Role of Asphaltenes in Inhibiting Corrosion and Altering the Wettability of the Steel Surface

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ABSTRACT

Asphaltenes (heptane insolubles) from a variety of crude oils have been identified previously as contributors to inhibition of internal corrosion of mild steel pipelines. However, the mechanism of inhibition is unknown. To explore the mechanism, carbon dioxide (CO_2) corrosion rates and wettability (oil/water contact angles) have been measured using Arab Heavy crude oil and its asphaltenes. Inhibition of CO_2 corrosion rates for carbon steel was measured using electrochemical methods in a glass cell; wettability was assessed using contact angle measurements in a multiphase goniometer. The phase behavior of asphaltenes in corrosion and wetting was evaluated in the crude, toluene (C_7H_8), or heptol (70:30 mixture of heptane [C_7H_{16}] and toluene). Inhibition on steel exposed to a hydrocarbon phase increased with the concentration of asphaltenes in toluene. Inhibition by asphaltenes dissolved in toluene appears to be more effective than in the whole crude, at equivalent concentrations of asphaltenes. At 5 wt% in toluene, asphaltenes form a strong protective layer on the carbon steel surface, which reduces the corrosion rate and makes the surface hydrophobic. When the solubility of the oil is altered to the point where asphaltenes start to flocculate, it enhances the corrosion inhibition greatly. However, the inhibition is not as persistent as for the fully dissolved asphaltenes, and the surface needs to be periodically wetted with the oil phase to maintain the protection.

KEY WORDS: asphaltenes, carbon dioxide corrosion, carbon steel, inhibition, wettability

INTRODUCTION

The tendency of crude oil to inhibit aqueous carbon dioxide (CO_2) corrosion has been observed in the field, but the mechanism of the inhibition has not been explained adequately. Some crude oils have good inhibitory effects and others do not. Differences are especially apparent in determining water cut at which corrosion becomes significant.[1] In recent years, the effect of crude oil chemistry on corrosion in oil-water two-phase flow has been investigated. Mendez, et al.,[2] found that corrosion inhibition results from a combination of effects from separated saturates, aromatics, or polars (resins plus asphaltenes). Hernandez, et al.,[3] considered numerous parameters, such as TAN (total acid number), metallic ions, total S, total N, API gravity, and type of crude oil. However, the only parameters found statistically significant in all cases were asphaltenes and resins. They proposed a prediction model of crude oil corrosion inhibition, which is an empirical function of saturates, aromatics, resins, and asphaltenes. Total N and total S were also included in the models for paraffinic and asphaltenic oils, respectively. In 2005, Hernandez, et al.,[4] revisited their data with a artificial neural network approach. A new model was developed that addressed the corrosion inhibition as a function of saturate, aromatic, resin, asphaltenes, acids, and porphyrinic metals. The underlying hypothesis is that surface-active species adsorb onto the metal surface creating a protective barrier. In the studies on a suite of Venezuelan crudes, asphaltenes were found to contribute to the inhibition;[4] however, the crudes were so diverse that
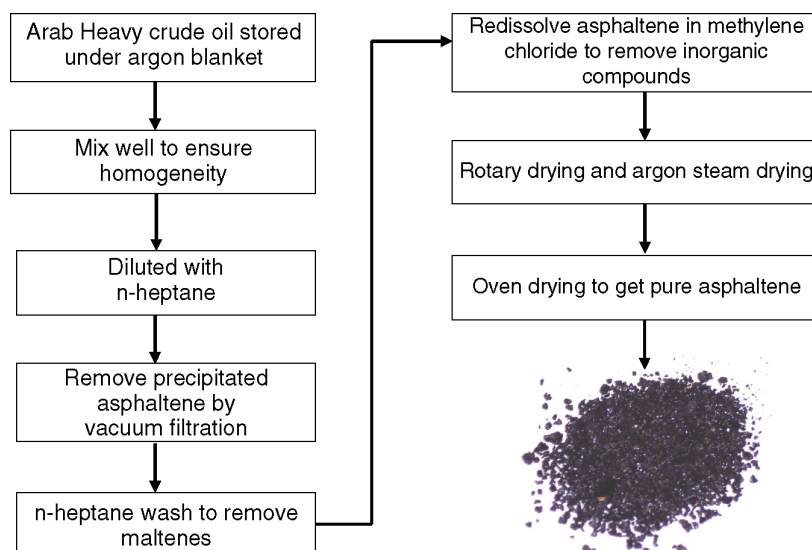
FIGURE 1: *Procedure used to extract asphaltenes from the crude oil.*[14]

their role in the inhibition was uncertain. Historically, Hackerman and Roebuck[5] demonstrated that polar compounds adsorbed onto metal surfaces and could act as acid corrosion inhibitors. This can be valid for polar compounds naturally found in the crude oil as well, including asphaltenes.

A Joint Industry Project (Water Wetting JIP)[1] has been investigating the mechanism by which chemical compounds present in the crude oil inhibit corrosion. The project attempted to determine behavior of model oil soluble polars in dynamic oil/water systems. Specifically, it examined the effects on partitioning, wetting, and the persistence of polars adsorbed onto carbon steel. Several surface-active model compounds were identified as active corrosion inhibitors, including acids, mercaptans. and basic nitrogen compounds (pyridine analogs).[6] These results suggested that high molecular weight polar compounds would be especially effective in providing "natural" corrosion inhibition.

Asphaltenes are the highest molecular weight and the most polar constituents in crude oil. However, asphaltenes are not homogeneous, and their characteristics change with the source of the crude oil.[7] Asphaltenes are typically defined as a solvent class; in the present case, asphaltenes will be defined as the toluene soluble/heptane insoluble fraction of a crude oil. These heptane insolubles include numerous S, N, and O functionalities with molecular weights from 500 u to >2,500 u. Asphaltenes from each crude are so complex and unique that there exist no model compounds for them. Because crude oils differ in saturates, aromatics, and resins as well as asphaltenes, comparisons among crudes are difficult to interpret.

Asphaltenes exist in crudes as nano-aggregates[8] solvated by the aromatics and resins; they stabilize emulsions to the greatest extent when they are near the point of flocculation.[9] Asphaltene deposition in well bores and flowlines is a major concern for flow assurance; again, asphaltene deposition is heaviest near the onset of asphaltene flocculation.[10] In the presence of water, asphaltenes adsorb onto surfaces by two mechanisms: ionic interaction, which depends on the composition of the aqueous and the solid phase, and deposition, which depends on the colloidal aggregation of asphaltenes.[11] Adsorption of asphaltenes onto metal powders reveals incomplete surface coverage in water-in-hydrocarbon emulsions; higher surface coverage was obtained when asphaltenes aggregate.[12] Deposition of asphaltene aggregates at interfaces (oil/water, oil/mineral, oil/metal) have been rationalized as a multi-step film formation process.[13]

In the present work, attention has been focused on asphaltenes isolated from Arab Heavy (sweet oil, ρ = 890 kg/m^3, API = 27.4, μ = 35.8 cP) in known solvent environments, which are then compared with results for the Arab Heavy crude oil. Figure 1 summarizes the extraction procedure for asphaltenes from the crude oil. The full extraction procedure is described in the literature.[14] The effects of asphaltenes on corrosion and contact angles were determined in toluene, heptol (70:30 heptane:toluene), and in the crude oil itself.

