Evaluation of the Protectiveness of a Paraffin Layer in CO_2 Corrosion of Mild Steel

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ABSTRACT

Crude oil composition is highly variable and complex. Its components can be broken down into four different classes by solubility characteristics such as: saturates, aromatics, resins, and asphaltenes. Within each class are myriad of chemical compounds, and many have the potential to interact with the pipeline wall to confer protection from corrosion. In this work the focus is on saturates, with the the n-paraffins chosen as being most relevant for the purposes of the present study. A representative pure model compound for the n-paraffins used in the experiments is eicosane ($C_{20}H_{42}$). A mixture of eicosane and a clear, inert model oil was prepared with a range of paraffin concentrations (0 – 50% eicosane). The chemical properties of the mixture were measured, including the Wax Appearance Temperature (WAT), density, viscosity and interfacial tension. The CO_2 corrosion rate for carbon steel was measured both below and above the WAT, using the linear polarization resistance (LPR) technique. The protectiveness of the long-chain paraffin layer was challenged by inducing flow (hydrodynamic shear stress) and by increasing temperature. The eicosane successfully conferred corrosion retardation at temperatures below the WAT; however, this protection did not withstand the effect of shear stress or increased temperature. Further analysis by using sessile drop contact angle measurements using a goniometer revealed that the protectiveness by the eicosane is related to changes in the wettability of the surface. The hydrophobicity of the steel surface increased as the concentration of the paraffins in the synthetic paraffin-oil mixture was increased.

KEYWORDS: paraffin, wax, CO_2 corrosion, carbon steel, wettability

INTRODUCTION

Paraffinic petroleum may contain between 20-50 wt.% normal paraffins in the oil fraction.[1] Paraffin is a common name for alkane compounds, which are hydrocarbons with exclusively single bonds, also called saturates. Alkanes have the general formula C_nH_{2n+2} and are referred to as being a "wax" in their solid state. The name paraffin comes from Latin meaning "lacking affinity", which describes the absence of reactivity of the paraffins, including at the steel surface. Despite the lack of surface chemical activity, at low temperatures – below the so called wax appearance temperature (WAT), paraffins can precipitate and deposit on the pipe surface. When the wax layer covers the steel surface, it can slow down corrosion processes by hindering the diffusion of corrosive species to the surface. However, if the temperature stays below the WAT for extended period of time, the wax layer becomes thicker with time, and can, in the long run, cause partial or total blockage of the pipe.

The effect of compounds in the crude oil on CO_2 corrosion in oil-water flow has been investigated previously. In 1989, Efird and Jasinski[2] found that crude oils can generate corrosion inhibition, but the extent of inhibition varied from one crude oil to another. They determined that the conferred corrosion inhibition was derived from the chemistry of the crude oils themselves rather than crude oil simply forming a "protective coating". A study of Venezuelan crude oils[3-7] revealed that resins and asphaltenes were very influential when it came to corrosion inhibition, as well as sulfur and nitrogen containing compounds. When surface active compounds found in crude oils were studied separately, it was found that some of the sulfur and nitrogen containing compounds provided excellent corrosion protection, while others provided only moderate or negligible protection.[8] Ajmera et al.[9] found that asphaltenes have a direct effect on corrosion inhibition as well as wettability of steel surfaces. In addition, dos Santos, et al.[10] investigated the roles of crude oil polar components, including asphaltenes and naphthenic acids, on steel surface wetting by contact angle measurements and concluded that their removal transitioned the behavior of the surface from being oil wetted to water wetted.

These studies showed some examples how the chemistry of the crude oil can influence corrosion protection but few considered the role of saturates such as paraffins. When saturates are looked at in isolation they are generally not found to directly affect the corrosion rate.[4] However, the corrosion retardation properties of paraffins are not derived from their surface active characteristics; rather it is due to their relatively high freezing point (also called WAT) which causes the paraffins to deposit as a waxy layer on the steel surface. Therefore, in order to study the effect of paraffins, the testing needs to be done at temperatures below the paraffin freezing point (WAT). Morales et al.[11] found that the presence of a paraffin wax film on the surface promotes a significant reduction of general corrosion rates, although localized corrosion was observed relating to loss of integrity of the paraffin layer.

In the present paper, the effect of paraffin concentrations on corrosion and wettability is investigated, both above and below the WAT for comparison. The persistency of the corrosion retardation achieved below the WAT is then tested with high shear stresses and at increased temperature.

EXPERIMENTAL PROCEDURE

A paraffin-oil mixture is used to isolate the effect of paraffins. The paraffin-oil mixture is composed of a hydrotreated light distillate, LVT200[(1)] (ρ = 825 kg/m^3 (density), μ = 2 mPa.s (viscosity), σ = 40.0 mN/m (interfacial tension with water)) consisting of low molecular weight hydrocarbons (C9-C16) in which a laboratory grade normal paraffin (n-paraffin) eicosane ($CH_3(CH_2)_{18}CH_3$) is added at different concentrations. The model oil is categorized as paraffinic and is clear and colorless with its components not precipitating even at relatively low temperatures (0ºC). Furthermore, the model oil does not affect the corrosion rate or the wettability of the steel surface.[12] Therefore, the effects measured during the experiments are attributed to the added long-chain paraffin eicosane.

Oil Properties

Since the effects of paraffins on CO_2 corrosion and wettability are studied using a long-chain paraffin-oil mixture, it is necessary to study the properties of the mixture and how they change depending on the concentration of eicosane therein. The chosen mixtures are 0% (pure model oil), 10%, 30% and 50% eicosane, based on weight.

Density was measured by weighing 100 ml of the paraffin-oil mixture using a balance and a pre-weighed graduated cylinder. The weight of the cylinder is subtracted from the total weight and the density calculated by dividing the liquid weight by its volume.

The viscosity is tested using a falling ball viscometer at an ambient temperature. The principle of falling ball is based on Stokes' Law for a sphere falling in a viscous fluid under the effect of gravity. The measurement is made by measuring the time it takes the ball to fall between two set marks in a column filled with the testing fluid. The viscosity, $\mu = t(\rho_b - \rho_f)K$, is calculated in mPa.s with t as the ball's falling time (s), ρ_b the density of ball (g/cm^3), ρ_f the density of test fluid (g/cm^3) and K, which is a constant specific to the ball.

