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CRUDE OIL CHEMISTRY EFFECTS ON INHIBITION OF CORROSION AND PHASE WETTING

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ABSTRACT

The effect of crude oil chemistry on corrosion processes is poorly understood. A simple mechanistic model that takes into account the combined effects of corrosion inhibition and wettability alteration, due to the adsorption of polar molecules onto the steel surface, is proposed. While the inhibition effect is dominant in oil-water stratified flow, the wettability alteration is dominant in turbulent flow. Consequently, both effects have to be taken into consideration in order to predict corrosion in oil-water pipe flow. The objective of this study is to identify chemicals present in crude oil which have an effect on inhibition and wettability. The likeliest molecules to adsorb onto a metal surface are polar compounds. Nine polar compounds containing nitrogen, sulfur and oxygen have been studied. Corrosion rates were recorded, the change of the steel wettability has been quantified and the mass adsorbed onto the metal surface measured with a quartz-crystal-microbalance. Results show that certain groups of chemicals have strongly inhibitive effect on corrosion and wettability while others had only a negligible effect.

Keywords: adsorption, corrosion, crude oil, inhibition, mercaptans, naphthenic acid, polar compound, pyridinic, pyrrolic, sulfide, thiophenes, wettability

INTRODUCTION

The objective of this study is to determine which groups of chemicals present in crude oil have an effect on crude oil inhibition of corrosion and phase wetting. This information is necessary in order to predict corrosion rates in pipelines where crude oil and water are flowing in a mild steel pipe. However, the molecular composition of crude oil is very complex and crude oil chemistry varies from field to field. It is therefore impossible to study the effect of each and every chemical present in crude oil.

The main phenomenon studied here was the adsorption of particular surface active compounds naturally present in crude oil: aromatics as well as oxygen, sulfur, and nitrogen containing compounds. Only a few compounds were chosen for this study each representative of a particular chemical class. The adsorption of surface active compounds at the metal surface can create an organic protective film leading to corrosion inhibition[1,2,3]. The presence of an organic film at the metal surface in oil-water two-phase flow can also change the steel/water and steel/oil interfacial tension, thus changing the wettability of the steel. Wettability has a direct effect on the corrosion rate[4], *i.e.* steel wet by oil does not corrode.

Another phenomenon studied was the accumulation of surface active compounds at the oil-water interface. This accumulation of surface active compounds changes the oil-water interfacial tension[5,6] which influences the break-up process of the water phase by the oil phase[7].

Surface active compounds adsorption effects on inhibition of corrosion and wettability have been studied both qualitatively and quantitatively in the past[8-13]. However, these effects were studied only by using corrosion measurements. The use of one single experiment cannot distinguish which effect has the largest influence on corrosion. Therefore, in this study each effect will be investigated separately without the interference of the others. The main aim is to achieve a better understanding of corrosion in oil-water two-phase flow.

Hypothesis: Crude oil chemistry has three effects on corrosion

Surface active compounds are known for their affinity towards iron surfaces, where they can adsorb either *via* weak interactions such as van der Waals forces (characteristic of physisorption) or strong covalent bonding (characteristic of chemisorption)[14,15]. Adsorption processes can create a very thin organic film on metal surfaces. This accumulation of surface active compounds at the metal surface, where the oxidation of iron by protons occurs, can slow down corrosion rates. Furthermore, the accumulation of the surface hydrophobic active compounds can change the wettability of iron, which is hydrophilic by nature[16,17].

Another hypothesized effect of surface active compounds in crude oil-water two-phase flow is in the change of the minimum velocity needed in order to disperse the water phase in droplets[4] due to a change of the oil-water interfacial tension.

The current study is thus based on the three following hypotheses:

1 - Corrosion inhibition is induced by the accumulation of surface active compounds at the metal surface.

2 - Wettability of steel is altered by accumulation of surface active compounds at the metal surface.

3 - Flow pattern is modified by accumulation of surface active compounds at the oil-water interface.

Surface active compounds tested

As explained earlier, it is impossible to study the effect of each and every compound present in crude oil on inhibition of corrosion and phase wetting. However, based on the three hypotheses above, only surface active compounds have the potential to adsorb onto an iron surface. There are four dominant classes of surface active compounds in crude oil: aromatics, oxygen containing compounds, sulfur containing compounds and nitrogen containing compounds. For each class the subclasses will be identified and tested (Table 1).

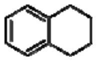
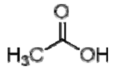
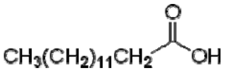
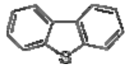
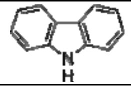
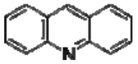
Aromatic compounds – adsorb onto the steel surface by sharing π-electron density from the aromatic ring with the metal surface[15]. This binding can possibly decrease corrosion rates or change the steel-oil interfacial tension. The aromatic chosen for this study is 1,2,3,4-tetrahydronaphthalene.

Oxygen containing compounds – 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[18]. The resulting physical interaction blocks the metal's active site and therefore decreases the corrosion rate[19]. The class of oxygen containing compounds with the highest potential for adsorption in crude oil is organic acids. Organic acids adsorb onto the steel surfaces via the electrons on the carbonyl oxygen. While small chain organic acids are known to increase corrosion rates[20], long chain organic acids are used as corrosion inhibitors in industry[21,22]. Acetic acid will be used as representative of small molecule organic acids and myristic acid will represent long chain organic acids. Moreover, to validate the results found with the myristic acid, a mixture of naphthenic acids extracted from kerosene (sold by TCI America) will be tested. The molecular formula used for the naphthenic acids tested is $R\text{-}CH_2\text{-}COOH$ where R represents a mixture of 0 to 3 ring saturated 5- and 6-membered ring structures. Average molecular weight for the naphthenic acids tested (TCI) is 214 $g \cdot mol^{-1}$. Mass spectrometry suggests that two ring structures are prevalent.

Sulfur containing compounds – these can adsorb in an analogous fashion to oxygen containing compounds, using unshared electrons, although they have a greater tendency to chemisorb *via* formation of sulfur-metal bonds. Sulfur containing compounds are subdivided in two categories: non-polar (sulfide, thiophenes) and polar forms (thiols commonly known as mercaptans)[23]. Dioctyl sulfide, dibenzothiophene and tetradecanethiol were tested to represent sulfide, thiophenes and mercaptans, respectively.

Nitrogen containing compounds – these compounds can adsorb in an analogous fashion to both oxygen and sulfur containing compounds. Nitrogen containing compounds are subdivided in two categories: pyridinic forms (known as basic nitrogen) and pyrrolic forms (known as neutral nitrogen)[23]. Acridine was chosen to represent pyridinic compounds and carbazole to represent pyrrolic compounds.

Table 1: Description of the surface active compounds used in the present research.