EXPERIMENTAL PROCEDURES

Corrosion Inhibition

A three-electrode glass cell (Figure 2) configuration was set up with a C1018 (UNS G10180)[2] carbon steel cylinder as the working electrode; a silver/silverchloride (Ag/AgCl) saturated with 4 M potassium

chloride (KCl) solution as the reference electrode and a concentric platinum ring as the counter electrode. The corrosion rate was measured with linear polarization resistance (LPR) and the corrosion rate was calculated with a B value of 0.013 V.

The glass cell was filled with 1.8 L of deionized water with 1 wt% sodium chloride (NaCl) and kept at 25°C. The solution was deoxygenated with CO_2 gas for 40 min to 1 h. The pH of the solution was adjusted to pH 5 by adding a deoxygenated sodium bicarbonate solution. The working electrode was introduced in the solution and rotated at 1,000 rpm. When a stable open-circuit potential (OCP) was obtained, the corrosion rate measurements were carried out.

The asphaltenes from Arab Heavy crude oil were dissolved in either toluene or heptol (70:30 heptane:toluene) in concentrations of 0, 0.1, 1, and 5 wt% asphaltenes.

Each test in a glass cell was performed in four consecutive steps: precorrosion, partitioning, direct inhibition, and persistency:

—First, in the precorrosion step, the corrosion rate of the rotating electrode (at 1,000 rpm) is measured before the oil phase (Arab Heavy crude oil or asphaltene dissolved in toluene or heptol) is introduced, but after the initial conditions (deoxygenation, pH adjustment, and stable OCP) have been established.

—Next, in the partitioning step, the working electrode was kept rotating at 1,000 rpm in the water phase while 0.2 L of the oil phase was added slowly on top of the water. At this point the glass cell (Figure 2, courtesy of Institute for Corrosion and Multiphase Technology, Ohio University) consists of two layers, a water layer (1 wt% NaCl solution, purged with CO_2) at the bottom and an oil layer (which can be either Arab Heavy crude oil or toluene/heptol with different concentration of asphaltenes) on top. These two layers are immiscible and stay separated during the testing. The corrosion rate was measured every 20 min in the water phase over a period of 5 h to 10 h to see if the asphaltenes partitioned from the oil phase into the water phase, affecting the corrosion rate.

—Then, in the direct inhibition step, which took place immediately after the partitioning step, the working electrode was moved from the water phase and up into the oil phase (within the same electrochemical cell), while CO_2 was being continuously purged and the working electrode rotated in the oil phase at 1,000 rpm for 15 min to expose the working electrode to the oil phase. The electrode was then moved back into the water phase and the corrosion rate was measured. This was repeated (expose the electrode to the oil phase, measure corrosion rate in the water phase) every 20 min for
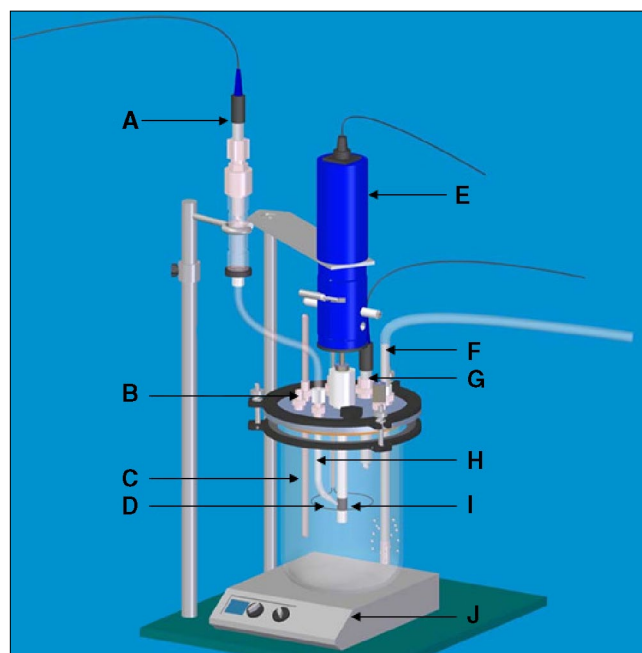

FIGURE 2. *Schematic of a glass cell setup with rotating cynlinder electrode (RCE). The parts of the setup are: (A) reference electrode, (B) gas outlet, (C) temperature probe, (D) platinum counter electrode, (E) rotator, (F) gas inlet, (G) pH electrode, (H) Luggin capillary, (I) working electrode, and (J) hot plate.*

10 h to 15 h to see how much the asphaltenes will adsorb on the working electrode and how that affects the corrosion rate.

—Finally, during the persistency step, which took place immediately after the corrosion inhibition step, the working electrode was kept in the water phase continuously, rotating at 1,000 rpm, while the oil phase remained on top, and the corrosion rate was recorded every 20 min for 5 h to 10 h to see if the corrosion rate established during the corrosion inhibition step would remain stable or change over time.

Contact Angle Measurements

A multiphase goniometer (Figure 3)[15] has been developed in-house, capable of measuring the contact angle of either a water droplet in the oil phase (water-in-oil) or an oil droplet in the water phase (oil-in-water). The contact angle was taken as the angle between the steel and oil/water surfaces measured via the water phase (Figure 4).

The water phase for the contact angle measurements was the same as that used for the corrosion rate measurements, i.e., 1 wt% NaCl deionized (DI) water solution, deoxygenated with CO_2, and pH adjusted to pH 5. Three different sets of contact angle measurements were performed:

