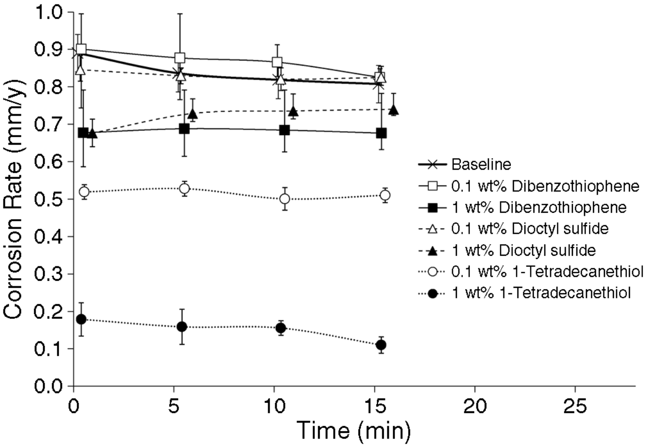


**FIGURE 5.** *Corrosion rate measured with LPR after the steel surface has been exposed to sulfur-containing compounds representative of thiophenes, sulfides, and mercaptans dissolved in model oil.*

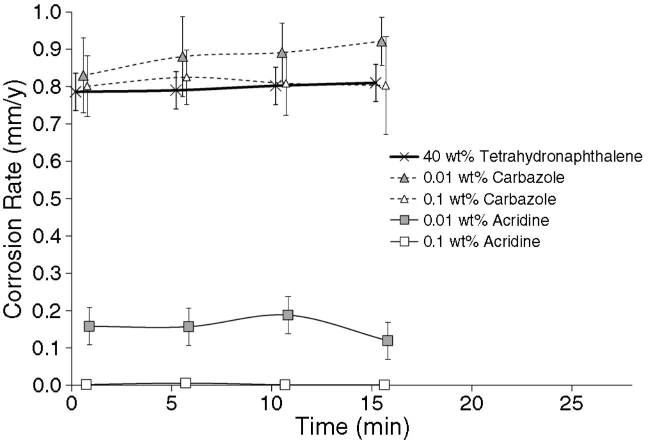


**FIGURE 6.** *Corrosion rate measured with LPR after the steel surface has been exposed to nitrogen-containing compounds representative of pyrrolic and pyridinic compounds dissolved in model oil mixed with an aromatic.*

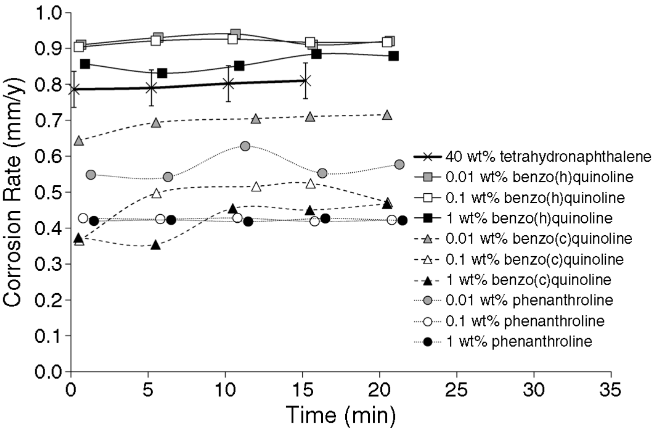


**FIGURE 7.** *Corrosion rate measured with LPR after the steel surface has been exposed to additional pyridinic compounds dissolved in model oil mixed with an aromatic.*

**TABLE 4**

*Synergistic Corrosion Rate for Acridine and Myristic Acid*

| Myristic Acid (wt%) | Acridine (wt%) | Polarization Resistance, $P_R$ (Ω) | Corrosion Rate (mm/y) |
|---|---|---|---|
| 0 | 0.1 | 16,200 | $1.7\times10^{-3}$ |
| 0.1 | 0.1 | 11,400 | $2.5\times10^{-3}$ |
| 1 | 0.1 | 3,560 | $7.9\times10^{-3}$ |

tested as well. The chemical composition of the quinolines is the same as for acridine, but the chemical structure is slightly different. The chemical structure of phenanthroline differs from that of the benzo(h)quinoline by an additional nitrogen atom replacing a CH group on an aromatic ring structure.

