

The 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 previously identified as contributors to inhibition of internal corrosion of mild steel pipelines. However, the mechanism of inhibition is unknown. To explore the mechanism, CO₂ corrosion rates and wettability (oil/water contact angles) have been measured using Arab Heavy crude oil and its asphaltenes. Inhibition of CO₂ corrosion rates for carbon steel was measured by 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 or heptol (70:30 mixture of heptane and toluene). To evaluate the strength of the asphaltene interactions, tests were repeated on solutions containing mixtures of asphaltenes with acridine (previously identified as surface active using these tests). Inhibition on steel exposed to hydrocarbon phases increased with concentration of asphaltenes in toluene. Inhibition by asphaltenes in toluene appears to be more effective than in the whole crude. At 5% in toluene asphaltenes form a strong protective layer on the carbon steel surface, which reduces the corrosion rate and makes the surface hydrophobic. Heptol appears to have little effect on the wetting. However, in heptol, inhibition begins at lower asphaltene concentrations and is nearly complete at 5%.

KEY WORDS: Asphaltenes, acridine, CO₂ corrosion, carbon steel, wettability, inhibition

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INTRODUCTION

The tendency of crude oil to inhibit aqueous CO₂ corrosion has been observed in the field, but the mechanism of the inhibition has not been adequately explained. Some crude oils have good inhibitory effects and others do not. Differences are especially apparent in determining water cut at which corrosion becomes significant¹. 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 proposed prediction model of crude oil corrosion inhibition, which is an empirical function of saturates aromatics, resins and asphaltenes. In 2005, Hernandez et al.⁴ updated their previous model and addressed that the corrosion inhibition capacity of crude oil is a function of saturate, aromatic, resin, asphaltenes, acids, and metallic ions. The underlying hypothesis made by all these workers 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 inhibition⁴; however, the crudes were so diverse that their role in the inhibition was uncertain. Historically, Hackerman⁵ demonstrated that polar compounds in crude oil adsorbed onto metal surfaces and could act as acid corrosion inhibitors.

A Joint Industry Project (Water Wetting JIP)⁽³⁾ has been investigating the mechanism by which chemical compounds present in the crude oil inhibit corrosion. The project aimed to determine behavior of model oil soluble polars in dynamic oil/water systems. Specifically, it examined the effects on partitioning, wetting and 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 most polar constituents in crude oil. However, asphaltenes are not homogeneous, and their characteristics change with the source of the crude oil⁷. 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 to >2500 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 solvated by the aromatics and resins; they stabilize emulsions to the greatest extent when they are near the point of flocculation⁸. Asphaltene deposition in well bores and flowlines is a major concern for flow assurance; again, asphaltene deposition is heaviest near the onset of asphaltene flocculation⁹. In the presence of water, asphaltenes adsorb onto mineral surfaces by two mechanisms; ionic mechanisms, which depend on the composition of the aqueous phase and mineral, compete with adsorption of colloidal asphaltene aggregates in making surfaces oil-wet¹⁰. Adsorption of asphaltenes onto metal powders reveals incomplete surface coverage in water-in-hydrocarbon emulsions; higher surface coverage was obtained when asphaltenes self-associated¹¹. Adsorption of asphaltenes at a toluene-water interface has been rationalized as a multi-step film formation process¹².

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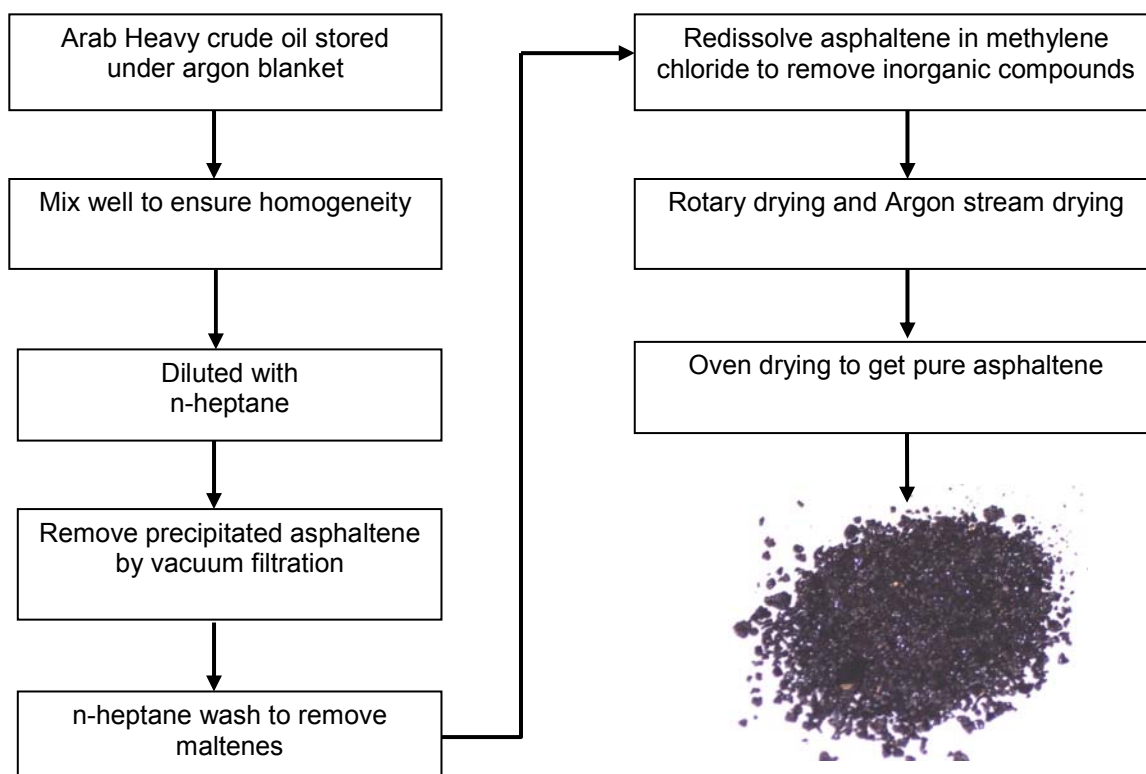