—oil-in-water, water pre-wet surface
—water-in-oil, oil pre-wet surface
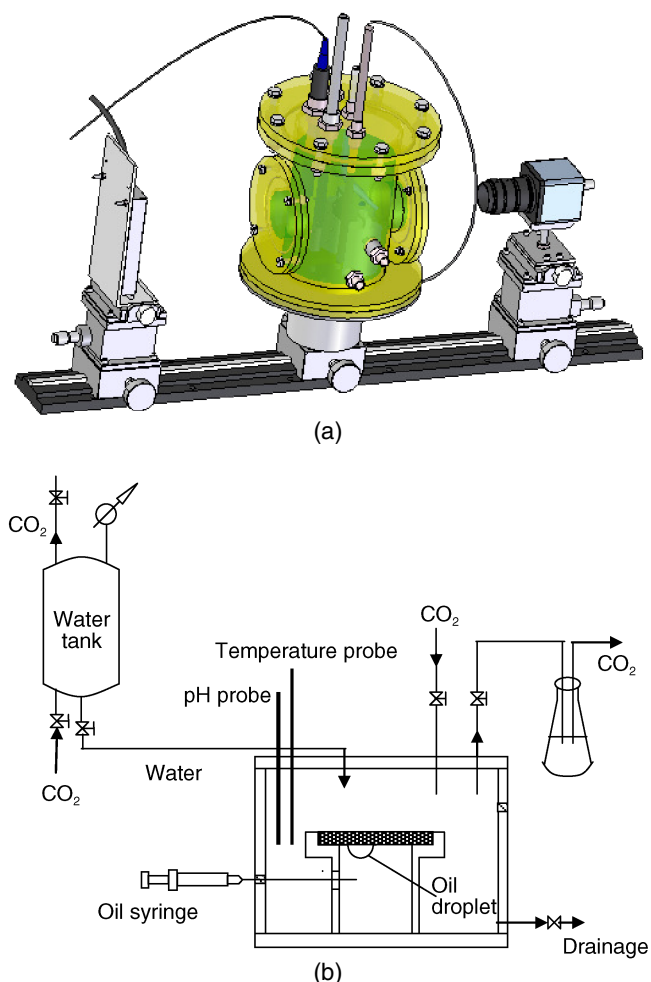—oil-in-water, oil pre-wet surface

(a)

(b)

FIGURE 3. *(a) Stainless steel goniometer cell in the center, with a camera on the right and a backlight on the left; (b) schematic presentation of the cross section of the goniometer cell with an oil droplet being deposited underneath the specimen's surface.[15]*
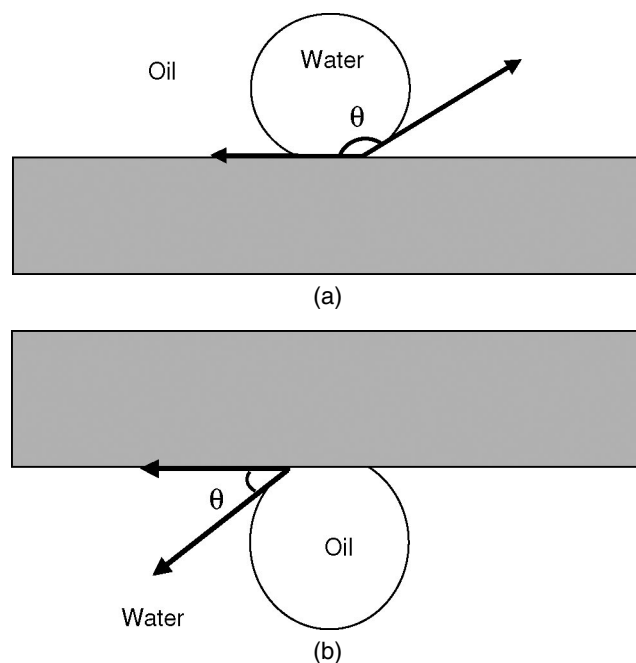

FIGURE 4. *Contact angle of (a) water droplet in oil phase (water-in-oil) and (b) oil droplet in water phase (oil-in-water). The contact angle (θ) is taken in respect to the water phase.*

men holder in the middle of the goniometer. Subsequently, CO_2 was purged through the cell for another hour. The droplet was then injected with a microsyringe through an injection point (for oil droplet) or from the top lid (for water droplet). An image of the droplet was captured with a camera and the contact angle was measured with image analysis software.

RESULTS AND DISCUSSION

Asphaltenes are a solubility class, rather than a chemical compound, and are defined as being soluble in toluene (where they exist as nano-aggregates[8]). However, the asphaltenes are insoluble in alkanes, such as heptane or pentane, which will cause the asphaltenes to flocculate and may precipitate if the alkane concentration gets too high. As noted in the Introduction, the behavior of asphaltenes is most evident at the point of incipient precipitation. To test for this phenomenon, the tests were conducted both with toluene for the corrosion inhibition behavior of dissolved asphaltenes and with heptol, which is a 70:30 mixture of heptane and toluene, to study the corrosion inhibition behavior of the asphaltenes at the point of flocculation. At this ratio of heptanes to toluene, 38 wt% of asphaltenes will precipitate and 62 wt% remains in solution.[7]

Corrosion Inhibition — Asphaltenes in Toluene

Partitioning — During the partitioning step, the working electrode was kept rotating in the water phase while the oil phase was placed on top. The
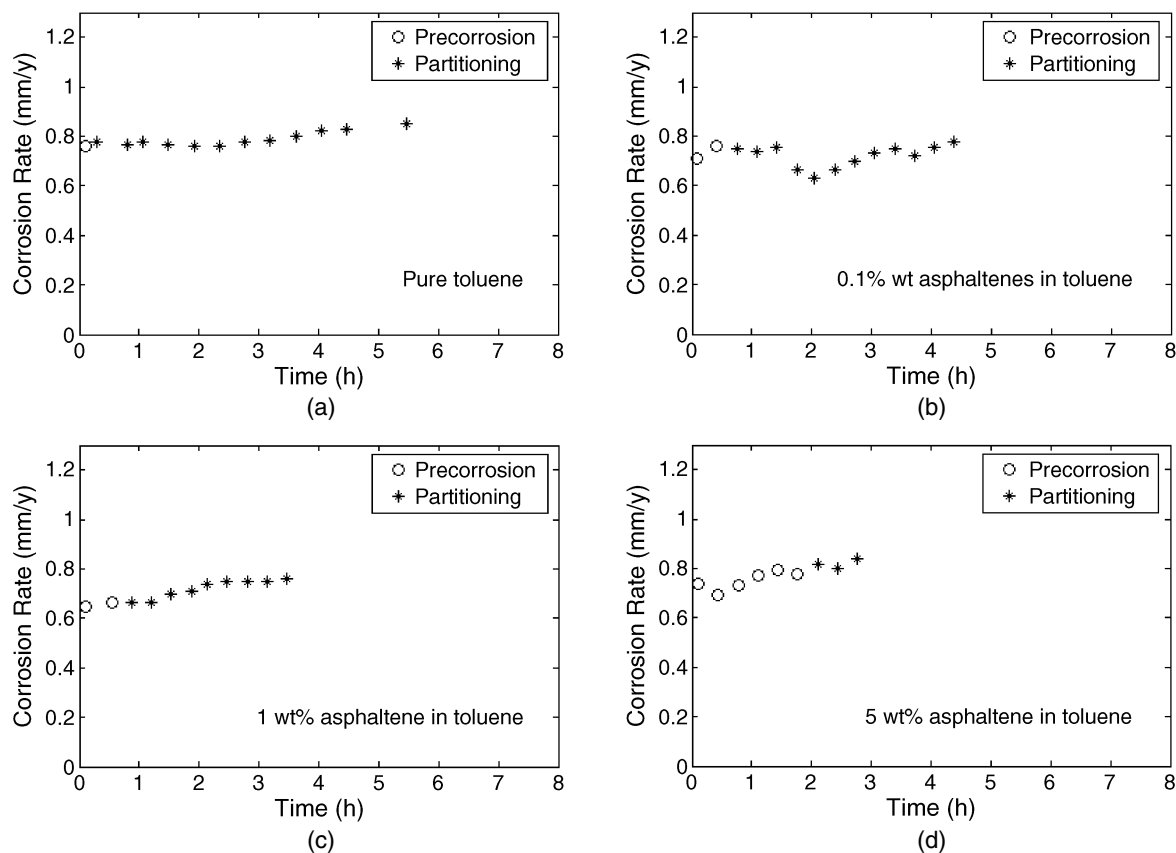
The first set is a straight-forward oil-in-water contact angle measurement, where the mild steel sample is immersed in the water phase and an oil droplet is deposited on the surface immediately thereafter. In the second set, the specimen was first immersed in the asphaltenic oil phase (oil pre-wet) before it was transferred into a clear model oil (LVT200†), and a water droplet was deposited on the surface from above. The clear model oil was used because the asphaltenic oil phase can be opaque, in which case the water droplet cannot be seen. In the third set of experiments, the specimen was pre-wet in the oil phase in the same manner as in set number 2, but was then transferred into a water phase and an oil droplet was deposited on the surface from below.