The additional pyridinic compounds were tested at 0.01 wt%, 0.1 wt%, and 1 wt% concentrations and the results are given in Figure 7. The benzo(h)quinoline had no corrosion inhibitive behavior, while benzo(c)quinoline and phenanthroline had a modest corrosion inhibition of 50%. The effect of the acridine is therefore more of a steric effect caused by the structure of the acridine compound, allowing the molecules to line up so that the nitrogen atom is adsorbed on the surface, while the aromatic rings align with a π–π bonding between them, in which water molecules cannot penetrate.

Looking at individual compounds is very informative, but crude oils are a complex mixture of thousands of chemicals. It is possible to have a positive or negative synergy between two or more compounds so that the overall corrosion inhibition is more or less than the corrosion inhibition of the individual compounds. Furthermore, surface-active compounds can be acidic or basic, and it is possible these compounds could be neutralized, which could compromise their surface activity.

To test the synergistic corrosion inhibition of an acid and a base, a varying concentration of myristic acid is tested against a constant concentration of acridine (Table 4). The myristic acid does have a negative synergistic effect on the corrosion inhibition of acridine; but, although the corrosion rate has more than quadrupled with a tenfold concentration of myristic acid compared with acridine, the corrosion rate is still in the range of micrometers per year.

### *Contact Angle Measurements*

When a water-in-oil contact angle measurement is performed, the water droplet is deposited on top of the steel surface. As can be seen in Figure 8, the water droplet wets the surface and spreads out slowly until equilibrium is obtained at 58° in this case of pure model oil.

The result of the baseline test shown in Figure 8 is displayed in Figures 9 and 10 along with the results of the water-in-oil contact angles measured for different surface-active compounds added to the oil phase. Figure 9 shows the contact angles measured after 5 min of exposure, while Figure 10 shows the contact angle after a 2 h exposure. Contact angles less than 90° indicate a hydrophilic surface, while contact angles greater than 90° indicate a hydrophobic surface.

For the aromatic compound (tetrahydronaphthalene) the contact angle water-steel remained at 180° for more than 30 s before it started to decrease, reaching 130° after 5 min and a stable value of 60° in less than 2 h, the surface turning from hydrophobic to hydrophilic in the process. The final contact angle of the aromatic is very similar to the one obtained with the model oil on its own, but the time needed to reach the final value is much longer. The aromaticity of tetrohydronaphthalene provides stronger adsorption than possible with only the paraffinic model oil. The straight-chained paraffinic hydrocarbons are only