Chemical class	**Name**	**Formula**	**Molecular weight g·mol^{-1}**
Aromatic	1,2,3,4-Tetrahydronaphthalene	$C_{10}H_{12}$ 	132.2
Oxygen containing compounds	Acetic Acid	CH_3COOH 	60.05
	Myristic acid	$CH_3(CH_2)_{12}COOH$ 	228.37
	Naphthenic acid mixture sold b y TCI America	$R–(CH_2)–COOH$	~214
Sulfur containing compounds	Dibenzothiophene	$C_{12}H_8S$ 	184.26
	Dioctyl sulfide	$CH_3(CH_2)_7S(CH_2)_7CH_3$	258.51
	1-Tetradecanethiol	$CH_3(CH_2)_{13}SH$	230.45
Nirogen containing compounds⊗	Carbazole	$C_{12}H_9N$ 	167.2
	Acridine	$C_{13}H_9N$ 	179.2

⊗ The nitrogen containing compounds tested in this study are insoluble in the model oil used (LVT-200) which is composed only of saturates. Therefore, the oil used in the test involving nitrogen compounds is composed of 60% LVT-200 and 40% 1,2,3,4-tetrahydronaphthalene. The aromaticity increases the solubility of the nitrogen containing compounds. Moreover, the ratio 60% saturate/40% aromatic is representative of crude oil.

Steel wettability

Hydrocarbons are hydrophobic. Their adsorption at the metal surface can change the affinity of the steel, which is hydrophilic in nature, to hydrophobic. This alteration of phase wetting at the metal surface is caused by a change of steel-oil and steel-water interfacial tension[8]. The difference between the steel-oil interfacial tension and the steel water interfacial tension is termed the equilibrium spreading coefficient, ψ [12] and is determined by Young's equation (Eq.1).

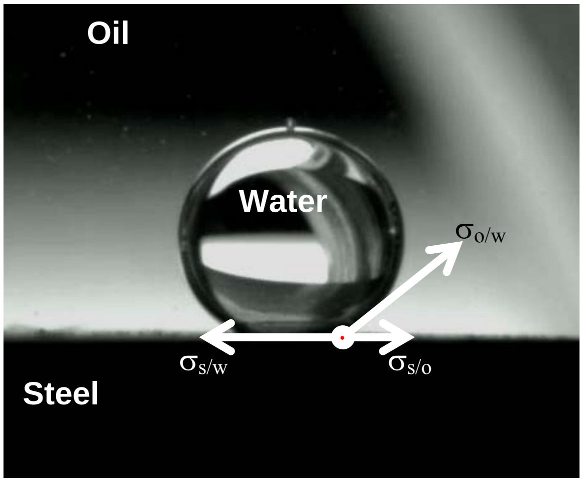


Figure 1: Interfacial tension forces applied to a water droplet in model oil resting on a steel surface. The shape of the droplet is determined by the interaction of the interfacial forces of oil-water ($\sigma_{o/w}$), steel-oil ($\sigma_{s/o}$) and steel-water ($\sigma_{s/w}$).

Young's equation:
$$\psi = -\sigma_{o/w}\cos\theta = \sigma_{s/o} - \sigma_{s/w} \tag{1}$$

If the contact angle is larger than 90° the equilibrium spreading coefficient ψ is positive. Therefore, the affinity of the steel for water ($\sigma_{s/w}$) is stronger than the affinity of the steel for oil ($\sigma_{s/o}$). On the other hand, if the affinity for the steel is stronger for oil, the water droplet will have a contact angle smaller than 90°. A strong affinity of the steel for oil is beneficial for preventing corrosion. In this condition, a water droplet approaching the wall surface will not wet the metal and therefore will not be corrosive.

Interfacial tension: effect of the flow on corrosion

The wetting of the internal surface of the pipe depends on what happens both at the steel surface and in the bulk (flow effect). If the turbulence of the oil phase is strong enough to break the water phase into droplets and entrain them in the flow, the water droplets theoretically never touch the pipe wall. This condition can be predicted by a set of four equations called the water wetting model (Eq.2), which was proposed by Nesic et.al[4]. When the condition described by (Eq.2) is satisfied, the model predicts that the water phase flows as droplets in a continuous oil phase. The pipe is therefore free from corrosion problems.

$$\max\left\{\begin{array}{c} 0.725\cdot\left(\frac{\rho_o}{\sigma}\right)^{-0.6}\cdot\left(\frac{2u_o^3 f}{D}\cdot\frac{\rho_m}{\rho_c}\cdot\varepsilon_o\right)^{-0.4} \\ 2.22\cdot D\cdot\left(\frac{\rho_o u_o^2 D}{\sigma}\right)^{-0.6}\left(\frac{\varepsilon_w}{\varepsilon_o}\right)^{0.6}\left(\frac{\rho_m}{\rho_o}\cdot\frac{1}{\varepsilon_o}\cdot f\right)^{-0.4} \end{array}\right\} < \min\left\{\begin{array}{c} \frac{3}{8}\cdot\frac{\rho_o}{\Delta\rho}\cdot\frac{f\cdot u_m{}^2}{g\cdot\cos\beta} \\ 0.632\cdot\sqrt{\frac{\sigma}{(\rho_w-\rho_o)\cdot\cos\beta'\cdot g}} \end{array}\right\} \quad (2)$$

The prediction of the model depends on hydrodynamic parameters such as oil velocity, water velocity, water cut, density of the oil, inclination and size of the pipe and also on the oil-water interfacial tension (σ). The crude oil chemistry does not have a direct effect on hydrodynamic parameters but it can change the oil-water interfacial tension. Polar compounds can be present which have a hydrophilic head attached to a hydrophobic tail. The head can be in the aqueous phase while the tail resides in the oil phase. The accumulation of such polar compounds at the oil-water interface decreases the oil-water interfacial tension[26].

The oil-water interfacial tension is a key parameter in the breaking process of the water phase into entrained droplets by the turbulence of the oil phase. Strong oil-water interfacial tension makes it more difficult for the turbulence to break the water phase into droplets. Therefore, it is easier to obtain a stratified flow, which can be corrosive since water is then in direct contact with the pipe wall.

EXPERIMENTAL PROCEDURE

Each hypothesis will be tested by a specific experimental technique. The first hypothesis, that surface active compounds that accumulate at the metal surface induce corrosion inhibition, is tested by corrosion measurements. The second hypothesis, that surface active compounds that accumulate at the metal surface change the wettability of the steel, is tested by contact angle measurements. The third hypothesis, that surface active compounds at the oil-water interface have an effect on the flow pattern, is tested by interfacial tension oil-water measurements.