The wax appearance temperature (WAT) is measured using an ice bath and a thermocouple. The prepared paraffin-oil mixtures are placed in a beaker in an ice bath. The WAT is recorded with the thermocouple as the temperature at which solid is first visually observed in the paraffin-oil mixture.

The oil and water interfacial tension was measured with a ring-pull tensiometer. The principle of the tensiometer is that when the withdrawal force (upward) exerted externally on a platinum ring is larger than the force (downward) caused by interfacial tension between oil and water, the film at the interface on the platinum ring breaks. The interfacial tension is measured in dyne per centimeter (dyne/cm), which is equivalent to milliNewtons per meter (mN/m).

Corrosion Rate

The corrosion testing was performed in a glass cell (Figure 1) using three electrodes: a rotating cylinder as the working electrode, a silver/silver-chloride (Ag/AgCl) saturated with 1 M KCl solution as the reference electrode located in a Luggin capillary tube and a concentric platinum ring as the counter electrode. The linear polarization resistance (LPR) technique was used to measure the corrosion rate.
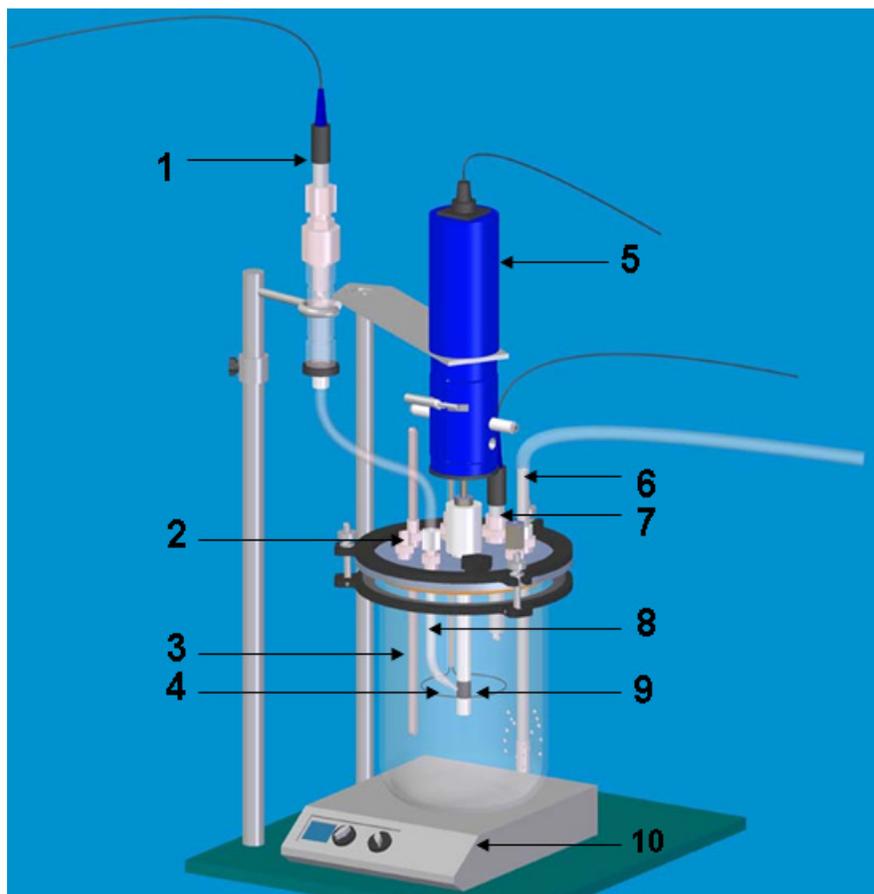

[(1)] Trade name.

Figure 1: Schematic of a glass cell set-up with rotating cylinder electrode (RCE). The parts of the set-up are: 1. reference electrode, 2. gas outlet, 3. temperature probe, 4. platinum counter electrode, 5. rotator, 6. gas inlet, 7. pH-electrode, 8. luggin capillary, 9. working electrode and 10. hot plate.

Initial Conditions

Initially, the glass cell including the Ag/AgCl reference electrode and the platinum counter electrode was filled with 1.75 L of 1.0 wt.% NaCl solution , deoxygenated by purging with CO_2 for 1 hour. Deoxygenation was maintained by purging the test solution with CO_2 gas throughout the test. When the desired temperature of the electrolyte was attained (5°C - 30°C), the pH of the test solution was adjusted from the equilibrium pH to pH 5.0 by adding a deoxygenated sodium bicarbonate ($NaHCO_3$) solution, monitored by a pH probe. The working electrode, a carbon steel (X65) rotating cylinder, with an exposed surface area of 5.4 cm^2, polished with 600 grit sand paper, was inserted into the electrolyte as shown in Figure 1 with a rotation speed of 1000 rpm. The temperature of the solution was maintained at either 5°C for tests performed below the wax appearance temperature (WAT) or at 30°C for tests performed above the WAT. An additional test was performed where the temperature was increased stepwise by 5°C from 5°C to 30°C in order to assess any ramping affect. A potentiostat was connected to the three-electrode glass cell and the open circuit potential monitored. The electrochemical measurements were carried out after 5 to 30 minutes when a stable potential had been established. The procedure described above is the initial step and common for all the corrosion tests performed in the glass cells.

Corrosion above the Wax Appearance Temperature (WAT)

Three steps: partitioning, corrosion inhibition and persistency, were performed for tests at a temperature above the WAT, where the temperature is maintained at 30ºC and all of the eicosane is in the liquid phase. Prior to the 'partitioning' step, the initial conditions, as described above, are established.

Step 1: Partitioning.