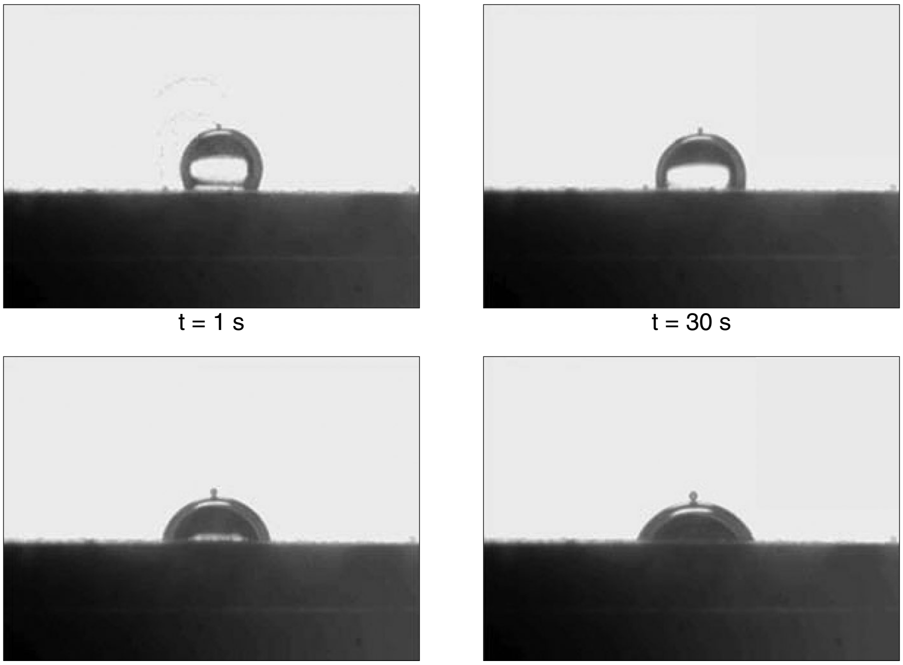

t = 1 s
t = 30 s
t = 180 s
t = 600 s

**FIGURE 8.** *The contact angle of a water droplet in model oil (water-in-oil) at different times (1, 30, 180, and 600 s) showing the spreading of the droplet over a span of 5 min.*

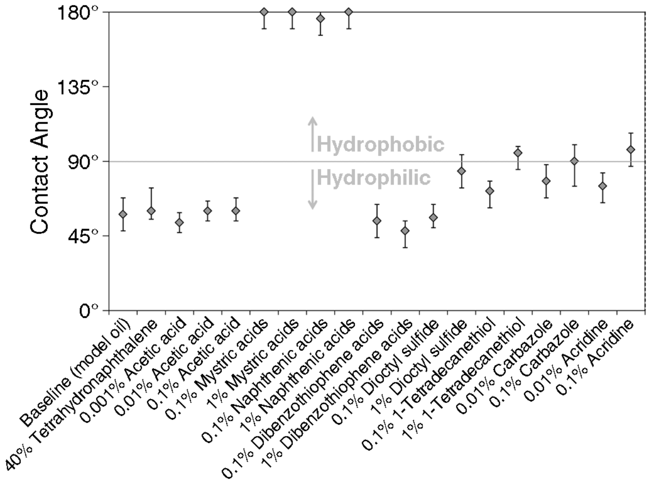


**FIGURE 9.** *Water-in-oil contact angle for different model compounds added to the model oil, with the exceptions of acridine and carbazole added to a mixture of model oil and tetrahydronaphthalene and acetic acid added to the water phase, after 5 min of exposure. All concentrations are in weight percent.*

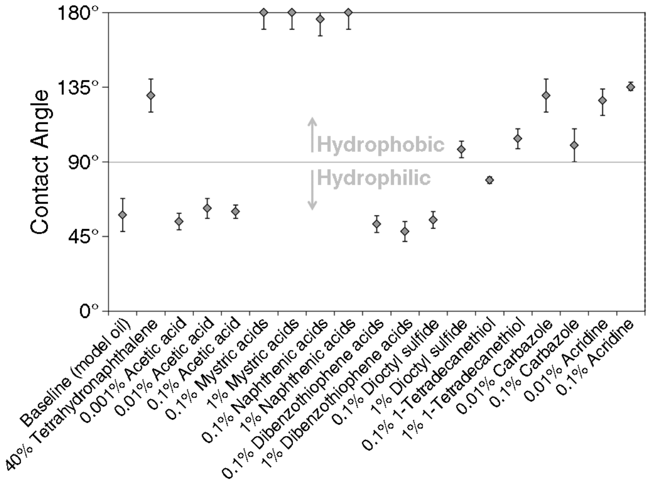


**FIGURE 10.** *Water-in-oil contact angle for different model compounds added to the model oil, with the exceptions of acridine and carbazole added to a mixture of model oil and tetrahydronaphthalene and acetic acid added to the water phase, after 120 min of exposure. All concentrations are in weight percent.*