Corrosion measurements

A 2 Liter glass cell apparatus mounted with a rotating electrode was used for the corrosion measurements. The working electrode (rotating cylindrical electrode, diameter 1.5 cm) is made from carbon steel. The composition of the steel is shown in Table 2. The counter electrode was a platinum ring and the reference electrode a silver/silver-chloride electrode connected to the solution by a salt bridge. Linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic sweep data were recorded.

Table 2: Steel composition in wt.% (Fe is in balance).

Al	As	B	C	Ca	Co	Cr	Cu	Mn	Mo	Nb
0.004	0.010	0.0002	0.19	0.002	0.007	0.13	0.16	0.83	0.042	0.003
Ni	P	Pb	S	Sb	Si	Sn	Ta	Ti	V	Zr
0.16	0.015	0.017	0.013	0.015	0.22	0.021	<0.001	<0.001	0.058	0.002

A specific experimental procedure was designed to understand the adsorption of a surface active compound present in the oil phase onto the metal surface. In a 2L glass cell, 1.8L of aqueous electrolyte was introduced (1 wt. % NaCl, 1 bar CO_2, pH 5.0). The working electrode was sequentially polished with 400 and 600 grit sandpaper then cleaned with acetone and isopropanol in an ultrasonic bath. The working electrode was then rotated (2000 rpm) in the glass cell. The corrosion rate was measured using LPR, after which 200 mL of model oil (LVT-200) was mixed with a particular surface active compound and introduced in the glass cell. The rotating working electrode was moved up into the oil phase for 20 minutes, and then moved down into the water phase. The corrosion rate was recorded every 5 minutes by LPR. Excellent agreement was found between LPR, EIS and polarization sweep data, therefore only LPR measurements will be presented in this paper.

Steel Wettability measurements

The wettability test procedure was as follows. One percent by weight of surface active compound was added to 1 L of model oil. The oil phase (model oil, 800mL) and water phase (1% NaCl, pH5, 1Bar CO_2, 200mL) are mixed together in a beaker for 1 hour, then left to settle overnight to equilibrate. A flat carbon steel coupon was cleaned with acetone and polished sequentially with 400 and 600 grit sandpaper, then further cleaned with isopropanol in an ultrasonic bath for 2 minutes. The coupon was then dried and immersed in the model oil. A droplet of water was then added on the top of the coupon. A video recording of the evolution of the droplet at the metal surface was taken over 10 minutes, allowing for the measurement of the contact angle water droplet-on the steel as a function of time.

Interfacial tension measurements

To determine the effect of flow on corrosion, interfacial oil-water tension was measured with a platinum ring tensiometer. The preparation of the solution was the same as outlined above for the contact angle measurements. One percent by weight of surface active compound was added to 1 L of model oil. The oil phase (model oil, 800mL) and water phase (1% NaCl, pH5, 1Bar CO_2, 200mL) were mixed together in a beaker for 1 hour and then left to settle overnight to equilibrate prior to testing.

Adsorption measurements

Hypothesis 1 and 2 are based on an adsorption mechanism*, i.e.,* the adsorption of surface active compounds onto iron. This adsorption can be recorded as a function of time by a Quartz Crystal Microbalance (QCM), the quartz crystal is covered with an iron layer. In each experiment, a new iron-coated quartz crystals was introduced into a 1L beaker containing 0.5L of model oil. After the quartz crystal frequency was stabilized, 0.5L of model oil mixed with one surface active compound was added into the beaker. The frequency of the quartz crystal was recorded throughout the whole experiment. The observed change in frequency is proportional to a change of mass. Therefore, the adsorption of surface active compounds was detected when the frequency of the quartz crystal decreased.

RESULTS AND DISCUSSION

Inhibition of corrosion

Aromatic compounds: Figure 2 shows the corrosion rate of the carbon steel coupon after being immersed in LVT (Base Line) and LVT/tetrahydronaphthalene for 20 minutes. Even with 40% Tetrahydronaphthalene, the corrosion rate does not change. Aromatics can adsorb onto a metal surface[15], but the molecule-surface interactions created are insufficiently strong to replace the water molecules adsorbed onto the iron surface, and therefore do not significantly decrease the corrosion rate.

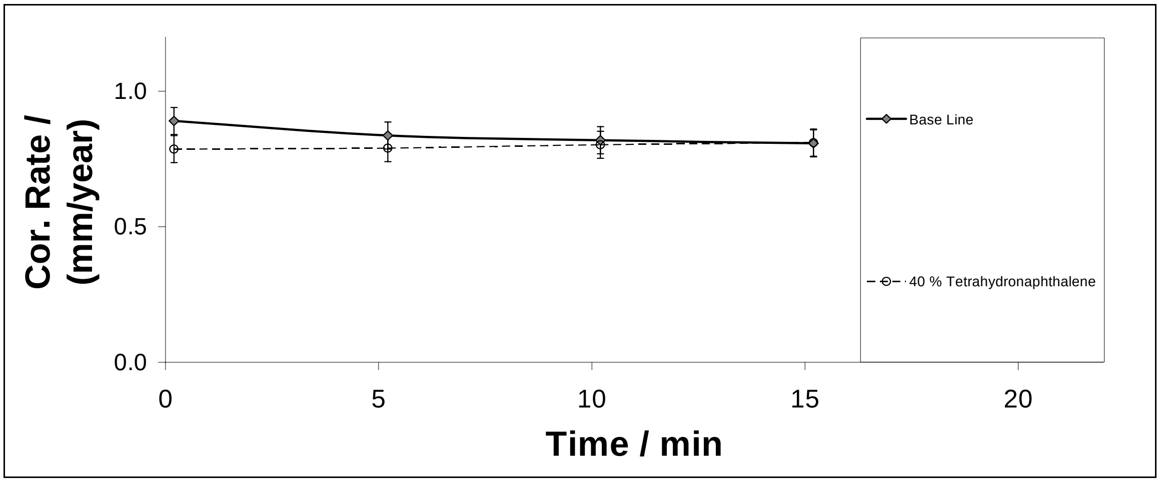


Figure 2: Corrosion measurements by LPR for aromatics added to the model oil (Base Line: model oil no Tetrahydronaphthalene) .

Oxygen containing compounds: Small molecule organic acids such as acetic acid $[CH_3CO_2H]$ are insoluble as a monomer in oil. Consequently, it was not possible to add acetic acid to the oil phase and record the corrosion rate. However, glass cell experiments were performed in aqueous conditions. The acetic acid corrosion rate was recorded by LPR experiments. The conditions were identical to those outlined for corrosion measurements in a previous section (1 wt. % NaCl, 1 bar CO_2, pH 5.0). The corrosion rate was recorded for 10 ppm, 100 ppm and 1000 ppm acetic acid and the results are shown in Table 3.

Table 3: Dependency of carbon steel's corrosion rate function of acetic acid concentration in aqueous solution.