The experiments were all carried out by putting the continuous phase (either water or oil phase) into the goniometer and purging it with CO_2 for at least 1 h before the steel specimen was placed on a speci-

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† Trade name.

FIGURE 5. *Corrosion rate measured when an oil phase consisting of (a) pure toluene, (b) 0.1 wt% asphaltenes in toluene, (c) 1 wt% asphaltenes in toluene, and (d) 5 wt% asphaltenes in toluene is added on top of the aqueous phase. "Precorrosion" refers to the corrosion rate measured before the addition of the oil phase and "partitioning" to the corrosion rate measured after the addition of the oil phase.*

addition of asphaltenes dissolved in toluene had no effect on the corrosion rate as compared to the precorrosion rate (corrosion rate before the oil phase was added on top of the aqueous phase), as shown in Figure 5. Therefore, it was concluded that during the duration of the test nothing partitioned from the asphaltene solutions into the water phase that affected the corrosion rate.

Direct Inhibition — The inhibition measurements started in the same solution immediately after the partitioning step ended, so to reflect this, the partitioning data from Figure 5 is carried over to Figure 6 to demonstrate whether inhibition occurred.

As can be seen in Figure 6(a), the toluene by itself did not have an inhibiting effect, and adding 0.1 wt% asphaltenes dissolved in the toluene, Figure 6(b), did not affect the corrosion rate either. However, for 1 wt% asphaltenes, Figure 6(c), the corrosion rate is steadily decreased with each exposure to the oil phase from 0.67 mm/y to 0.48 mm/y where repeated exposures after 7.5 h had limited effect. For 5 wt% asphaltenes, Figure 6(d), the decrease in the corrosion rate is more pronounced with each exposure than for 1 wt% asphaltenes, and the corrosion rate goes from 0.70 mm/y to 0.32 mm/y over a 7-h period.

In Figure 7, the corrosion rate measured during the direct inhibition step is plotted for different concentrations of asphaltene dissolved in toluene, along with results from Arab Heavy, which is the crude oil from which the asphaltenes were extracted, and has been reported to contain as much as 6.7% to 9.0% asphaltenes.[9,14,16-18] The figure shows clearly that the lower concentration (0, 0.1 wt%) are not inhibitive, while higher concentration (1, 5 wt%) of dissolved asphaltenes are, producing inhibition of 28% and 54%, respectively, for 1 wt% and 5 wt% dissolved asphaltenes. By comparing the corrosion inhibition of 5 wt% asphaltenes dissolved in toluene to the corrosion inhibition of Arab Heavy crude oil of 49%, it can be suggested that the deposition of dissolved asphaltenes on the steel surface contributes to the corrosion inhibitive property of Arab Heavy crude oil.

Persistency — The persistency measurements started in the same solution immediately after the direct inhibition ended, so to reflect this, the direct inhibition data from Figure 6 is carried over to Figure 8, to demonstrate whether any inhibition that was measured was persistent.

After the periodic exposures of the steel sample to the asphaltenic oil were stopped, the corrosion rate
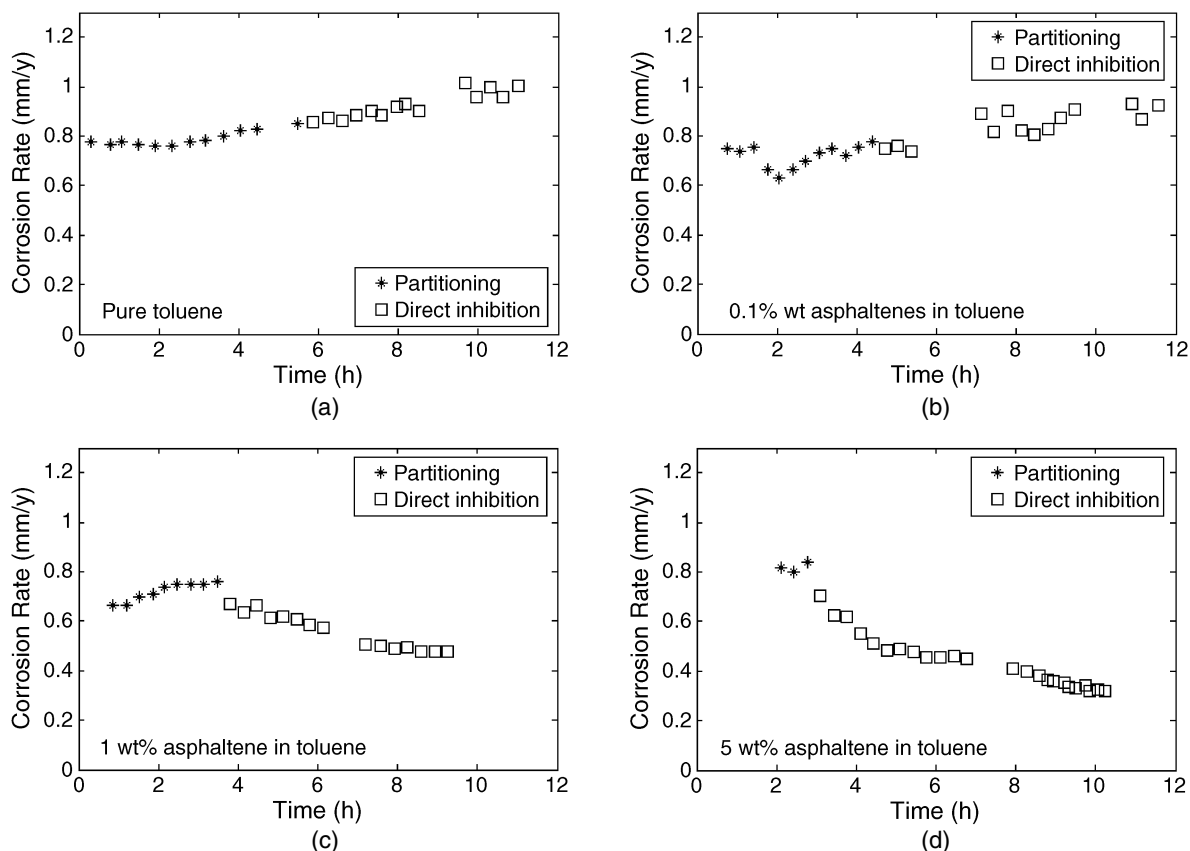
FIGURE 6. *Corrosion rate measured when the working electrode is exposed to the oil phase consisting of: (a) pure toluene, (b) 0.1 wt% asphaltenes in toluene, (c) 1 wt% asphaltenes in toluene, and (d) 5 wt% asphaltenes in toluene. "Partitioning" refers to the corrosion rate measured with the oil phase sitting on top of the aqueous phase and "direct inhibition" when the working electrode is exposed to the oil phase for 15 min at a time.*
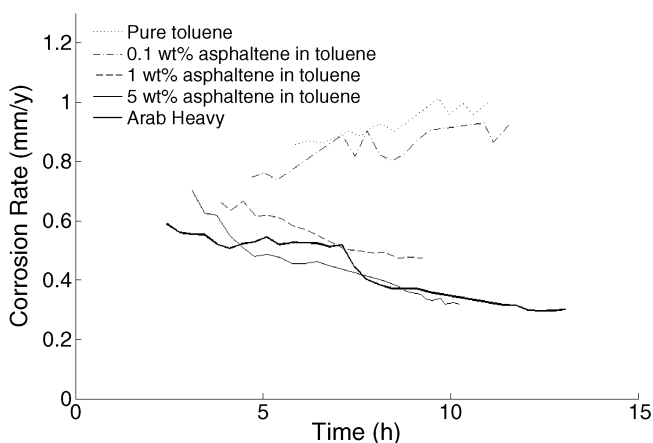