FIGURE 1: Procedure used to extract asphaltenes from the crude oil¹³

In the present work, attention has been focused on asphaltenes isolated from Arab Heavy (sweet oil, $\rho = 890 \text{ kg/m}^3$, $\text{API} = 27.4$, $\mu = 35.8 \text{ cP}$) in known solvent environments and compared with results for the whole crude. FIGURE 1 summarizes the extraction procedure for asphaltenes from the crude oil. The full extraction procedure is described in the literature¹³. 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 PROCEDURE

Corrosion Inhibition

A three-electrode glass cell (FIGURE 2) configuration was set up with a C-1018 carbon steel cylinder as the working electrode; a silver/silver-chloride (Ag/AgCl) saturated with 4M 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 mV.

The glass cell was filled with 1.8 liters of de-ionized water with 1wt% of NaCl and kept at 25°C. The solution was deoxygenated with CO₂ gas for 40 minutes to 1 hour. 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 1000 rpm. When a stable open circuit potential was obtained, the corrosion rate measurements were carried out.

The asphaltenes from Arab Heavy crude oil were dissolved in either toluene or heptol in concentrations of 0, 0.1, 1 and 5 wt% asphaltenes

Each test in a glass cell was performed in three consecutive steps: partitioning, corrosion inhibition and persistency:

- First, in the *partitioning step*, the working electrode was kept rotating at 1000 rpm in the water phase while 0.2 L of the oil phase was added slowly on top. The corrosion rate was measured every 20 minutes for 5-10 hours to see if the asphaltenes partition into the water phase and affect the corrosion rate.
- Next, in the *corrosion inhibition step*, the working electrode was moved up into the oil phase and rotated there at 1000 rpm for 15 minutes. The electrode was then moved back to the water phase and the corrosion rate was measured each time. This was repeated for 10-15 hours to see how much will the asphaltenes adsorb on the working electrode and how that affects the corrosion rate.
- Finally, during the *persistency step*, the working electrode was kept in the water phase continuously, rotating at 1000 rpm, and the corrosion rate was recorded every 20 minutes for 5-10 hours to see if the corrosion rate recorded in the previous step would remain stable or if it will be changed over time.

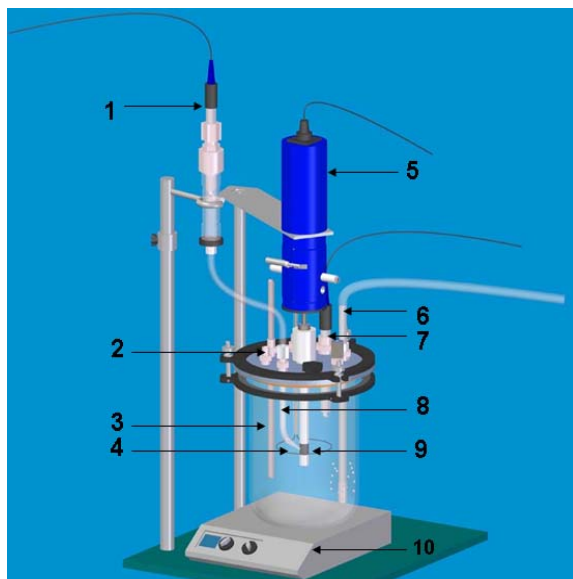


FIGURE 2: Schematic of a glass cell set-up with rotating cylinder electrode (RCE) (courtesy of Haitao Fang). The parts of the set-up are: 1. reference electrode, 2. gas outlet, 3. temperature probe, 4. platinum counter electrode, 5. rotator, 6. gas inlet, 7. pH-electrode, 8. luggin capillary, 9. working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

Contact Angle Measurements

A multiphase goniometer (FIGURE 3) 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).