Concentration of acetic acid (ppm)	0	10	100	1000
Corrosion rate (mm/year)	0.79	0.84	0.96	1.47

Corrosion rate increases with acetic acid concentration. However, as shown in Figure 3, long chain organic acids such as myristic acid [$CH_3(CH_2)_{12}COOH$] and naphthenic acids (TCI) decrease the corrosion rate.

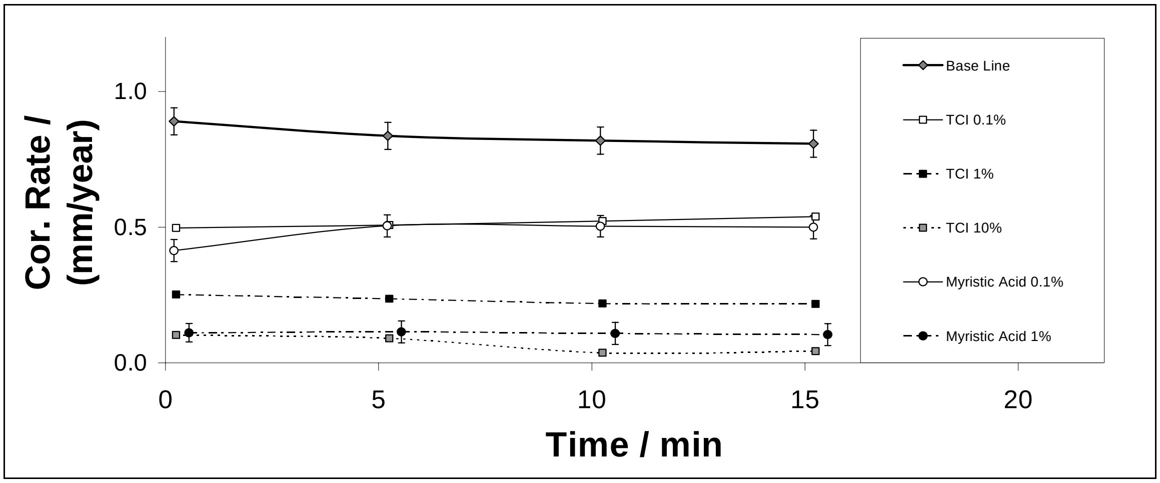


Figure 3: Corrosion measurements by LPR for oxygen containing compounds added to the model oil phase.

Long chain organic acids are able to significantly decrease the corrosion rate. Only 0.1% concentration of myristic acid gives a 48% inhibition of corrosion, while a 1% concentration gives 88% of inhibition of corrosion. Naphthenic acids (TCI) present the same behavior. These results were expected, the protection against corrosion by organic acid is well known[21,22]. Moreover, EIS experiments showed that organic acids have negligible effect on the corrosion mechanism and polarization sweeps showed that only the cathodic reaction is inhibited by organic acid while the anodic reaction stays unchanged.

Sulfur containing compounds: Figure 4 shows the results obtained with sulfur containing compounds. Dibenzothiophene and dioctyl-sulfide have no significant effect on the corrosion rate. However, with the addition of 1-tetradecanethiol (a mercaptan) the corrosion rate decreases significantly. Only 0.1% of 1-tetradecanethiol produces a 44% inhibition of corrosion and 1% of 1-tetradecanethiol gives 84% of inhibition of corrosion. This is in good agreement with the mercaptan literature[25]. As for the organic acids, EIS measurements show that the corrosion mechanism is unchanged. However, the polarization sweep shows that 1-tetradecanethiol induces a strong inhibition of both the anodic and cathodic processes.

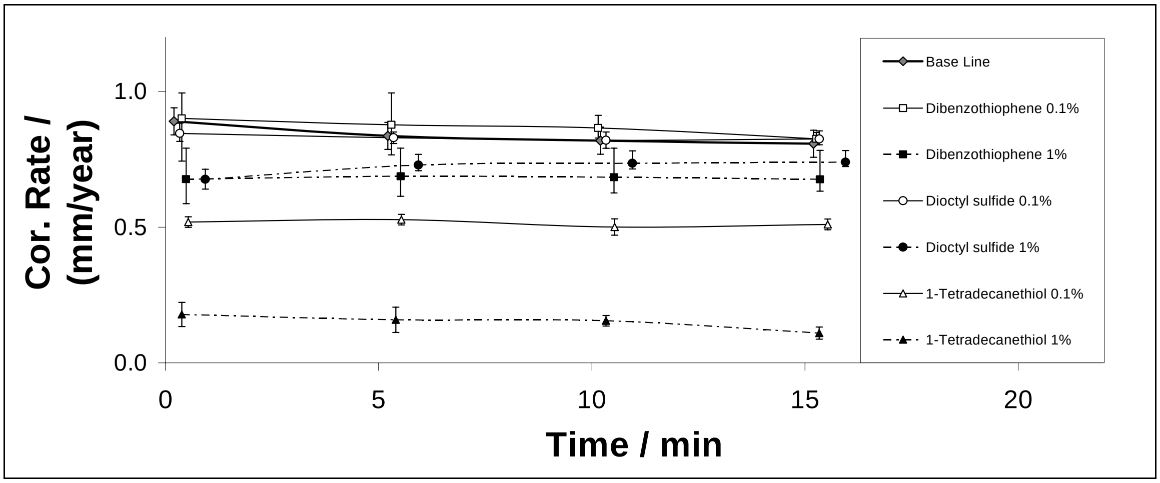


Figure 4: Corrosion measurements by LPR for sulfur containing compounds added to the model oil phase.

Nitrogen containing compounds: Figure 5 depicts results obtained with nitrogen containing compounds. While carbazole cannot adsorb onto iron surface and inhibit corrosion, acridine is able to adsorb at the metal surface and strongly inhibit corrosion. Only 0.01% of acridine added to the oil phase produces 83% inhibition of corrosion, while 0.1% acridine present in the oil phase induces a 100% corrosion inhibition. During EIS experiments polarization resistance as high as 15000 Ω were recorded. It should be noted that the 100% corrosion inhibition associated with acridine is too high to be representative of all "pyridinic type" compounds found in crude oil. Therefore, three nitrogen containing compounds have been identified for further study: benzo[h]quinoline, phenanthridine and 1,10-phenanthroline.