The partitioning step is employed to show whether any chemical from the paraffin-oil mixture will partition into the water phase from the oil phase and influence the corrosion rate. In this step 0.25 L of the paraffin-oil mixture was heated to the same temperature (30ºC) as the brine solution and added slowly on the top of the water phase. Because of the lower density of the oil, the oil mixture will float on top of the water phase. Thus, the carbon steel rotating cylinder is always immersed in water. The open circuit potential was carried out until a stable potential is established. Corrosion rate was measured every 20 minutes for 8 hours.

Step 2: Corrosion inhibition.

The corrosion inhibition step immediately follows the previous partitioning step. The corrosion inhibition step is done to verify how the eicosane-oil mixture will influence the corrosion rate of the working electrode. In this step the working electrode was moved up into the oil phase, which floats on top of the water phase, and rotated there at 1000 rpm for 15 minutes. The aim of moving the working electrode up and keeping it in the oil mixture is to sufficiently expose the working electrode to the eicosane-oil mixture. The working electrode was then placed back into the water phase and the corrosion rate measured. This "up-and-down" process was repeated every 20 minutes for 8 hours.

Step 3: Persistency.

When the corrosion inhibition step is completed, the next step is to measure the persistency of any effect observed in the previous 'corrosion inhibition' step. After the last repeated cycle in Step 2, the working electrode was kept steadily in the water phase. Corrosion rate measurements were conducted every 20 minutes for another 10 hours.

Corrosion below the Wax Appearance Temperature (WAT)

Initial conditions were established as described above, with temperature of the electrolyte adjusted to and maintained at 5ºC during the whole measurement. At this temperature, the eicosane-oil mixture becomes solid.

Step 1: Partitioning.

In this test 0.25 L of the eicosane-oil mixture, which is slightly above the WAT, was added slowly on the top of the water phase and the temperature of both water phase and oil phase adjusted to 5ºC. This made the oil phase on top of the water phase solidify with the carbon steel rotating cylinder below and surrounded by the aqueous electrolyte. The open circuit potential measurements were carried out until a stable potential was established, after which the corrosion rate was measured every 20 minutes for 4-5 hours.

Step 2: Corrosion inhibition and persistency.

The working electrode was prepared according to the initial step and immersed in the eicosane-oil mixture at a temperature slightly above the WAT (1ºC higher than the WAT of each mixture) for 15

minutes. It was then extracted from the mixture and cooled at 5ºC for 5 minutes until a wax layer visible to the naked eye appeared on the carbon steel surface. Meanwhile, a glass cell was prepared following the same procedure as described above for the initial condition with the temperature adjusted to 5ºC. The freshly prepared working electrode was inserted into the water phase of the glass cell to measure the corrosion rate every 20 minutes for 22 hours. The aim of this step is to test whether the layer of the synthetic paraffin-oil mixture, which coats the working electrode, can significantly reduce the corrosion rate when the temperature is below the WAT, and if so, whether the corrosion retardation is persistent.

Effect of Shear on Corrosion Protection due to Long Chain n-Paraffins

The aim of this test is to determine whether the wax layer on the specimen surface can be physically removed by shear stress. After preparing the working electrode according to the procedure described for corrosion inhibition below the WAT (see above), the specimen with a wax layer was inserted into the water phase in the glass cell at 5 ºC and the corrosion rate was measured every 20 minutes at 1000 rpm, which equals a linear velocity at the specimen surface of 0.6 m/s and a shear stress of 2.1 Pa,[13, 14] for 4-6 hours. After the corrosion rate became stable, the rotating speed was temporarily increased up to 9000 rpm, which equals a linear velocity at specimen surface of 5.6 m/s and a shear stress of 87 Pa, for 1 hour. Then the rotation speed was slowed down to 1000 rpm and the corrosion rate measured. This procedure was repeated until the corrosion rate is stable following the increase in the rotation speed.

Effect of Temperature on Corrosion Protection due to Long Chain n-Paraffins

This test was carried out to see how the corrosion protection achieved by the eicosane below the WAT was affected by increasing the temperature. The working electrode was immersed in the eicosane-oil mixture at a temperature slightly above the WAT (1ºC higher than the WAT of each eicosane-oil mixture) for 15 minutes, then moved out and cooled at 5ºC in air until a wax layer appeared and was clearly visible. Next, the specimen was inserted into the water phase in the glass cell at 5 ºC and the corrosion rate was measured every 10 minutes at 5ºC for half an hour. The temperature was then increased in 5°C increments up to 30ºC. The rotation speed of the working electrode was kept at 1000 rpm. At each temperature, the corrosion rate was measured every 10 minutes for half an hour.

Contact Angle Measurements

One of the objectives of this project was to investigate the effect of a long chain paraffin on steel wettability, which was performed by measuring the contact angle of an oil droplet on a steel surface, surrounded by a water phase (oil-in-water) or a water droplet in oil phase (water-in-oil) at temperatures both above the WAT and below the WAT. An oil-in-water droplet is representative of an oil droplet wetting the steel surface under the condition of continuous water layer and a water-in-oil droplet is representative of a water droplet wetting the steel under the condition of a continuous oil layer. Figure 2a) shows the oil-in-water contact angle of an oil droplet which is placed beneath the steel surface surrounded by the water phase. In this case the surface is hydrophobic and the oil droplet spreads out and the contact angle is > 90°. Figure 2b shows the water-in-oil contact angle of a water droplet which is placed on the steel surface surrounded by an oil phase. In this case the surface is hydrophilic and the water droplet spread out making a contact angle < 90°. The contact angle is defined as the angle between the surfaces of the droplet and the solid substrate line in contact with the water phase. A goniometer (Figure 3) is an instrument used for contact angle measurement. The goniometer is composed of the test cell, which is filled with the continuous liquid (oil or water) into which the steel sample is inserted, backlight, video camera and image capturing system.
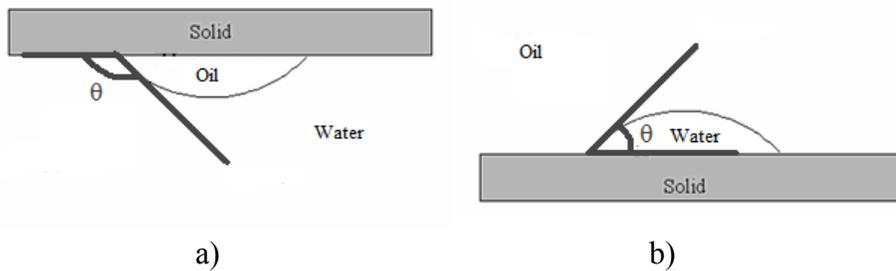
a)   b)