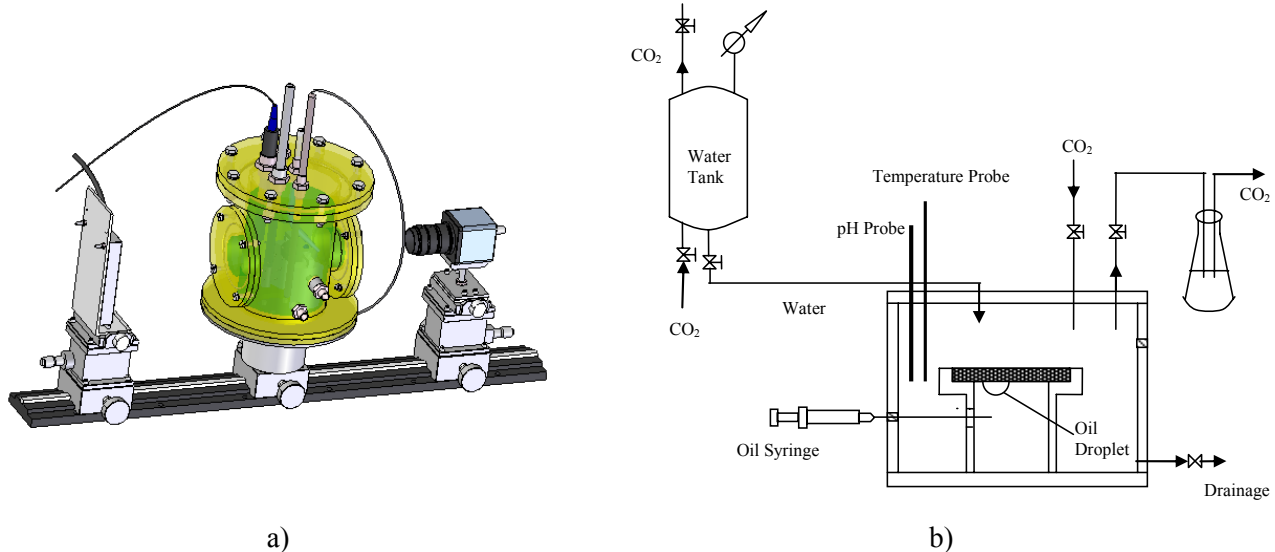


FIGURE 3: a) Stainless steel goniometer cell in the center, with a camera on the right and a backlight on the left, b) schematic presentation of the cross section of the goniometer cell with an oil droplet being deposited underneath the specimen's surface.

The water phase for the contact angle measurements was the same as that used for the corrosion rate measurements, i.e. 1 wt% NaCl DI water solution, deoxygenated with CO₂ and pH adjusted to pH5. 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

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. 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.

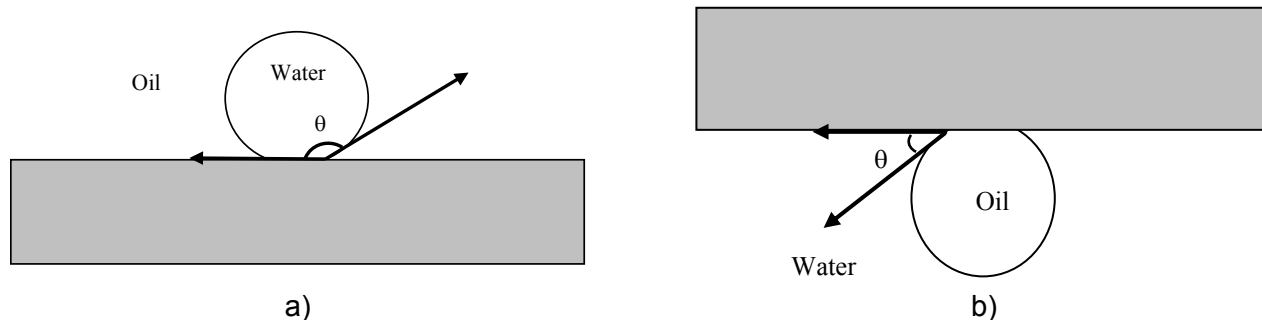


FIGURE 4: Contact angle of: a) water droplet in oil phase (water-in-oil) and b) oil droplet in water phase (oil-in-water). The contact angle (θ) is taken in respect to the water phase.

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 hour before the steel specimen was placed on a specimen 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

By definition asphaltenes are soluble in toluene (although they may exist as nano-aggregates). However, the crude oil can contain alkanes, such as heptane or pentane, which will cause the asphaltenes to flocculate (aggregate) 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. In order to test for this phenomenon, the tests were conducted using heptol, which is a 70:30 mixture of heptane and toluene. At this ratio of heptane:toluene, 38 wt% of asphaltenes gather as aggregates and 62 wt% remains in solution⁷. Preliminary study established that toluene and heptol alone do not affect the corrosion rate or the surface wettability of the carbon steel.

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 addition of asphaltenes dissolved in toluene had no effect on the corrosion rate as compared to the water baseline (corrosion rate without the presence of the oil phase), as shown in FIGURE 5. Aside from the usual scatter seen in different repeats of the experiment, all solutions show the corrosion rates over the period tested to be approximately 0.7 mm/y. Thus, it was concluded that nothing partitioned from the asphaltene solutions into the water phase that affected the corrosion rate. Likewise nothing appears to have partitioned into the water phase from the whole Arab heavy crude.