FIGURE 7. *The corrosion rate during the direct inhibition step, where the working electrode is exposed to the oil phase for 15 min before returning to the water phase for each LPR measurement.*

in the aqueous phase was followed for an additional period of time (Figure 8). In the cases where no inhibition was observed (pure toluene and 0.1 wt% asphaltene), the corrosion rate does not significantly change, but fluctuations are observed. The corrosion inhibition that was observed for 1 wt% and 5 wt% asphaltene in Figure 6 appears to persist over time, with no fluctuation in the corrosion rate, although the corrosion rate starts to increase slightly (from 0.47 mm/y to 0.52 mm/y) for 1 wt% after 10 h past the last exposure to the oil phase. It cannot be concluded whether this increase in the corrosion rate is a beginning of a complete loss of inhibition or whether it is just a small adjustment in the corrosion rate.

The corrosion inhibition obtained by exposure to Arab Heavy crude oil (Figure 7) is persistent, as can be seen in Figure 9. There is, however, a small adjustment of the corrosion rate in the beginning of the persistency step, suggesting that the deposited film, from the earlier inhibition step, is not as uniform for the crude oil as for the dissolved asphaltenes and part of it is lost, resulting in slightly higher corrosion rates.

Corrosion Inhibition — Asphaltenes in Heptol

The results for the corrosion inhibition measured after exposure to asphaltene in heptol focuses on two concentrations, one at a low concentration (0.1 wt% asphaltene) and the other one at a high concentration (5 wt% asphaltene), compared to the asphaltene concentration of the Arab Heavy crude oil (6.7 wt% to 9 wt%).
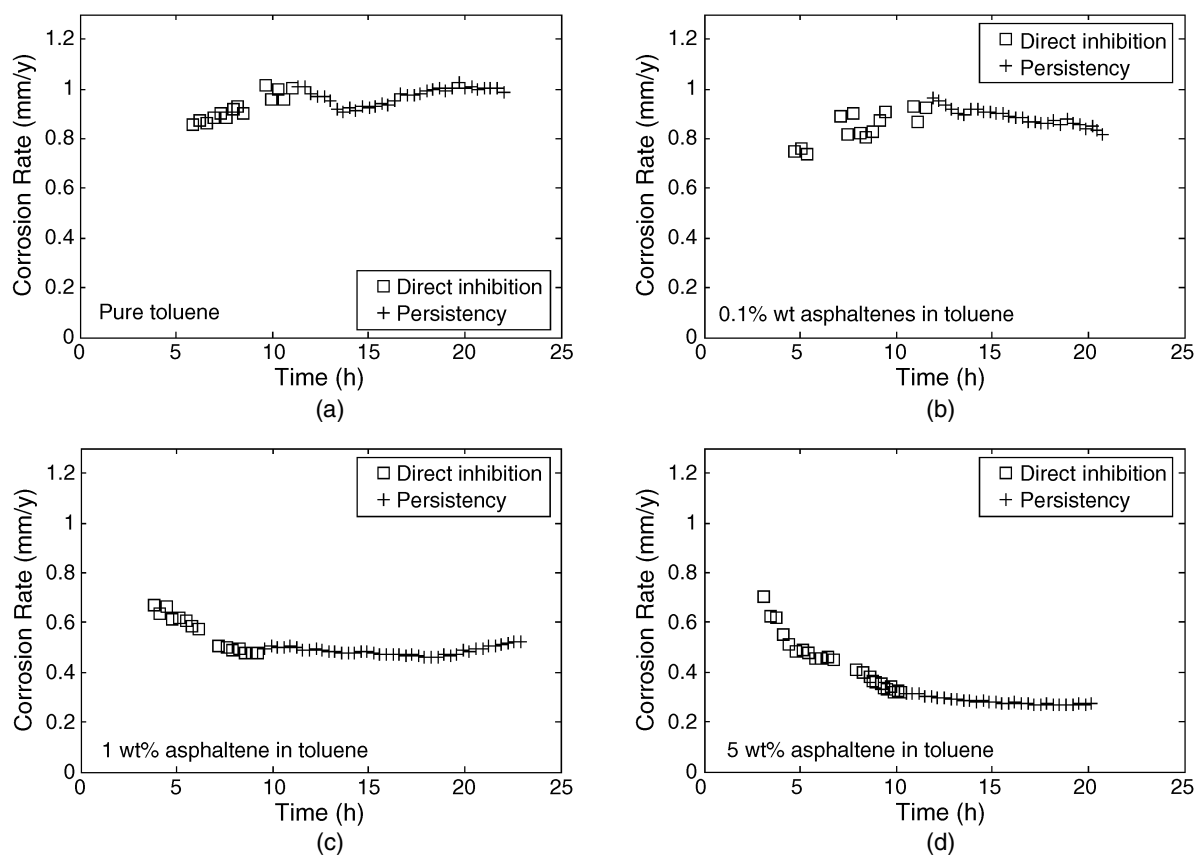
FIGURE 8. *Corrosion rate measured after the working electrode has been repeatedly exposed to an oil phase consisting of: (a) pure toluene, (b) 0.1 wt% asphaltenes in toluene, (c) 1 wt% asphaltenes in toluene, and (d) 5 wt% asphaltenes in toluene. "Direct inhibition" refers to the corrosion rate measured during exposure to the oil phase (Figure 6) and "persistency" to the corrosion rate measured after the exposure had ended.*