Figure 2: Sketch of the contact angle, θ, of: (a) oil droplet (oil-in-water) (b) water droplet (water-in-oil).
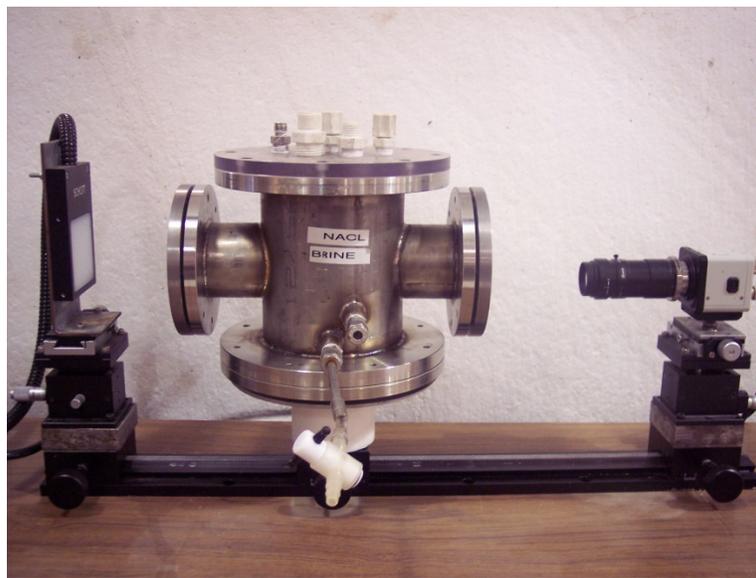

Figure 3: Goniometer setup with the video camera and a backlight.

Two kinds of contact angle measurements were conducted, oil-in-water and water-in-oil. The oil-in-water contact angles were conducted by filling the vessel of the goniometer system with 1 wt.% NaCl at pH 5.0 and saturating it with CO_2. Meanwhile the X65 steel sample was polished to a 600 grit finish and then pre-wetted by inserting it into a beaker with the paraffin – model oil mixture, which had been purged with CO_2, at a temperature slightly (~1°C) above the WAT (30°C) for 15 minutes. For measurements taken below the WAT (5°C), the sample was maintained at 5°C after the pre-wetting until a wax layer formed on the surface. This was then inserted into the goniometer vessel and the measurements taken with a drop of the eicosane-model oil mixture. The water-in-oil contact angles were measured with the vessel of the goniometer filled with the eicosane – model oil mixture, purged with CO_2, at temperatures above the WAT, but with the vessel filled with the model oil only for temperatures below the WAT. The sample preparation was the same as for the oil-in-water contact angle measurements described above, including the pre-wetting procedure. The water phase was prepared in the same fashion as for the oil-in-water procedure described above.

RESULTS AND DISCUSSION

Properties of the Eicosane – Model Oil Mixture

The properties of the eicosane – model oil mixture, such as wax appearance temperature, density, viscosity and interfacial tension, are presented in Table 1. No wax is formed when the model oil is cooled without adding eicosane. With 10 wt.% of long chain paraffin (eicosane) added to the model oil, the wax appearance temperature (WAT) is measured at 7°C, and it increases as the amount of paraffins is increased up to 35°C for pure eicosane (100 wt% long chain paraffin). The density of the eicosane – model oil mixture decreases proportionally as the amount of the eicosane added to the model oil is increased and at the same time the viscosity is increased as the larger paraffin eicosane molecules are added to the mixture. However, the interfacial tension is unaffected by the addition of the long chain paraffin eicosane, which is expected since paraffins are not surface active compounds.

Table 1
Physical properties of the eicosane - model oil mixture at difference concentration of paraffins (eicosane)

	Wax Appearance Temperature (°C)	Density (kg/m^3)	Viscosity (mPa.s)	Interfacial tension (mN/m)
Model oil	-	825.1	2.78	44.1
10 wt% eicosane	7	818.9	3.11	43.0
30 wt% eicosane	20	809.5	3.58	45.5
50 wt% eicosane	27	805.4	4.08	44.4
100 wt% eicosane	35	788.6	-	-

Corrosion above the Wax Appearance Temperature (WAT)

Figure 4 shows the corrosion rate measured for each of the three steps for the tests performed at 30°C (above the WAT), partitioning, corrosion inhibition and persistency. There is no significant difference in the corrosion rate among different concentrations of the long chain paraffin eicosane and they are comparable to the corrosion rate measurwith only the water phase and with the pure model oil (0% eicosane). Furthermore, there is no indication that the paraffins influence the corrosion process when dissolved in the oil above the WAT. There is no reduction in the corrosion rate during the partitioning phase, which is unsurprising since the paraffins are non-polar hydrocarbons and will not mix with water, which is polar. The partitioning step does provide the information that there are no contaminants in the paraffin-oil mixture that will cause corrosion inhibition.