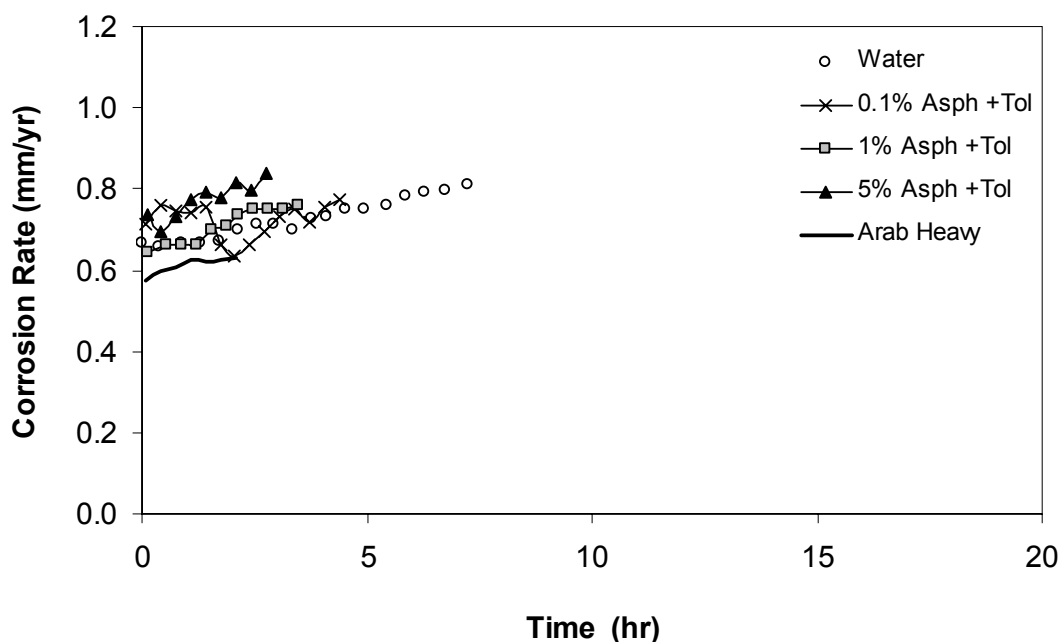


FIGURE 5: Corrosion rate measured during the partitioning step for asphaltenes (Asph) in toluene (Tol) compared to the results for Arab Heavy crude oil.

Inhibition. The inhibition measurements started in the same solution immediately after the partitioning step ended so to reflect this, the new data is simply added to FIGURE 5 in order to yield FIGURE 6. Each corrosion measurement was made in water after the working electrode was exposed to the hydrocarbon phase for the desired period. While the 0.1 wt% asphaltenes dissolved in toluene did not affect the corrosion rate, higher concentrations did. For 1 wt% asphaltenes, there is a significant reduction of the corrosion rate from 0.75 to 0.48 mm/y where repeated exposures after 7.5 hrs had limited effect (see FIGURE 6). For 5 wt% asphaltenes, the corrosion rate continued to decrease with each exposure (from 0.84 to 0.32 mm/y). Exposure to Arab Heavy crude oil resulted in the same final corrosion rate (0.30 mm/y). Approximately 5% asphaltenes is contained in the Arab Heavy crude used in these experiments, therefore the match can be considered to be excellent; other samples of Arab Heavy have been reported to contain as much as 8.3% asphaltenes¹³. These findings suggest that the corrosion inhibitive property of Arab Heavy crude oil can come from the deposition of asphaltenes on the steel surface.

Persistence. After the periodic exposures of the steel sample to the asphaltenic oil were stopped, the corrosion rates in the aqueous phase were followed for an additional period of time (see FIGURE 7). The corrosion inhibition by the asphaltenes appeared to persist over time with possibly a slight shift in the case for the whole crude. This may imply that the adsorption of asphaltenes in toluene on the steel surface was more uniform than from the Arab Heavy crude oil itself, i.e. that some other compounds adsorbed from the crude oil and contributed to the corrosion inhibition which were subsequently lost.