Partitioning — Figure 10 shows the partitioning data for both low concentration (0.1 wt%) and high concentration (5 wt%) of asphaltene in heptol compared to the precorrosion data. During precorrosion, only the aqueous phase is present in the glass cell and the partitioning data are taken after the addition of an oil phase on top of the water phase. The addition of the oil phase does not significantly change the corrosion rate; it remains steady compared to the precorrosion data. Therefore, it can be concluded that there is no partitioning from the oil phase in the short time frame measured here.

Direct Inhibition — For the direct inhibition, the working electrode was rotated in the oil phase for 15 min before returning to the aqueous phase for corrosion rate measurement by LPR. The corrosion inhibition from asphaltene in heptol (Figure 11) was significantly greater than the corrosion inhibition from both asphaltene in toluene and from the crude oil itself (Figure 6). In heptol, even 0.1 wt% asphaltene was enough to reduce the corrosion rate to 0.30 mm/y, which is comparable to the effect seen with 5 wt% asphaltene in toluene. The corrosion rate for direct inhibition in 5 wt% asphaltene in heptol brings the corrosion rate as low as 0.02 mm/y.
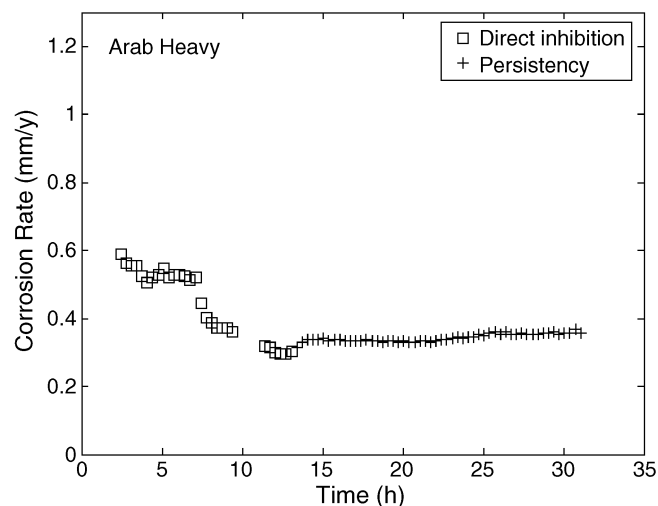

FIGURE 9. *Persistency of the corrosion inhibition that was obtained when the working electrode was exposed to Arab Heavy crude oil.*

The inhibitive properties of asphaltenes in heptol appear to result from asphaltene aggregation being partially in solution and partially flocculated. As a result of the flocculated precipitated asphaltenes, the oil phase became more viscous and a visible black
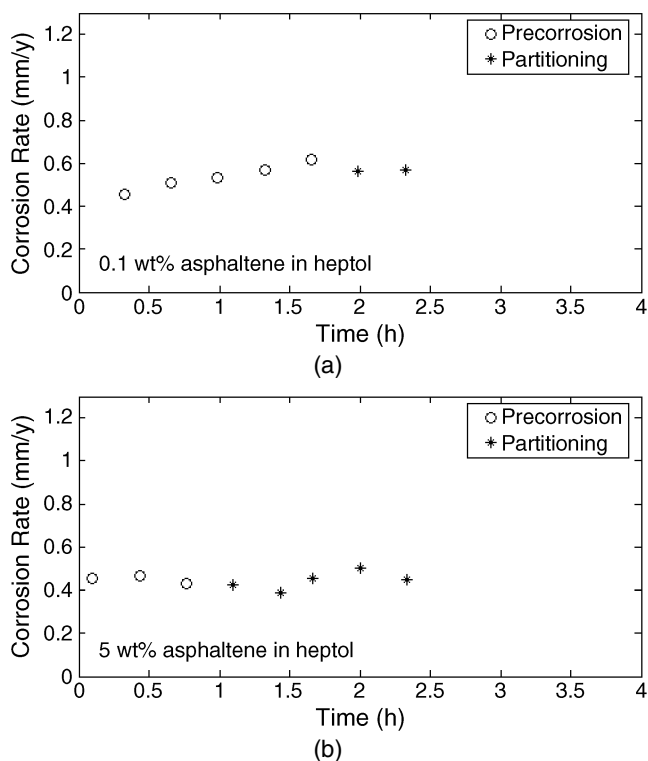
FIGURE 10. *Corrosion rate measured when an oil phase consisting of (a) 0.1 wt% asphaltene in heptol and (b) 5 wt% asphaltene in heptol is added on top of the aqueous phase. "Precorrosion" refers to the corrosion rate measured before the addition of the oil phase and "partitioning" to the corrosion rate measured after the addition of the oil phase.*
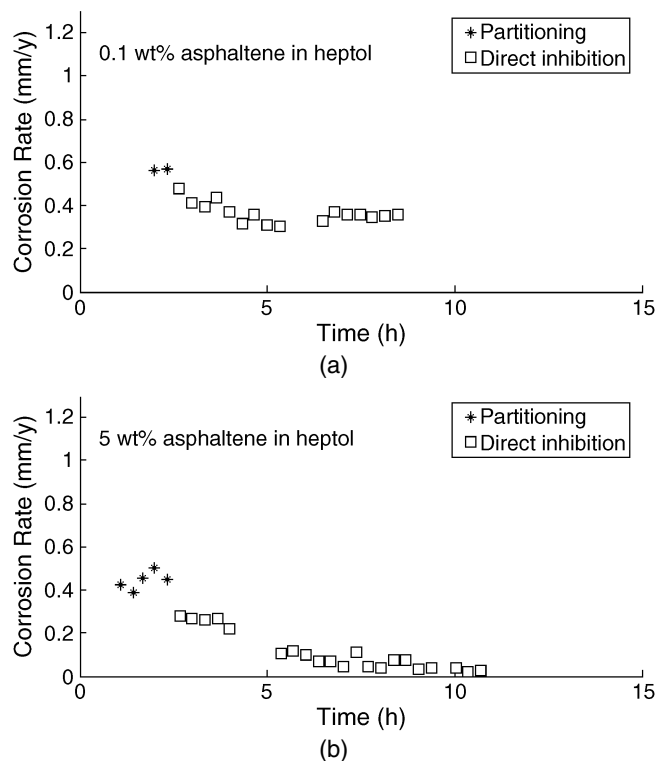