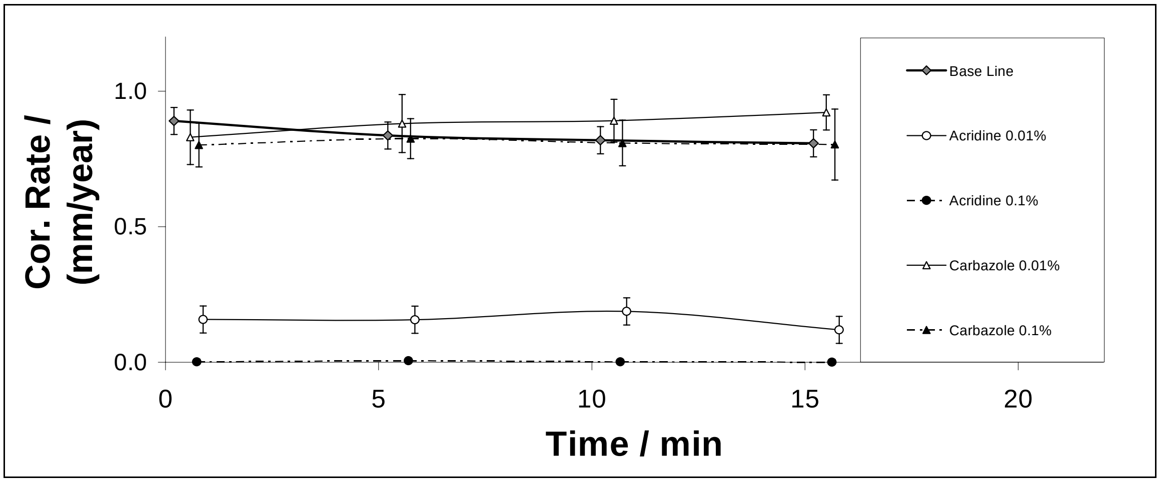


Figure 5: Corrosion measurements by LPR for nitrogen containing compounds added to the model oil phase.

In summary, four classes of compounds have been tested but only three were able to reduce the corrosion rate (oxygen, sulfur and nitrogen containing compounds). Aromatics were unable to have a significant effect on corrosion even in very large concentration (40%). Figure 6 shows that within the same class of compounds not every subclass was able to inhibit corrosion.

- Oxygen containing compounds: Small molecules organic acids increase the corrosion rate while large molecules organic acids have inhibitive properties.
- Sulfur containing compounds: Only mercaptans are able to decrease corrosion rates while dialkyl sulfides and thiophenes have no significant effect.
- Nitrogen containing compounds: Pyridinic compounds (basic nitrogen) can adsorb at the metal surface, this is proved by acridine strong inhibition of corrosion. However, pyrrolic compounds (neutral nitrogen) such as carbazole have no effect on corrosion.

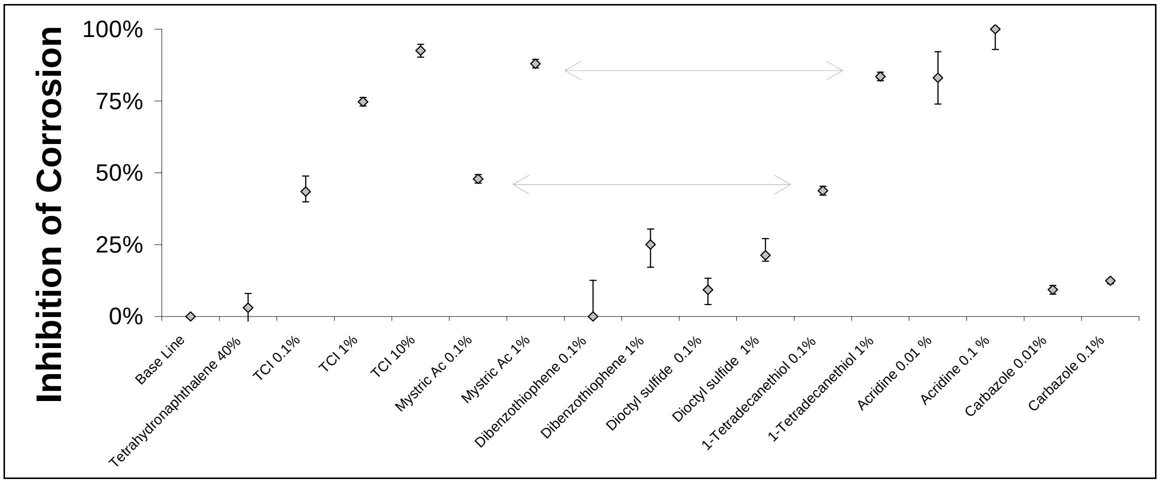
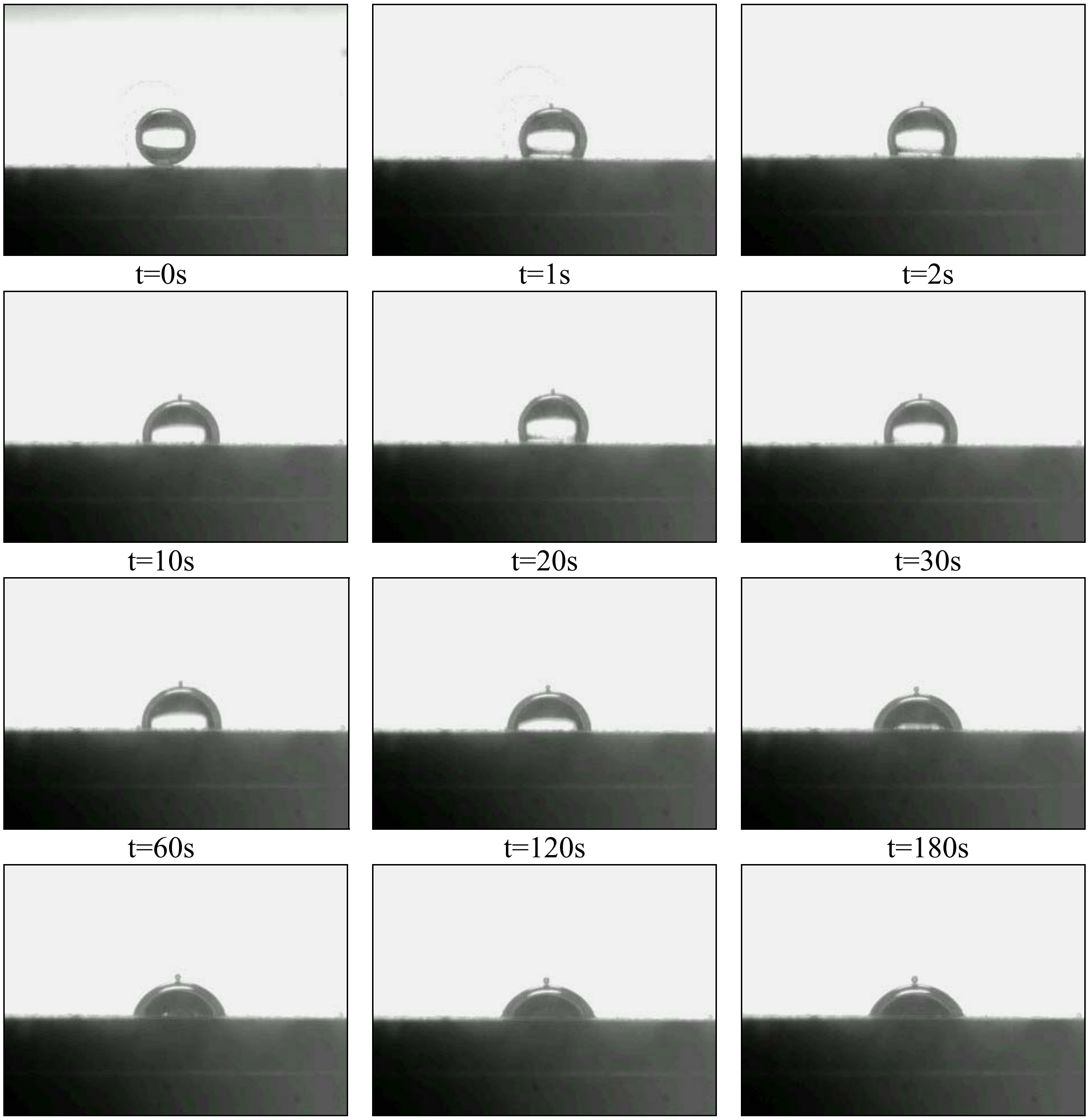