capable of forming weak van der Waals bonds to the surface, which are not as strong as the π-bonding possible with the aromatic ring structure. However, the π-bonding is not sufficiently strong to keep the surface hydrophobic, and the water phase slowly spreads on the steel surface, displacing the hydrocarbons and making the surface hydrophilic in the process. Because of the length of time it takes for the water to spread on the surface, it can be concluded that in a intermittent oil-water flow when the steel's surface is alternatively wetted with oil and water, aromatic compounds can play a protective role. This protection would be lost in the case of stagnant or stratified flow, since the water eventually would displace the aromatic compounds in the oil.

While acetic acid, representing the small-chain carboxylic acids, does not have an effect on steel wettability, the long-chain carboxylic acid (myristic acid)

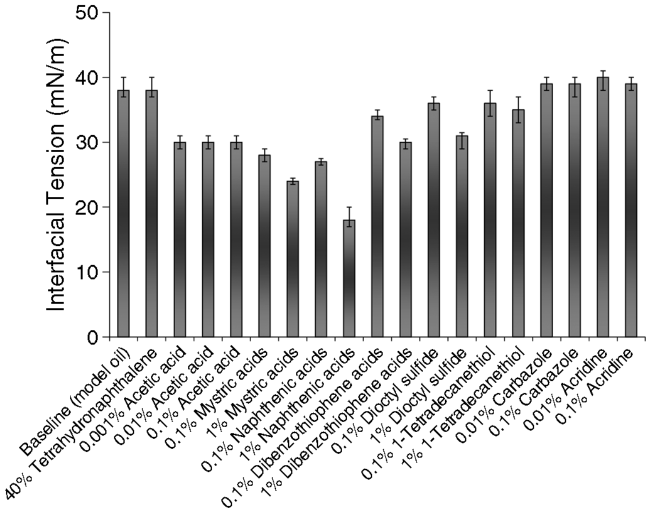


**FIGURE 11.** *Oil-water interfacial tension with the different compounds added to the oil phase with the exceptions of acridine and carbazole added to a mixture of model oil and tetrahydronaphthalene and acetic acid added to the water phase.*

and the cyclic carboxylic acids (naphthenic acids) had a very strong effect on the wettability of the steel, changing the contact angle from 58° to 180°, producing a completely hydrophobic surface. Even after 2 h of exposure, the water droplet never wetted the steel surface.

The effect of sulfur-containing compounds on surface wettability is less than the effect of the long-chain and cyclic carboxylic acids. Dibenzothiophene, which contains a cyclic ring structure just as the naphthenic acids, has no effect on the wettability of the steel, pointing to the importance of the carboxyl end group on the surface activity. The dioctyl sulfide, which has a sulfur atom with saturated aliphatic chains on either side, does raise the contact angle at a 1 wt% concentration, but this compound does not change the wettability of the steel surface from hydrophilic to hydrophobic. In the case of both the thiophene and sulfide compounds, the sulfur atom on its own is not able to form a strong bond with the surface. Tetradecanethiol, representing the thiols containing an active –SH group, is more efficient to adhere to the surface than the thiophene and the sulfide and changes the contact angle from 58° to 95°, making the surface slightly hydrophobic. However, comparing the wettability alteration of the tetradecanethiol to the one of myristic acid, which is also a C14 organic acid, it can be seen that the –SH end group adsorbs weaker on the steel surface than the carboxylic end group.

There was no effect of the nitrogen-containing compounds on the surface wettability detected. Measurements of the contact angle for acridine and carbazole mimicked the behavior of the aromatic (tetrahydronaphthalene), which was used to dissolve them.