The corrosion inhibition step seen in Figure 4 shows that the corrosion rates for the different concentrations of long chain paraffin in the eicosane-oil mixtures do not differ significantly from the corrosion rate of the water phase on its own, or the model oil without addition of long chain paraffin (0 wt.% eicosane). The corrosion rates for the different mixtures steadily increase from ~0.65 – 0.70 mm/year to ~0.85 – 1.05 mm/year, without any noticeable effect of the 'corrosion inhibition' step. The variance in the persistency step appears to be lower than for the 'corrosion inhibition' step, which could be an effect of some of the oil temporally adhering to the working electrode once it has been returned to the water phase for corrosion rate measurement during the 'corrosion inhibition' step. It can be concluded that the paraffins do not affect the corrosion process at temperatures above the wax appearance temperature (WAT).
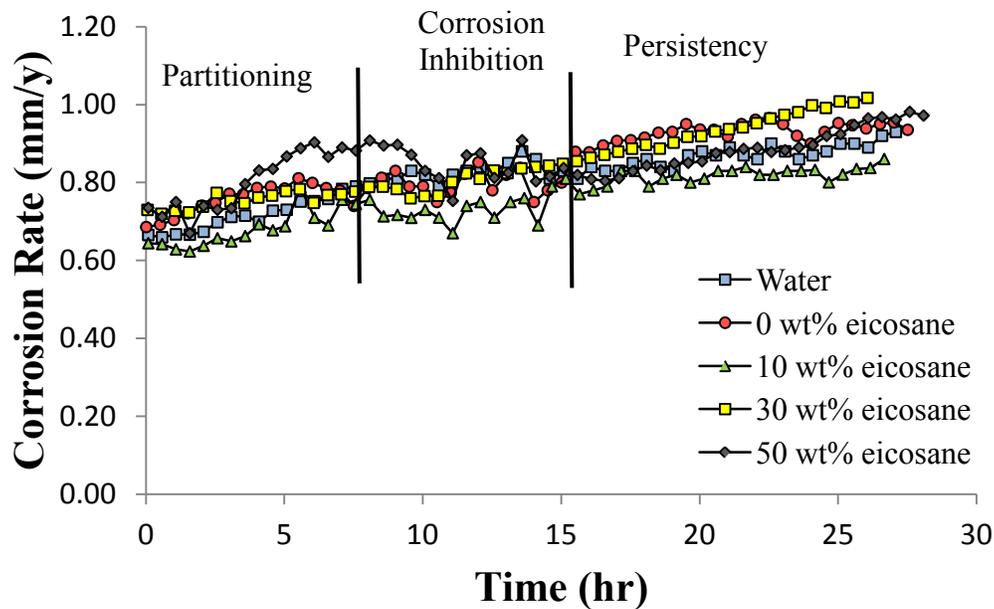
Figure 4: Corrosion rate measured at 30ºC (above the WAT) of different concentration of paraffins in the model oil, from 0 wt% (pure model oil) to 50 wt% of long chain paraffin (eicosane). The graph shows the corrosion rate during the three steps of partitioning, corrosion inhibition and persistency and compares the corrosion rate to the baseline (only water phase).

Corrosion below the Wax Appearance Temperature (WAT)

The corrosion rate during the partitioning step at 5°C (below the WAT) is 0.25 mm/year (Figure 5), which is much lower than the corrosion rate of 0.6 – 1.0 mm/year for 30°C (Figure 4) due to the slower kinetics at the lower temperature. It is also more stable, with little or no variance and no influence of the solid oil phase. No partitioning from the oil phase to the water phase was measured.
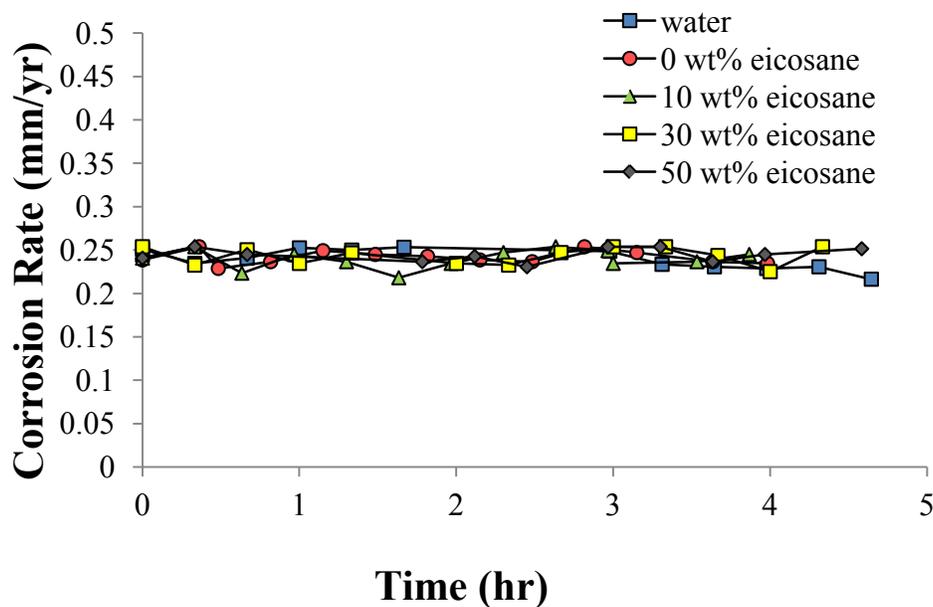

Figure 5: Corrosion rate measured at 5ºC (below the WAT) of different concentration of eicosane in the model oil, from 0 wt% (pure model oil) to 50 wt% of long chain paraffin (eicosane). The graph shows the corrosion rate during the partitioning step and compares the corrosion rate to the baseline (only water phase).

Figure 6 shows the corrosion rate (mm/yr) vs. time (hr) at different concentration of paraffins during the corrosion inhibition and persistency step at 5°C. By comparing the corrosion rates for the water and pure model oil (0 wt% paraffins), it is clear that the model oil on its own does not produce protection from corrosion. With a paraffin film created in the 10 wt% eicosane mixture, an initial corrosion protection of 40% is achieved, however, this protection is not permanent, and as the working electrode rotates at 1000 rpm, the protection of the paraffin layer is eventually lost as the final corrosion rate equals the baseline corrosion rate of water.

By using higher concentration of paraffins, more permanent corrosion protection is achieve. At concentrations of 30 wt% and 50 wt%, a strong enough paraffin film is formed on the working electrode to produce a corrosion protection of about 90%, which is very persistent in the time frame presented in Figure 6.