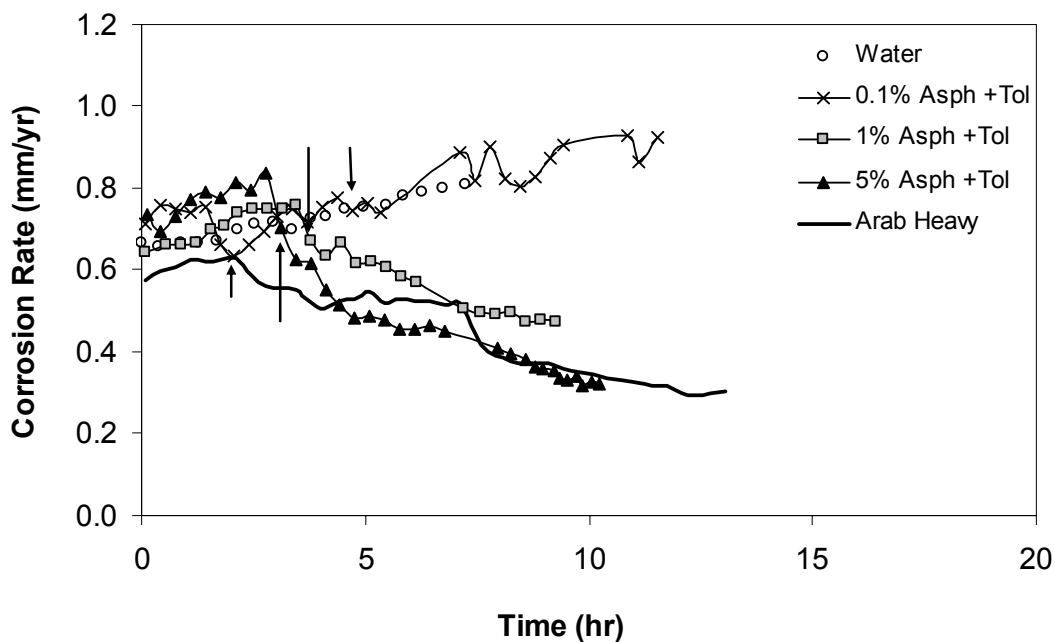


FIGURE 6: Corrosion rate measured during the partitioning and corrosion inhibition step for asphaltenes (Asph) in toluene (Tol) compared to the results for Arab Heavy crude oil. The arrows point to the first measurement of the inhibition step for each concentration of asphaltenes and Arab Heavy.

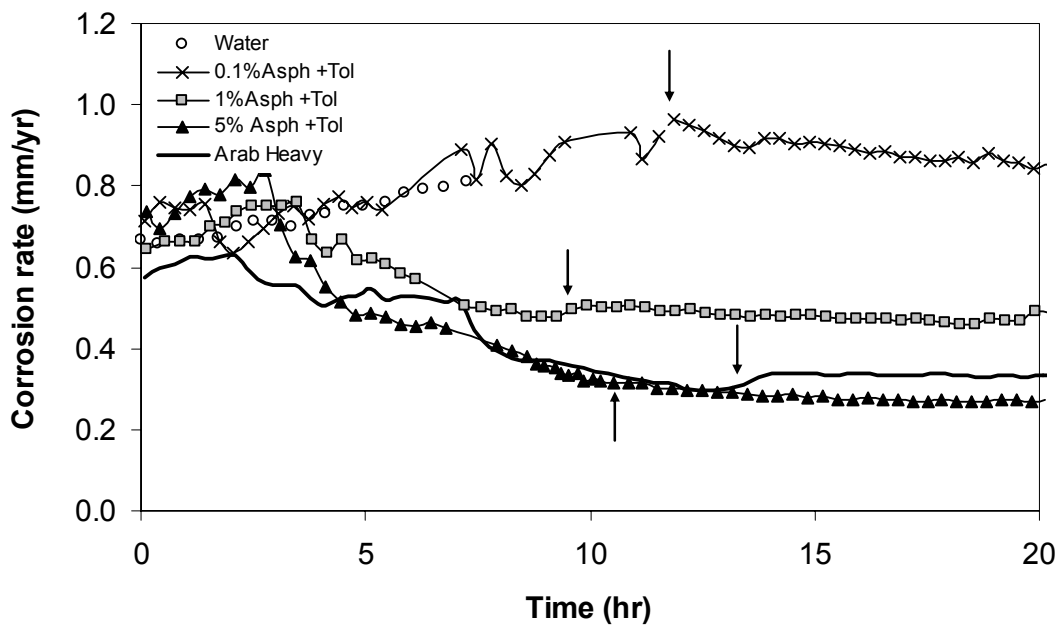


FIGURE 7: Corrosion rate measured during the partitioning, corrosion inhibition and persistency step for asphaltenes (Asph) in toluene (Tol) compared to the results for Arab Heavy crude oil. The arrows point to the first point of the persistency measurements for each concentrations of asphaltenes and Arab Heavy.

Inhibition - Asphaltenes In Heptol

Partitioning. Similar results were obtained when heptol was used as the solvent for the asphaltenes, which were in agreement with the results obtained in toluene shown above. The asphaltenic components from the hydrocarbon solution did not partition into the water phase to inhibit corrosion (see FIGURE 8).