### *Interfacial Tension Measurements*

One factor of minimizing the likelihood of corrosion is to minimize the contact between the water phase and the pipeline steel surface. In an oil-water flow, the dispersion of water in the oil phase is facilitated by a lower interfacial tension. Therefore, a decrease in the interfacial tension would promote corrosion protection. By looking at Figure 11, it can be seen that the effect of the tested surface-active compounds on the interfacial tension is limited. The aromatic compound (tetrahydronaphthalene) has no effect on the interfacial tension, and neither do the nitrogen-containing compounds (carbazole and acridine), which are dissolved in 40 wt% tetrahydronaphthalene–model oil mixture. The sulfur-containing compounds have a negligible effect, and the interfacial tension is 30 mN/m to 36 mN/m, compared to the interfacial tension for pure model oil and water of 38 mN/m.

The tested compounds that have the greatest effect on the interfacial tension are the carboxylic acids. Even the short-chained acetic acid have a slight effect on the interfacial tension, lowering it to 30 mN/m. The long-chain myristic acid (dissolved in the oil phase) has a slightly greater effect on the interfacial tension than the short-chain acetic acid with an interfacial tension of 24 mN/m at 1 wt% concentration (10,000 ppm). The naphthenic acids had an even greater effect than the long-chain acid, and the interfacial tension was 18 mM/m at 1 wt% naphthenic acid concentration. However, this drop in the interfacial tension with a relatively large concentration of carboxylic acids is not very significant compared to the effect of certain inhibitors[25] and/or surfactants,[26] which can reach ultralow interfacial tension (<0.01 mN/m) even at very low inhibitor concentrations (<10 ppm).

To get a sense of whether a 50% drop in the interfacial tension has a significant effect on the pipeline corrosion, a model proposed by Cai, et al.,[11] is used to predict how the change in interfacial tension affects the transition between stratified and dispersed flow. The model takes into account both hydrodynamic factors, such as the pipe diameter and the water and oil velocity, as well as the liquid properties, including interfacial tension, density, and viscosity. Figure 12 shows the predicted transition between stratified flow on the left of the transition and dispersed flow on the right. The graph shows how the transition moves to higher mixture velocities (total oil and water superficial velocity) as the water cut is increased. By adding 1 wt% naphthenic acids and reducing the interfacial tension in half, there is only a negligible effect on the dispersion of water into the oil phase. Although the interfacial tension can have an indirect effect on corrosion, that effect is negligible unless the interfacial tension is reduced to low enough values for a fairly stable water-in-oil emulsion to form.

## DISCUSSION

Surface-active compounds, representing naturally occurring crude oil compounds, have been found capable of promoting protection from corrosion in pipeline oil-water flow. However, not all surface-active compounds have the same effect on corrosion and interfacial properties. There are two characteristics of the surface-active compounds that dictate their efficiency, the hydrocarbon structure and the surface-active head group. The hydrocarbon structure has a pronounced effect on the corrosion inhibitive efficiency of the compounds. The long-chain structure is especially efficient in promoting corrosion inhibition as seen by the results from myristic acid and 1-tetradecanethiol, which both have a C14 tail group and a corrosion inhibition of 40% at 0.1 wt% concentration and ca. 85% at 1 wt% concentration. On the other hand, the short-chain structure of acetic acid has no corrosion inhibitive activities, and, in fact, acetic acid contributes to the corrosivity of the $CO_2$-saturated solution. Although the surface activity of the acetic acid is evident from interfacial tension measurements, the effect is very limited compared to the effect of the long-chain myristic acid.

The long-chain hydrocarbon structure promotes corrosion inhibition by forming an adsorbed monolayer at the surface, which prevents water from coming in direct contact with the surface. Naphthenic acids have the same surface-active head group as myristic acid and acetic acid but an aromatic ring structure, in addition to a straight hydrocarbon chain. The aromatic rings also can contribute to the adsorption process either by adsorbing on the surface or adsorbing on each other via π-bonds. The ability of the naphthenic acids to form a strongly hydrophobic surface indicates that they form a hydrophobic monolayer; however, the monolayer created by naphthenic acid does not seem to inhibit corrosion as efficiently as the monolayer created by myristic acid, probably because the naphthenic acids are a mixture of different molecules that all have affinity to the steel surface but will not form as a homogeneous layer as the myristic acid.