Figure 6: Summary of the inhibitive effect of the compounds tested in this study.

It should be noted that myristic acid and 1-tetradecanethiol have a similar chemical structure (Table 1). The comparison of these chemicals inhibitive properties suggests that once a chemical is adsorbed at the metal surface its functionality (oxygen or sulfur) may not be important and that the length of the carbon chain has the strongest effect on corrosion inhibition. This is a stearic effect.

Steel wettability

<u>Base line experiment (model oil)</u>: When a spherical water droplet touches a flat steel surface the water-steel contact angle is 180°. Interfacial forces act and the water droplet spreads across the steel surface displacing the oil. Therefore the contact angle decreases as a function of time. Figure 7 shows the evolution of a water droplet in model oil during the first 5 minutes. The final water-steel contact angle is 58°.



t=0s t=1s t=2s

t=10s t=20s t=30s

t=60s t=120s t=180s

t=240s t=300s t=600s

Figure 7: Evolution of a water droplet in model oil during the first 5 minutes
as the contact angle changes from 180° to 58°.

The same experiment was repeated with surface active compounds added to the oil phase. Heuristically, the chemicals that were able to have an effect on corrosion are supposed to have a similar effect on the steel wettability. Figure 8 shows the water-steel contact angle after 5 minutes and Figure 9 the water-steel contact angle after 2 hours for the chemicals used in this study.

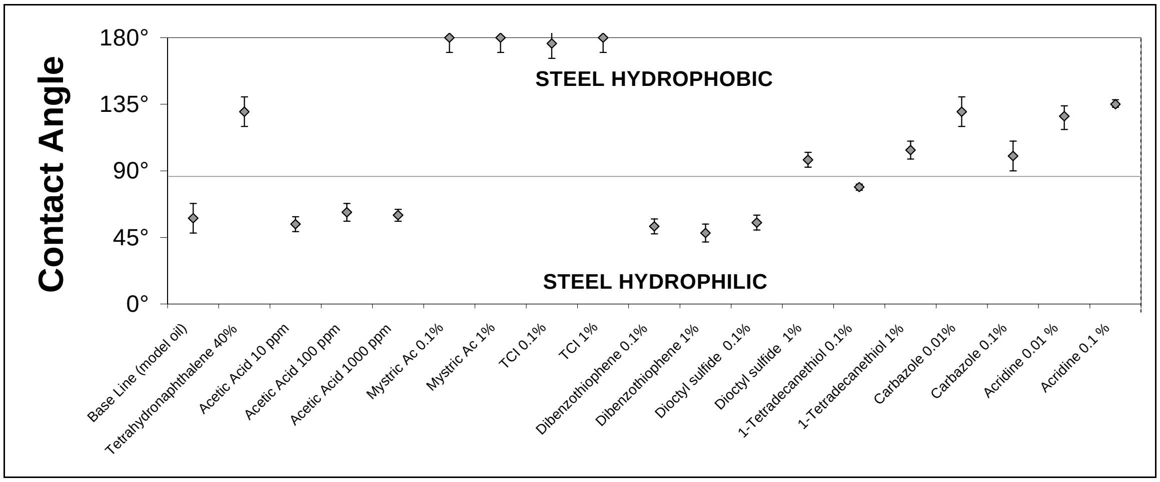


Figure 8: Water-Steel contact angle after 5 minutes. Organic acids have the strongest effect on steel wettability.

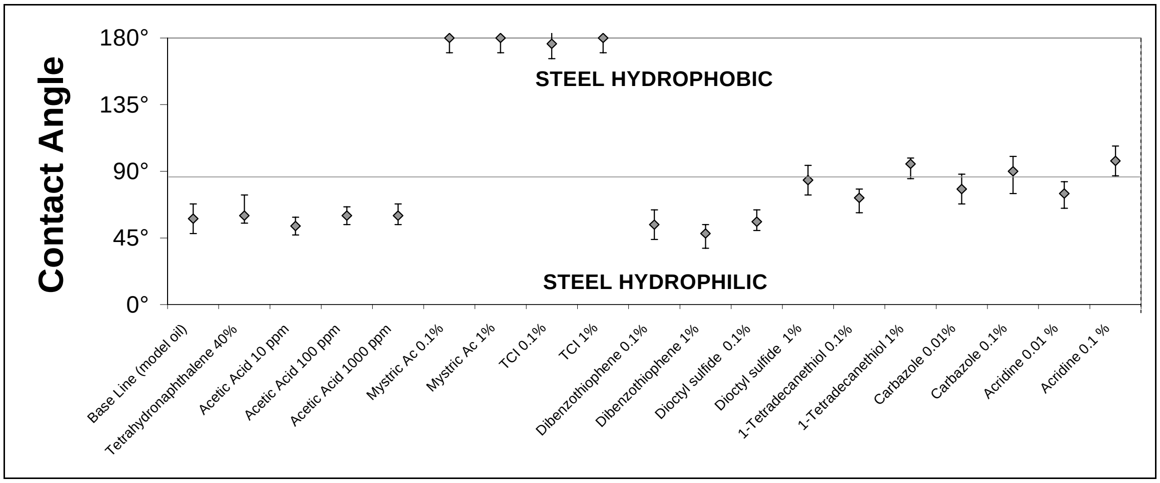


Figure 9: Water-Steel contact angle after 120 minutes. Organic acids effect on steel wettability is not dependant on time.

Aromatics: the contact angle water-steel remained at 180° (steel hydrophobic) for more than 30 seconds then started to decrease. It reached 130° after 5 minutes and then a stable value of about 60° in less than 2 hours (the steel surface becoming hydrophilic under 90°). Even if the final contact angle is the same as the one obtained with model oil, the time needed to reach the final value is much longer. In this experiment, it seems that the aromatics are adsorbed onto the metal surface and the water phase slowly displaces the adsorbed oil phase. This explains why no effects related to aromatics were found in the corrosion measurements.