It has been demonstrated in Figure 6 that with a large enough concentration of paraffins in the oil phase, a significant and persistent corrosion protection can be established due to the deposition of the paraffins on the steel surface. In order to determine if the paraffin layer provide lasting protection in the case of changing operating conditions such as increased shear or increased temperature, further testing was carried out to challenge the paraffin protective layer.
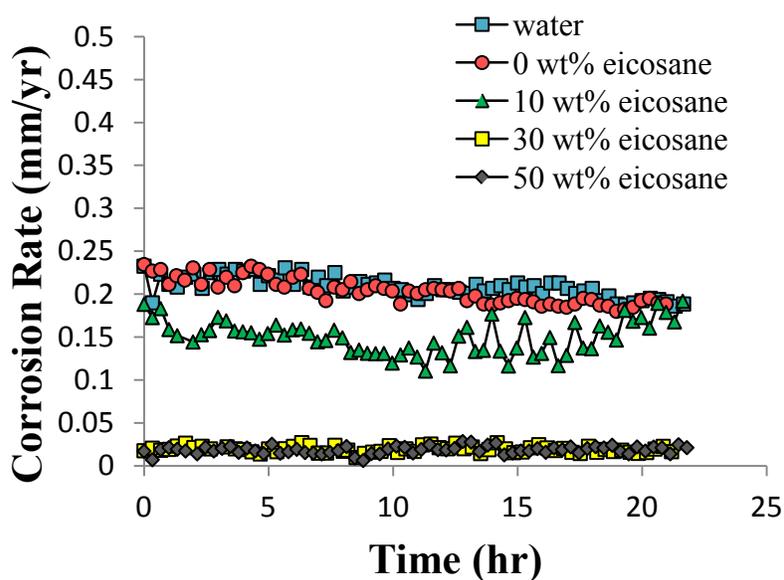

Figure 6: Corrosion rate measured at 5ºC (below the WAT) of different concentration of eicosane in the model oil, from 0 wt% (pure model oil) to 50 wt% of long chain paraffin (eicosane). The graph shows the corrosion rate during the corrosion inhibition and persistency step and compares the corrosion rate to the baseline (only water phase).

In Figure 7, a working electrode was prepared in the same way as for previous corrosion tests at 5°C using 30 wt% eicosane-model oil mixture. A corrosion rate of 0.02 mm/year is initially established at 1000 rpm as before (Figure 6), subsequently the rotation speed was increased to 9000 rpm for at least 1 hour before decreasing the rotational speed back to 1000 rpm to conduct more corrosion rate measurements. The periods where the rotational speed is set to 9000 rpm is indicated by arrows in Figure 7. The corrosion rate increases to 0.16 mm/year after the first two 1 hour periods of 9000 rpm rotational speed and no further increase in the corrosion rate is recorded. There is still some protection compared to the water baseline, or 36% compared to the initial corrosion rate, but it can be concluded that most of the corrosion protection has been lost due to the long chain paraffin layer being physically removed from the surface during the periods of increased shear.
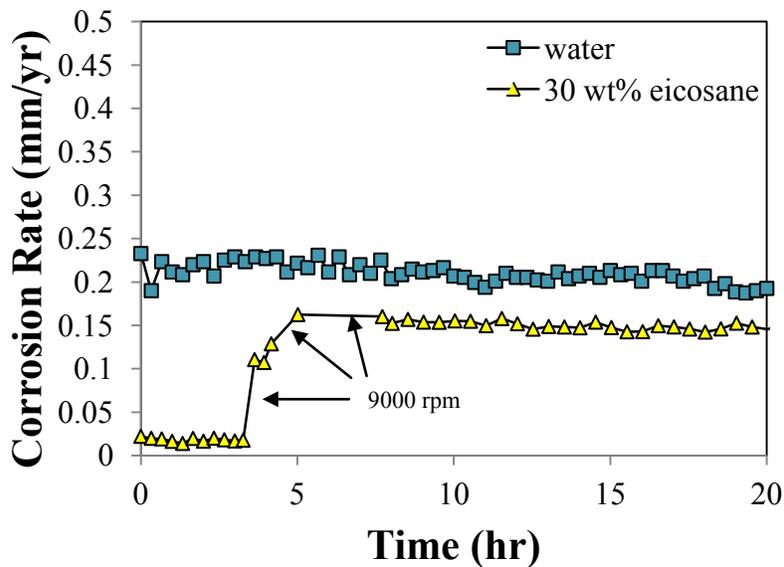
Figure 7: The effect of shear stress (9000 rpm) on the corrosion rate measured at 1000 rpm for 5ºC (below the WAT).

According to Figure 7 the protection of the long chain paraffin layer as shown in Figure 6 can be compromised during times of high shear. Figure 8 shows what happens to the corrosion rate of carbon steel under an eicosane film formed with 30 wt% long chain paraffin – model oil mixture when the temperature of the corrosion cell is increased. The corrosion rate is 0.02 mm/y at 5°C, then increases to 0.07 mm/y at 10°C, 0.14 mm/y at 15°C, 0.35 mm/y for 20°C, 0.50 mm/y at 25°C and finally ending at 0.71 mm/y at 30°C, which is comparable to the corrosion rate measured exclusively above the wax appearance temperature (Figure 4). The protection of paraffins can be assumed to be due to physisorption caused by relatively weak intermolecular forces such as van der Waals forces.
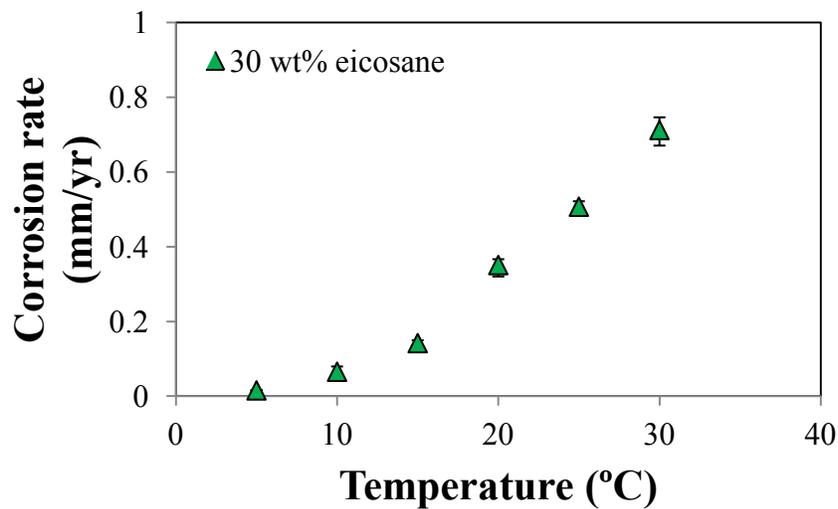

Figure 8: The effect of increased temperature on the corrosion rate measured at 5ºC (below the WAT) to 30 ºC (above the WAT).