By comparing compounds that have the same hydrocarbon tail but a different surface-active head group, namely, myristic acid with a –COOH head group and 1-tetradecanethiol with a –SH head group, it can be seen that although their corrosion-inhibitive properties are the same under the conditions tested in this research, their interfacial properties are quite different. While the myristic acid has a relatively large effect on the contact angle and the interfacial tension, the 1-tetradecanethiol has no significant effect. This is because the –SH end group has a much weaker dipole that does not form a hydrogen bond with the water, while the carboxylic end group (–COOH) is capable of forming a hydrogen bond through the –OH part of the end group and the carbonyl group (C=O) provides an additional bonding as well. Therefore, even if both of the compounds have the same corrosion inhibition measured in the water phase, the myristic acid has the additional protection of promoting oil-wet conditions in the pipeline in which case the water does not reach the steel's surface to corrode it.

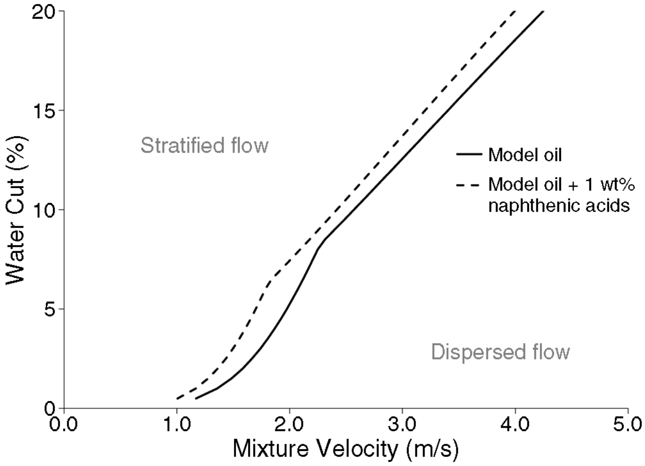


**FIGURE 12.** *Model simulation for the transition between stratified and dispersed flow in a 0.30 m (12 in) diameter horizontal oil-water pipeline for pure model oil (density = 825 kg/m$^3$, viscosity = 0.002 Pa.s, interfacial tension = 38 mN/m), and a model oil with 1 wt% naphthenic acids (interfacial tension = 18 mN/m).*

The majority of the tested compounds that had a heteroatom attached to a ring structure without an acyclic aliphatic structure (i.e., with exception of the naphthenic acids) have little or no corrosion-inhibitive properties. This effect seems to be at least partly a steric effect since the corrosion inhibition of acridine, with its exposed nitrogen atom and straight structure, is near 100% at 0.1 wt% concentration, while other pyridinic compounds did not produce a corrosion inhibition greater than 50% even at a tenfold (1 wt%) concentration. The strong inhibition is likely caused by the alignment of the molecules on the surface, where the nitrogen atom adsorbs on the steel while the aromatic rings align and bond with π–π bonding, forming a strong barrier that the water cannot penetrate.

## CONCLUSIONS

❖ The approach of measuring individual model compounds, rather than the whole crude, provides additional information on the mechanism of corrosion inhibition and the influence of interfacial activities, such as wettability and interfacial tension, compared to studying the whole crude. Interfacial tension is found to have only a minor effect on the corrosion mitigation of the pipeline through changes in flow patterns, while the wettability of the steel surface can have a substantial effect of lowering the likelihood of corrosion, although few compounds, most notably the large molecular carboxylic acids, are capable of forming a hydrophobic layer on the surface and thereby changing the wettability of the surface and producing substantial corrosion inhibition. The corrosion inhibition is found to depend strongly on the molecular structure of the compounds and their ability to bind to the surface, and even more importantly, to each other.

## ACKNOWLEDGMENTS

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