FIGURE 11. *Corrosion rate measured when the working electrode is exposed to the oil phase consisting of: (a) 0.1 wt% asphaltene in toluene and (b) 5 wt% asphaltene in toluene. "Partitioning" refers to the corrosion rate measured with the oil phase sitting on top of the aqueous phase and "direct inhibition" when the working electrode is exposed to the oil phase for 15 min at a time.*
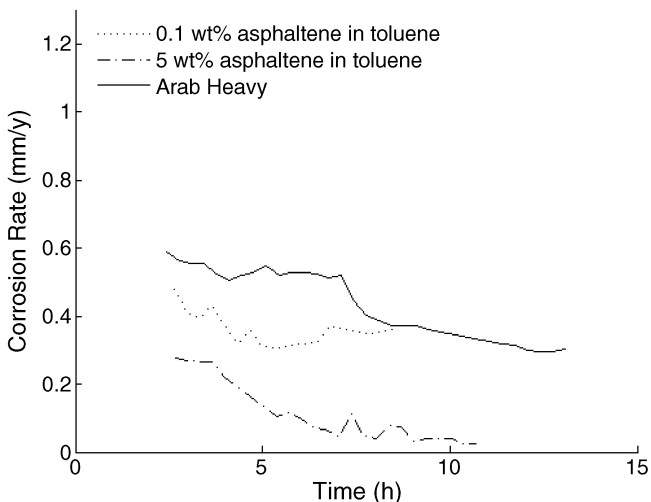

FIGURE 12. *The corrosion rate during the direct inhibition step, where the working electrode is exposed to the oil phase for 15 min before returning to the water phase for each LPR measurement.*

layer was formed on the working electrode, protecting it even further from corrosion. This is consistent with the prior observations that asphaltenes have their largest effect near incipient precipitation.[9-13] In the whole crude the asphaltenes appear less effective as

they are dispersed by resins and aromatics and less surface active.

When the corrosion rate obtained during the direct inhibition step for asphaltene in heptol is compared to the corrosion rate obtained for Arab Heavy crude oil (Figure 12), it can be seen that the corrosion rate is lower for asphaltene in heptol than for Arab Heavy, even for the low concentration (0.1 wt%) of asphaltene in heptanes. This result suggests that solubility changes of the crude oil, to the point of asphaltene precipitation, can have a beneficial effect on corrosion inhibition.

Persistency — The persistency step took place after the exposure of the working electrode to the oil phase was ceased, and the working electrode was kept rotating in the water phase. The corrosion inhibition observed for both 0.1 wt% and 5 wt% asphaltene in heptol was not persistent, as can be seen in Figure 13. The corrosion inhibition due to partially precipitated asphaltene is therefore dependent upon constant or periodical exposure to the oil phase.

Wettability — Contact Angles

The contact angle depicts the wettability of a surface by describing how much a droplet of oil or water spreads on it. A low contact angle (below 90°)

describes a hydrophilic surface, where water is the dominant phase and a high contact angle (above 90°) describes a hydrophobic surface, where oil is the dominant phase.

If the surface is oil wet, it will be protected from corrosion to occur. In a complex systems like a crude oil system, it is important to establish if there are species in the oil that can promote oil wetting by adsorption of the surface-active species found in the oil. This is accomplished by measuring the contact angles for steel pre-wet by each phase in the presence of the other.

Oil-In-Water, Water Pre-Wet Surface — This is a classic oil-in-water measurement, where the steel specimen is immersed in water and an oil droplet is injected just below the surface of the specimen. The oil droplet will then float up to the surface. Figure 14 shows the results for asphaltenes in both toluene and heptol as well as the results for Arab Heavy crude oil. In all cases, the surface remains hydrophilic, i.e., the oil phase is not able to displace the water on the surface. The contact angles of asphaltenes in solvent correspond to the contact angle of Arab Heavy crude oil, i.e., asphaltenes in either solvent behave like the crude from which they were isolated.

Water-In-Oil, Oil Pre-Wet Surface — Classic water in oil contact angle measurements cannot be made in the crude or asphaltene solutions because they are too dark to allow a water drop to be seen. Consequently, the surface of the specimen is immersed in the asphaltene phase before is it mounted in a clear model oil and a water droplet is dropped onto it above the surface. As the water droplet touches the steel's surface, it can either spread out (hydrophilic conditions) or not (hydrophobic condition). The results are shown in Figure 15, where it can be seen that the surface becomes more hydrophobic with the addition of asphaltenes and that the contact angles are independent of both the type of solvent (toluene or heptol) and the concentration of asphaltenes. For this case, the asphaltenic oil is slightly more hydrophobic than the crude oil, with a contact angle of 167° compared to 135° for Arab Heavy crude oil.

Oil-In-Water, Oil Pre-Wet Surface — In this case, the steel specimen is immersed in the oil phase before it is mounted in the continuous water phase and an oil droplet is placed on the surface of the specimen. The oil phase can be either pure solvent (toluene or heptol) or solvent with varying concentrations of asphaltenes. As can be seen in Figure 16, pre-wetting with the solvent by itself is not sufficient to change the wettability of the steel's surface. However, the addition of asphaltenes changes the wettability from hydrophilic to hydrophobic, and the greater the concentration of asphaltenes, the more hydrophobic the surface becomes.

By comparing Figures 14 and 15, it can be seen that the wettability of the surface is dependent on
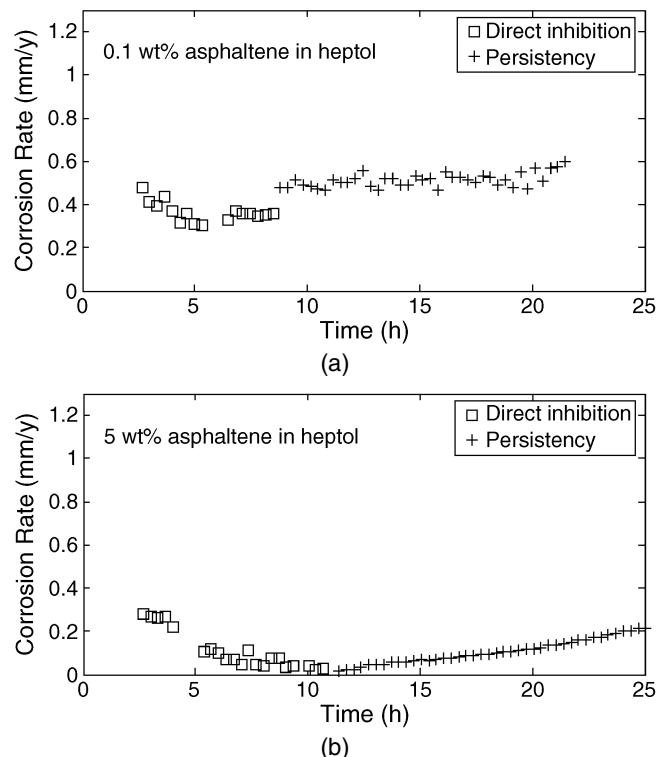