Contact Angle Measurements

Figure 9 shows the plot of oil-in-water contact angle measurements of oil droplets in 1 wt.% NaCl aqueous solution (water) phase when the carbon steel (X65) specimen is pre-wetted with different concentrations of a eicosane – model oil mixture at 5ºC and 30ºC. Above the WAT (at 30ºC), the contact angle of the eicosane-oil mixture is independent of the concentration of long chain paraffins in the mixture, or around 35º, which means there is no significant change in the wettability of the steel surface, and it remains hydrophilic. When the temperature is below the WAT (at 5ºC), the contact angle of a model oil droplet changes significantly from 37º without any long chain paraffin added during the pre-wetting to a complete wetting (180º) when a eicosane-oil – model oil mixture with a 50 wt% long chain paraffin concentration was used during the pre-wetting. The deposition of eicosane on the surface of the steel changes the wettability from hydrophilic to hydrophobic at sufficiently high long chain paraffin concentrations. For the method which the long chain paraffin film was prepared in the research, the eicosane concentration needs to be around 20 wt% for the wettability alteration to take place.
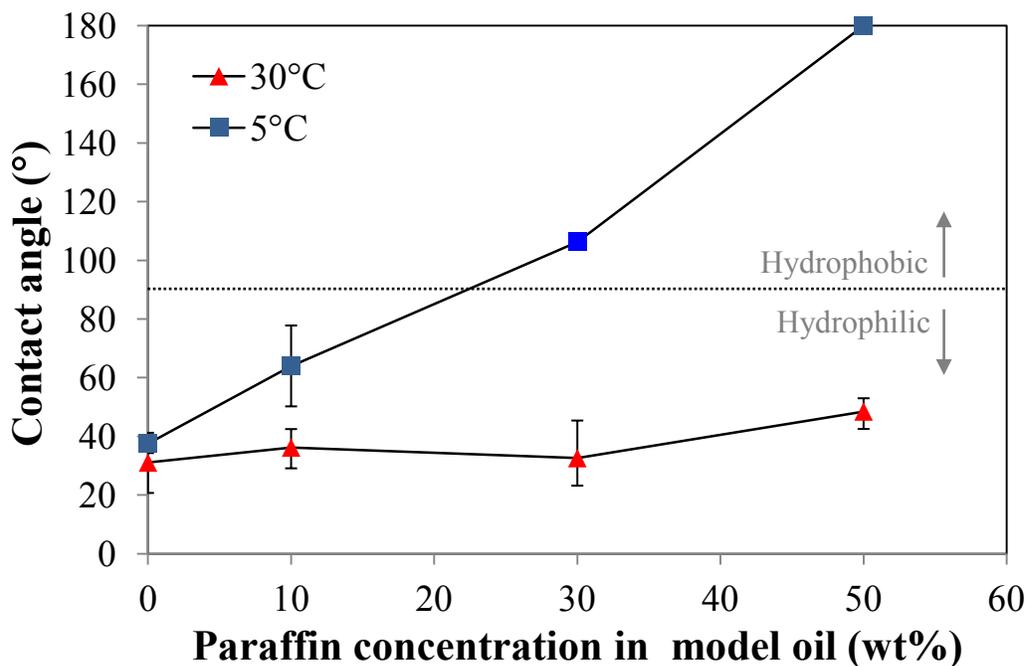

Figure 9: Oil-in-water contact angle measurements of eicosane – model oil mixture in 1 wt.% NaCl aqueous solution (pH5) at 30ºC (above the WAT) and 5ºC (below the WAT) with carbon steel (X65) pre-wetted with the eicosane - oil mixture as the substrate. For the measurements below the WAT, the substrate was pre-wetted in the paraffin – model oil mixture, but the measurements were carried out with droplets of pure model oil.