The oil layer is displaced more rapidly when the oil is free of aromatics. Even if the final value of the contact angle is the same, the effect of aromatics must not be neglected, particularly in intermittent oil-water two-phase flow. When a water droplet touches the pipe wall, this droplet either wets the pipe or rebounds from it. Without compounds added to the model oil the water immediately wets steel, while when aromatics are added to the oil phase water droplets can bounce on surface without wetting it. This effect can strongly limit the corrosiveness of dispersed oil-water flow.

Oxygen containing compounds: small molecule organic acids do not have an effect on steel wettability. However, the strongest effect is found with the high molecular weight organic acids. While steel is naturally hydrophilic, once it is wet with model oil and myristic acid or naphthenic acids, steel becomes completely hydrophobic. Even after a long period of time, the water droplet touching the steel surface never wetted it. The contact angle never went below 180°.

The effect of naphthenic acids on wettability is even stronger than the effect of aromatics. It is possible to conclude that if a straight pipe is pre-wetted with oil and naphthenic acids, dispersed water droplets in the oil flow are not going to be corrosive.

Sulfur containing compounds: the effect on wettability is weaker than for the organic acids. Dibenzothiophene and dioctyl sulfide do not change the steel wettability. Even tetradecanethiol, which is a good corrosion inhibitor, is only able to change the contact angle from 58° to 95°. It is a significant change in the wettability of the steel. However, this change of contact angle is not sufficient to affect the wettability and reduce corrosion significantly by itself. Once a water droplet wets the pipe, corrosion happens irrespectively from the contact water-steel angle.

Nitrogen containing compounds: were tested using model oil and 40% tetrahydronaphthalene. No significant effect on the steel wettability is found for the nitrogen containing compounds. It is possible that the strong effect of the aromaticity of the oil is masking the effect of the nitrogen containing compounds

Effect of the flow on corrosion

Oil-water interfacial tension measurements were conducted and the results are shown in Figure 10. None of the chemical tested are able to significantly decrease the interfacial oil-water tension except for the long chain organic acids (myristic acid and naphthenic acids). Organic acids are able to change the interfacial tension, 1% TCI reduces the interfacial oil-water tension by half.

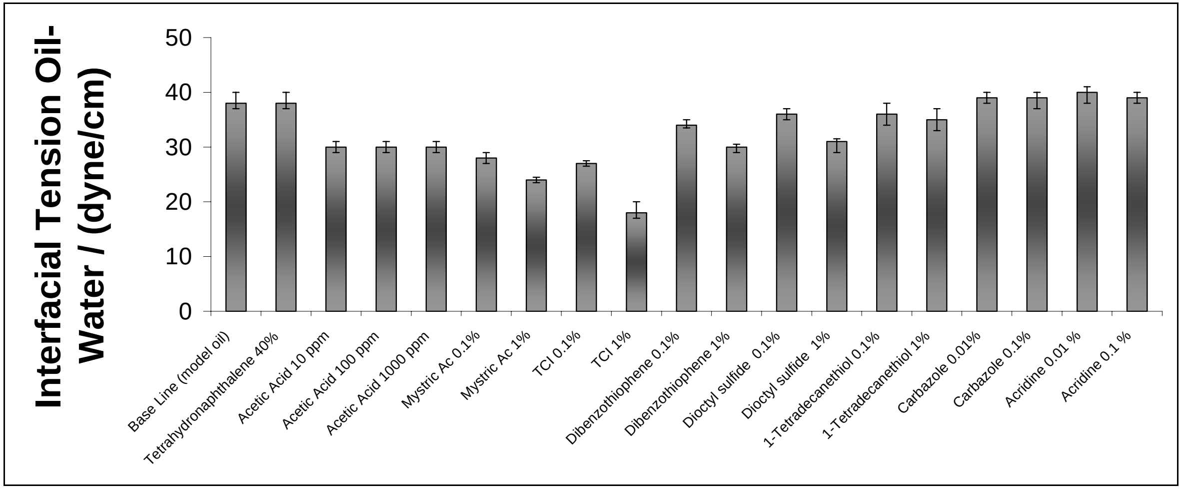


Figure 10: Water-oil interfacial tension function of the chemicals added to the oil phase (acetic acid is added to the water phase).

Figure 11, shows the effect of naphthenic acids (TCI) on the transition line water-wetting to oil-wetting calculated using Equation 2. Such a major change in the interfacial tension has only a small effect on the flow. A decrease in the oil-water interfacial tension is beneficial from a corrosion point of view (water is more easily dispersed in the oil flow). However, to have a significant change in the flow pattern, the oil-water interfacial tension reduction has to be much bigger that 50%.

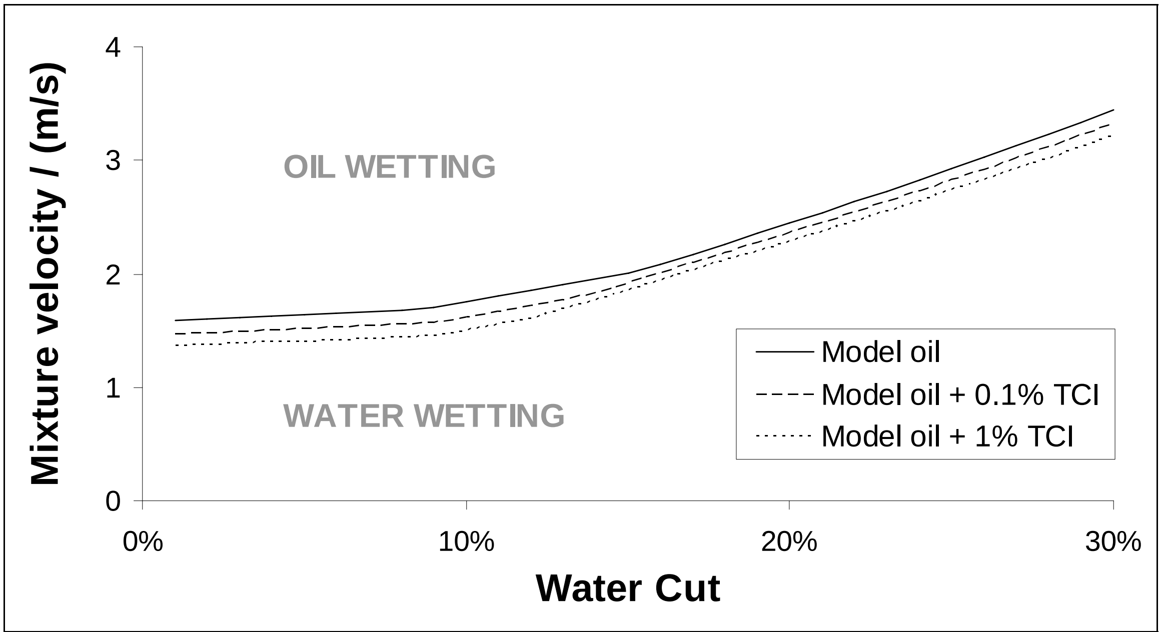


Figure 11: Phase wetting map for model oil (with TCI) calculated using Equation 2.