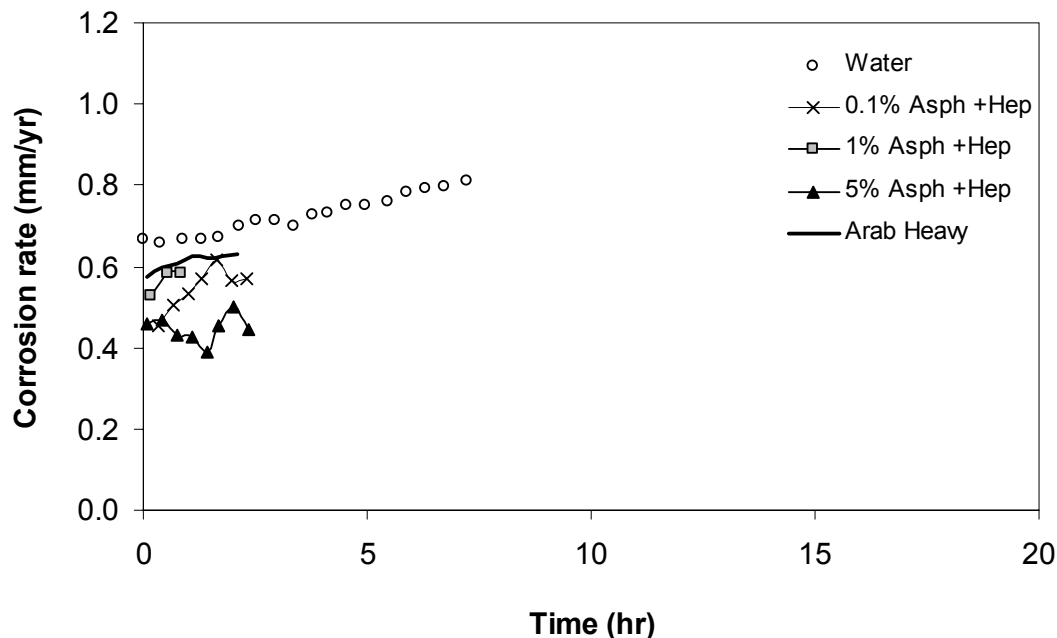


FIGURE 8: Corrosion rate measured during the partitioning step for asphaltenes (Asph) in heptol (Hep) compared to the results for Arab Heavy crude oil.

Inhibition. The corrosion inhibition of asphaltenes from heptol (FIGURE 9) was significantly greater than that from the asphaltenes in toluene (FIGURE 6). In heptol, even 0.1 wt% asphaltenes was enough to reduce the corrosion rate to 0.30 mm/y, which is comparable to the effect seen with 5 wt% asphaltenes in toluene. The corrosion rate for 1 wt% asphaltenes in heptol was around 0.2 mm/y and for 5 wt% asphaltenes in heptol the corrosion rate becomes as low as 0.02 mm/y.

The inhibitive properties of asphaltenes in heptol appear to result from asphaltene aggregation being partially in solution and partially flocculated. Due to the flocculated precipitated asphaltenes, the oil phase became more viscous and a visible black 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 precipitation⁸⁻¹². In the whole crude the asphaltenes appear less effective as they are dispersed by resins and aromatics and less surface active.

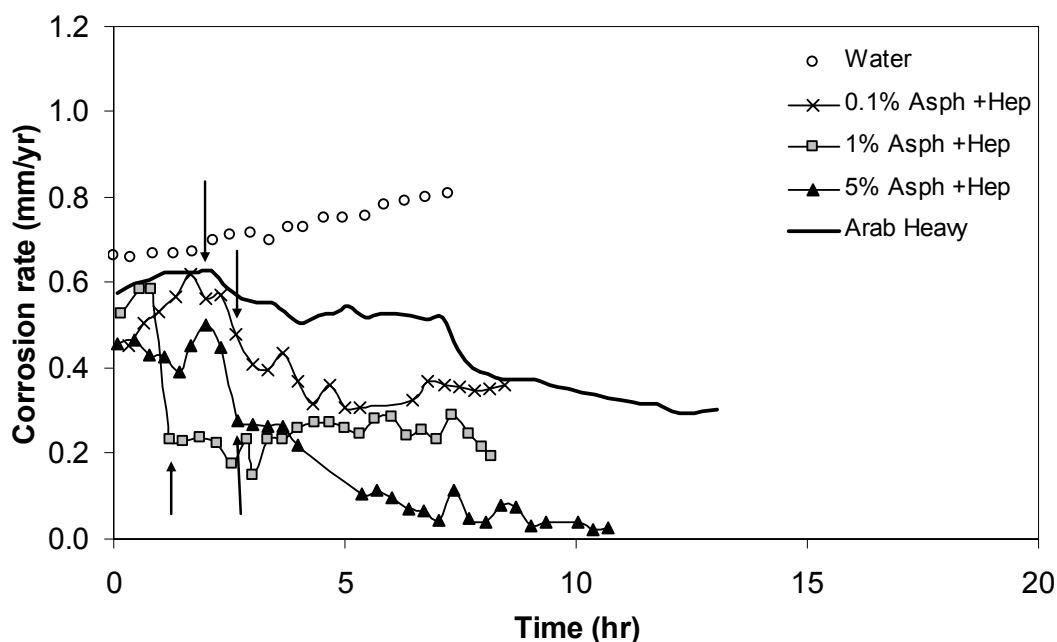


FIGURE 9: Corrosion rate measured during the partitioning and corrosion inhibition step for asphaltenes (Asph) in heptol (Hep) compared to the results for Arab Heavy crude oil. The arrows point to the first point of the inhibition measurement for each concentration of asphaltenes and Arab Heavy.

Persistence. The corrosion inhibition observed for 0.1 wt% asphaltenes in heptol was not permanent as can be seen in FIGURE 10. The corrosion inhibition for 1 wt% asphaltenes and 5 wt% asphaltenes in heptol was more persistent and the final corrosion rate detected was 0.15 mm/y for 1 wt% asphaltenes and 0.04 mm/y for 5 wt% asphaltenes in heptol. These results suggest that inhibition was reversible for low concentrations, but exposure at higher asphaltene concentrations allows for the formation of a permanent tightly adherent, three dimensional film.