Water-in-oil contact angles are depicted in Figure 10 for water droplets in oil phase with the carbon steel (X65) specimen pre-wetted with different concentrations of long chain paraffin (eicosane) in a eicosane-oil mixture at 5ºC (below the WAT) and 30ºC (above the WAT). For measurements above the WAT, the contact angle changes from 75° without paraffins to 106° with the paraffins added to the model oil, independent of the concentration of the paraffins. When the temperature is below the WAT the contact angle changes from 59º when no paraffins are added to the model oil to 135º when 30 wt% of paraffins are added to the model oil for pre-wetting.
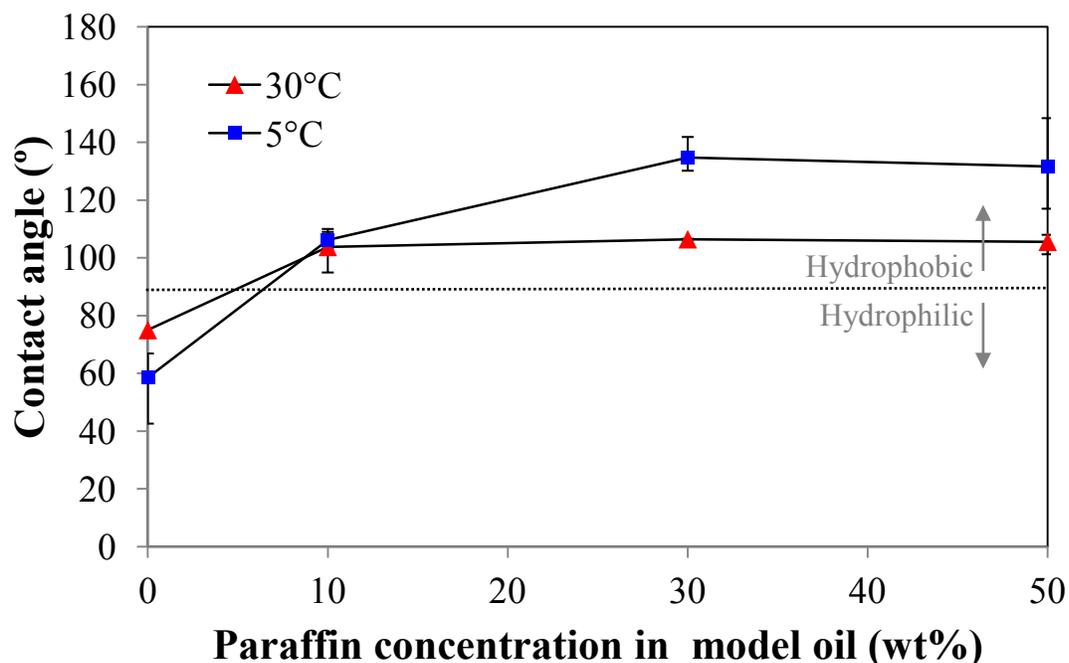
Figure 10: Water-in-oil contact angle measurements of 1 wt% NaCl aqueous solution (pH5) in eicosane – model oil mixture at 30ºC (above the WAT) and 5ºC (below the WAT) with carbon steel (X65) pre-wetted with the eicosane - oil mixture as the substrate. For the measurements below the WAT, the substrate was pre-wetted in the eicosane – model oil mixture, but the measurements were carried out with the pure model oil as the continuous phase.

Comparing Figure 9 and 10, it can be seen that at a temperature above the WAT, long chain paraffins are more effective altering the wettability from hydrophilic to hydrophobic when the oil phase is the continuous phase, possibly due to the larger molecular size of the paraffins (C20 compared to C9-C16 of the model oil) that are more difficult for the water to displace. However, at temperatures below the WAT this tendency of increased hydrophobicity when the continuous phase is oil is not observed. There is a certain challenge involved in measuring high (close to 180°) water-in-oil contact angles because even if the water droplet does not wet the surface at all, it still sits on the steel sample with an apparent contact angle lower than 180° due to the weight of the water droplet slightly flattening it.

CONCLUSIONS

Long chain paraffin layers can provide a substantial corrosion protection and wetting alteration at temperatures below the Wax Appearance Temperature. However, they should not be counted upon for corrosion protection since they interact weakly with the metal surface by van der Waals interactions and can be removed with heat and/or shear possibly resulting in a localized attack on the steel surface.

ACKNOWLEDGEMENTS

REFERENCES

1. Speight, J. G. In *The Chemistry and Technology of Petroleum;* Marcel Dekker: New York, NY, 1999; Vol. 3, pp 918.

2. Efird, K. D.,Jasinski, R. J. *Effect of the Crude-Oil on Corrosion of Steel in Crude-Oil Brine Production.* Corrosion, 1989, 45(2), 165-171.

3. M. Castillo, H. Rincon, S. Duplat, J. Vera, E. Baron, "Protective Properties of Crude Oils in CO_2 and H_2S Corrosion"*, CORROSION/03, paper no. 00005 (Houston, TX: NACE, 2003).

4. C. Mendez, S. Duplat, S. Hernandez, J. Vera, "On the Mechanism of Corrosion Inhibition by Crude Oils"*, CORROSION/01, paper no. 01044 (Houston, TX: NACE, 2001).

5. S. Hernandez, S. Duplat, J. Vera, E. Baron, "A Statistical Approach for Analyzing the Inhibiting Effect of Different Types of Crude Oil in CO_2 Corrosion of Carbon Steel"*, CORROSION/02, paper no. 02293 (Houston, TX: NACE, 2002).

6. S. Hernandez, J. Bruzual, F. Lopez-Linares, J.G. Luzon, "Isolation of Potential Corrosion Inhibiting Compounds in Crude Oil", CORROSION/03, paper no. 03330 (Houston, TX: NACE, 2003).

7. S. Hernandez, S. Nesic, G. Weckman, V. Ghai, "Use of Artificial Neural Networks for Predicting Crude Oil Effect on CO_2 Corrosion of Carbon Steels", CORROSION/05, paper no. 05554 (Houston, TX: NACE, 2005).

8. F. Ayello, W. Robbins, S. Richter, S. Nesic, "Crude Oil Chemistry Effects on Inhibition of Corrosion and Phase Wetting", CORROSION/11, paper no. 11060 (Houston, TX: NACE, 2011).

9. P. Ajmera, W. Robbins, S. Richter, S. Nesic, "The Role of Asphaltenes in Inhibiting Corrosion and Altering the Wettability of the Steel Surface", CORROSION/10, paper no. 10329 (Houston, TX: NACE, 2010).

10. dos Santos, R. G., Mohamed, R. S., Bannwart, A. C., Loh, W. *Contact Angle Measurements and Wetting Behavior of Inner Surfaces of Pipelines Exposed to Heavy Crude Oil and Water.* Journal of Petroleum Science and Engineering, 2006, 51(1-2), 9-16.

11. J. L. Morales, J.J. Perdomo, M. Ramirez, A. Viloria, "Effect of Crude Oil Contaminants on the Internal Corrosion in Gas Pipelines", CORROSION/2000, paper no. 00040 (Houston, TX: NACE, 2000).

12. Yang, S. Effect of Paraffins on Carbon Dioxide Corrosion and Water Wetting in Oil-Water Systems, Thesis, Ohio University, 2010.

13. Silverman, D. C. *ROTATING CYLINDER ELECTRODE FOR VELOCITY SENSITIVITY TESTING.* Corrosion, 1984, 40(5), 220-226.

14. Silverman, D. C. *The Rotating Cylinder Electrode for Examining Velocity-Sensitive Corrosion - A Review.* Corrosion, 2004, 60(11), 1003-1023.