Adsorption measurement

The results of the adsorption measured with a QCM are shown in the Figure 12. The mass adsorbed has been converted to a film thickness assuming that the film created during the adsorption is homogenous.

Aromatics were not tested since the high concentration of tetrahydronaphthalene changes the viscosity of the model oil. A change in the viscosity implies a change in the quartz crystal's frequency much larger than the effect of the mass adsorbed.

For oxygen containing compounds acetic acid was not tested. The results for myristic acid and naphthenic acid (TCI) are shown in Figure 12. The adsorption of myristic acid and TCI are similar, a rapid adsorption with a maximum about $1\mu g \cdot cm^{-2}$. This quick response suggests that the adsorption of organic acids is physisorption: *i.e.,* rapid adsorption through weak intermolecular interactions (Van der Waals forces).

The adsorption of sulfur containing compounds gave two different responses. Dibenzothiophene and dioctylsulfide have a rapid adsorption rate with a maximum about $0.5\mu g \cdot cm^{-2}$. The 1-tetradecanethiol adsorption was slow but steady. The maximum mass adsorbed measured was $0.9\mu g \cdot cm^{-2}$. Such slow adsorption is likely to be chemisorption.

Nitrogen containing compounds were not tested for the same reason as stated for aromatics.

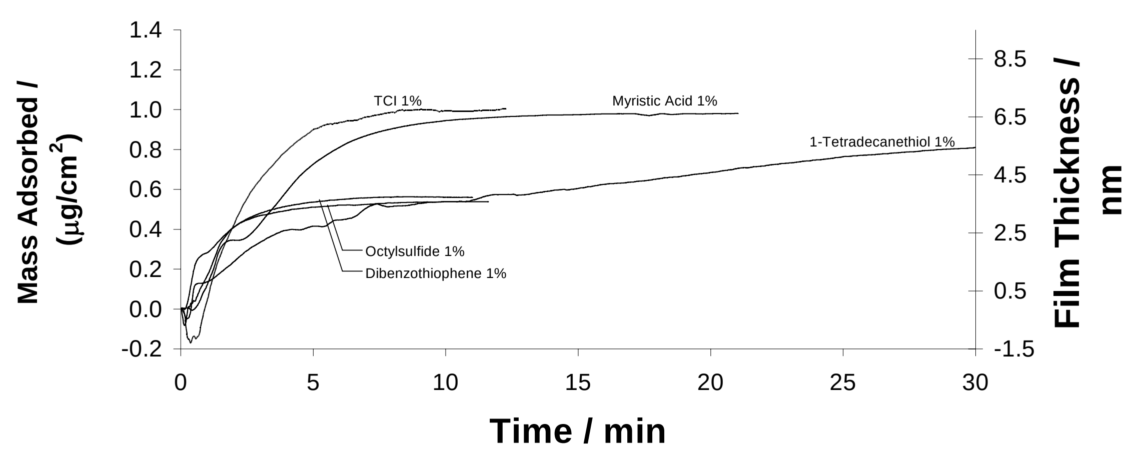


Figure 12: Evolution of the mass adsorbed for different surface active compounds tested as a function of time

Using the corrosion measurement (Figure 6) and the results of the QCM (Figure 12), a graph that correlates inhibition and adsorption can be generated. Each chemical tested produces one data point and the results are shown in Figure 13. The results indicate a linear relationship between inhibition of corrosion and the mass adsorbed at the metal surface. However, testing of only 5 chemicals is insufficient for the development of a universal conclusion.

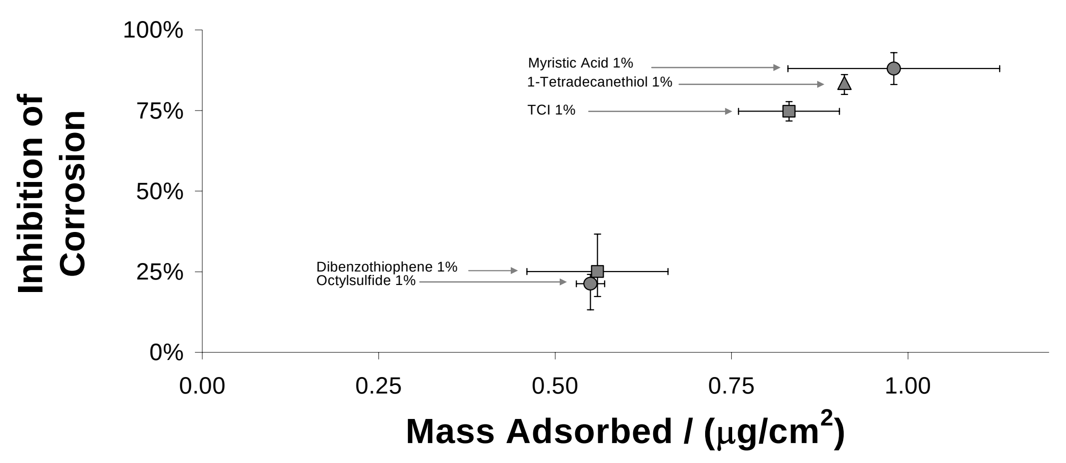


Figure 13: Relationship between mass adsorbed and inhibition of corrosion

CONCLUSION

This study was conducted to test three hypotheses related to corrosion inhibition and alteration of phase wetting of a mild steel surface by compounds found in crude oil:

1 - Corrosion inhibition is induced by the accumulation of surface active compounds at the metal surface.

2 - Wettability of steel is altered by accumulation of surface active compounds at the metal surface.

3 - Flow pattern is modified by accumulation of surface active compounds at the oil-water interface.

All three hypotheses are confirmed. Surface active compounds found in the crude oil adsorb onto the metal surface as the QCM measurements unambiguously demonstrated. The effect of these compounds on corrosion has been quantified, the effect on steel wettability has been measured and change of the oil-water interfacial tension has been recorded. However, as expected, not all surface active compounds produced the same effect on corrosion, wettability and change of the flow pattern.

NOTATION

D	Internal diameter of the pipe
f	Friction factor
g	Gravity constant

u	Velocity
β	Pipe inclination
ε	Percentage of fluid
ρ	Density
σ	Interfacial tension oil-water
$_m$	Mixture oil-water
$_o$	Oil
$_s$	Steel
$_w$	Water

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