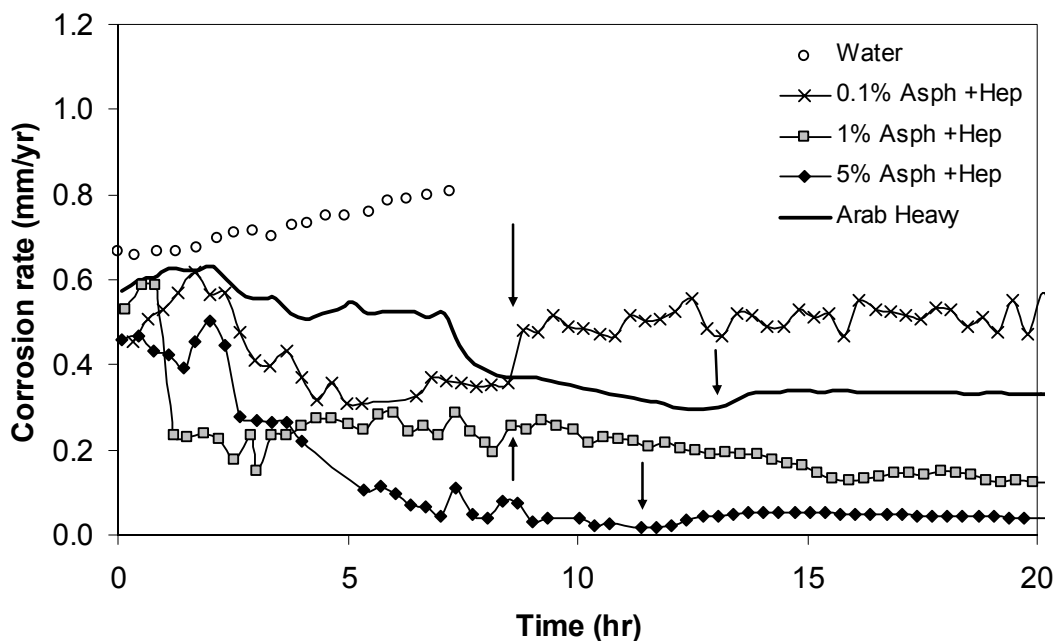


FIGURE 10: Corrosion rate measured during the partitioning, corrosion inhibition and persistency step for asphaltenes (Asph) in heptol (Hep) compared to the results for Arab Heavy crude oil. The arrows point to the first point of the partitioning measurement for each concentration of asphaltenes and Arab Heavy.

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. Most contact angle measurements are made for drops of one fluid onto a surface immersed in another. For corrosion inhibition, the surface must be protected from water, i.e. it must not get water wet. In complex systems like crude oil, it is important to establish if there are species in the oil that can displace water from a water wet surface and conversely to establish if water can displace oil-derived surface active compounds from the surface. 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 11 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.

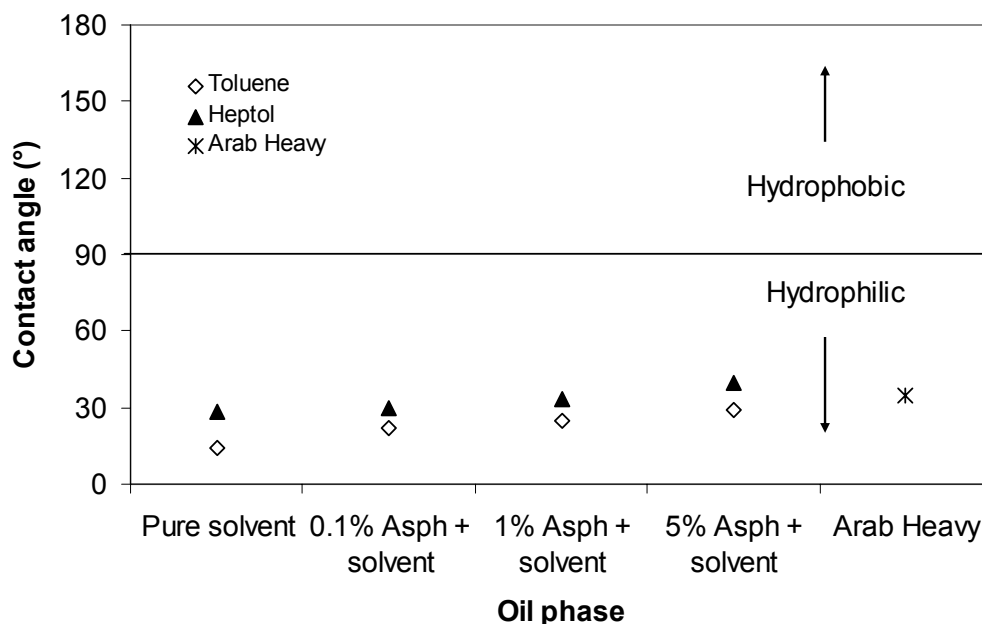


FIGURE 11: Contact angles of oil droplets in water phase. The oil phase consists of asphaltenes (Asph) dissolved in toluene or heptol and Arab Heavy crude oil. In all cases the surface remains hydrophilic.