FIGURE 13. *Corrosion rate measured after the working electrode has been exposed repeatedly to an oil phase consisting of: (a) 0.1 wt% asphaltenes in heptol and (b) 5 wt% asphaltenes in heptol. "Direct inhibition" refers to the corrosion rate measured during exposure to the oil phase and "persistency" to the corrosion rate measured after the exposure had ended.*
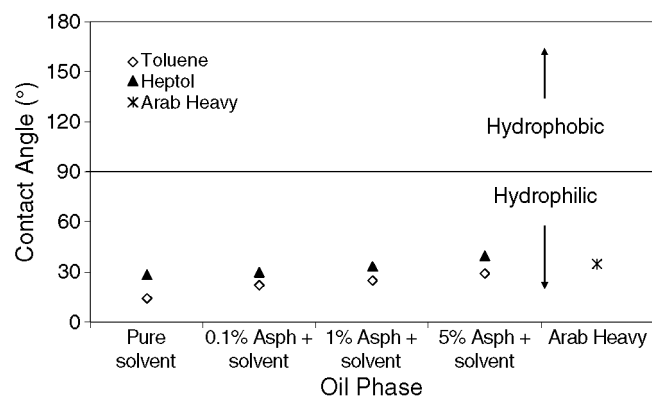

FIGURE 14. *Contact angles of oil droplets in the water phase. The oil phase consists of asphaltenes (Asph) dissolved in toluene or heptol and Arab Heavy crude oil. In all cases, the surface remains hydrophilic.*

the predominant phase, which wets the surface first. When the surface is pre-wet with water, it remains hydrophilic, and when the surface is pre-wet with oil, it remains hydrophobic. When the specimen is pre-wetted with oil and placed into a continuous water phase (Figure 16), the solvent on its own is not sufficient to retain the wettability of the surface as hydro-
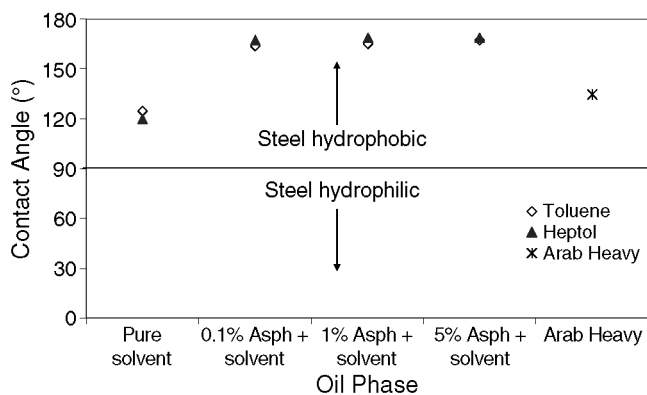
FIGURE 15. *Contact angles of water droplets in model oil phase with either toluene or heptol as the solvent. The steel specimen is pre-wet with the asphaltenic oil phase and Arab Heavy crude oil. In all cases, the surface remains hydrophobic.*
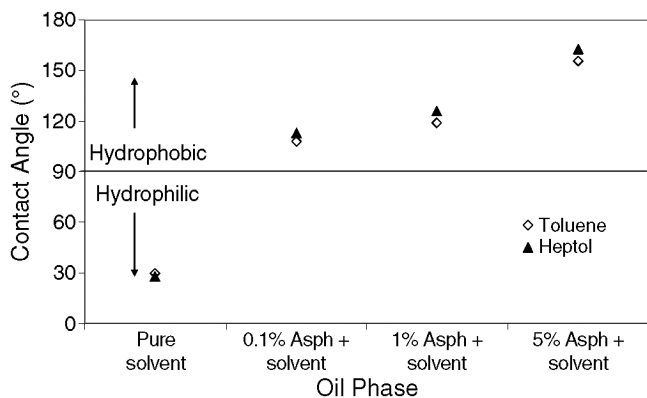

FIGURE 16. *Contact angles of oil droplets in water when the steel specimen is pre-wet with the oil phase, which consists of asphaltenes (Asph) with either toluene or heptol as the solvent.*

phobic, but with the addition of asphaltenes, the steel surface will preserve its hydrophobicity. The higher the concentration of asphaltenes, the more persistent this tendency will be.

As noted at the outset, asphaltene behavior is intimately connected to flow assurance in the field. The difference between asphaltene precipitation and deposition is a subject of intense interest.[9-10,13] If asphaltenes precipitate and adhere to pipe walls extensively, plugging is a major concern; if asphaltenes precipitate but do not deposit aggressively, they may contribute emulsions in oil-water separators. The results obtained in this study suggest an intermediate role for asphaltenes, i.e., a slow development of a protective organic film that resists water-phase removal. As long as a robust oil-wet film exists in the pipeline, corrosion will be "naturally" inhibited. The work of Hernandez and coworkers demonstrates that corrosion rates cannot be related simply to the total asphaltene content nor other routine analyses.[3-4] Workers concentrating on asphaltene deposition have noted the factors contributing to

development of an asphaltic layer on pipelines.[9-10,13] As in that work, additional study is required to rationalize the difference between crude oils and their asphaltenes in their ability to affect water-wetting and corrosion inhibition.

CONCLUSIONS

❖ Asphaltenes can provide considerable corrosion inhibition when fully dissolved in the oil, comparable to the inhibition experienced by the crude oil itself. The inhibition is dependent on the oil phase covering the metal surface to allow for adsorption of the asphaltene on the surface. When the solubility of the oil is altered to the point where asphaltenes are at the point of flocculation, the asphaltenes are more active and provide even more corrosion inhibition than by the dissolved asphaltene. However, the inhibition of the flocculated asphaltenes is not as persistent as for the dissolved asphaltene, and to maintain the inhibition, it is required that the surface is covered periodically with the oil phase.

❖ In a bulk aqueous environment, asphaltenes cannot displace water from a steel surface and it remains water-wet (hydrophilic). If a water-wet surface is exposed to asphaltenes in an oil phase, however, the inhibition data show that the asphaltenes can displace a water film. A steel surface pre-wet with asphaltenes remains oil-wet (hydrophobic), even when surrounded by a bulk aqueous phase unless exposed prolonged periods as indicated by the persistence data. Because asphaltene characteristics are unique to each crude, the conclusions presented herein are characteristic only of Arab Heavy and its asphaltenes. Other crude oil asphaltenes may yield different results.

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