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 it is mounted in a clear model oil and a water droplet is dropped onto it above the surface. As the water droplet touches the steel surface, it can either spread out (hydrophilic conditions) or not (hydrophobic condition). The results are shown in FIGURE 12, 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.

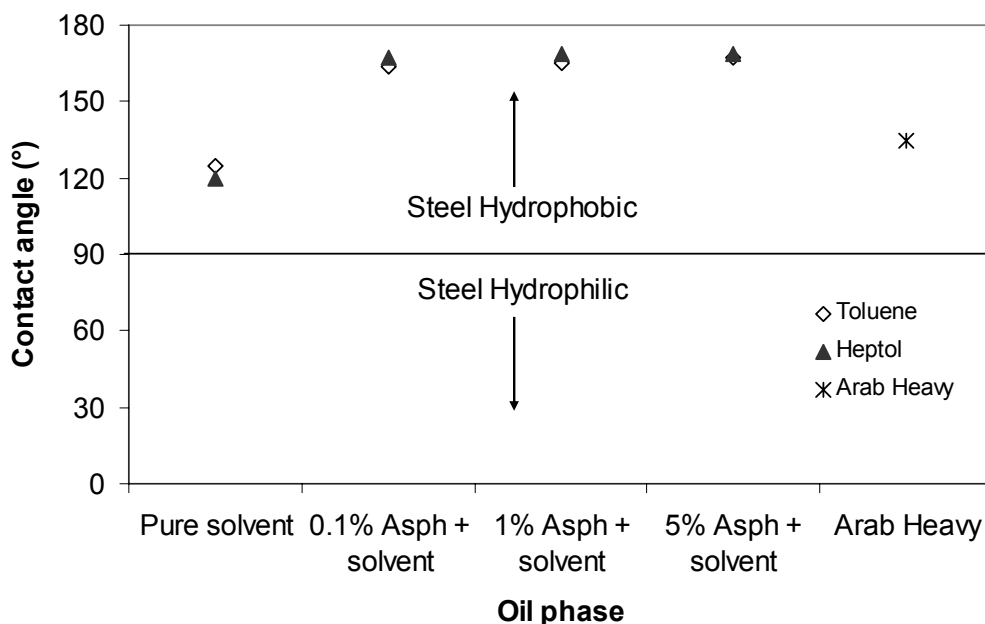


FIGURE 12: Contact angles of water droplets in model oil phase with either toluene or heptol as the solvent. The steel specimen is pre-wet with the asphaltenic oil phase and Arab Heavy crude oil. In all cases the surface remains hydrophobic.

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 concentration of asphaltenes. As can be seen in FIGURE 13 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 FIGURE 11 and FIGURE 12, it can be seen that the wettability of the surface is dependent on 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 13), the solvent on its own is not sufficient to retain the wettability of the surface as hydrophobic, 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.

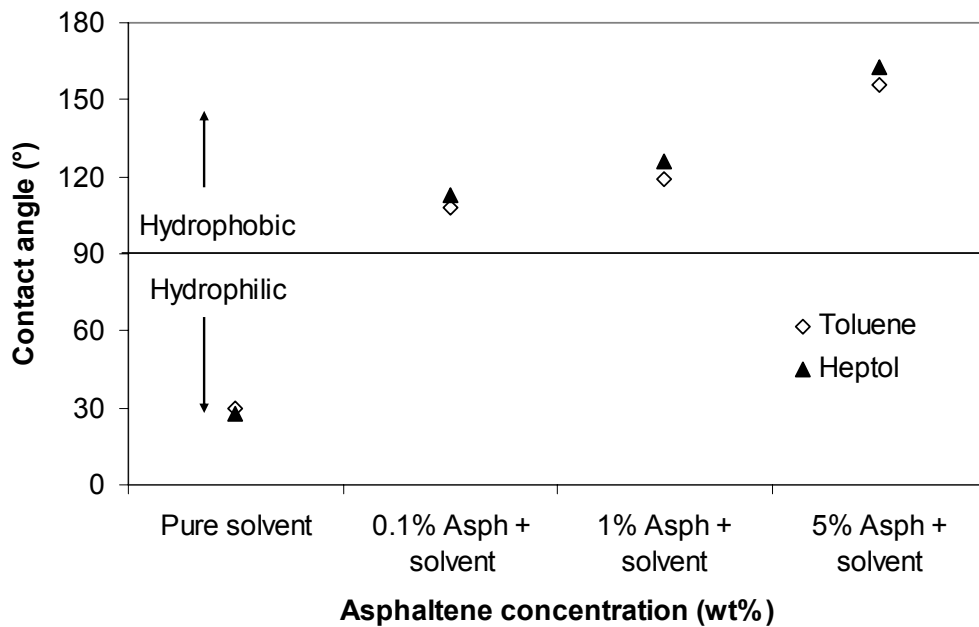


FIGURE 13: Contact angles of oil droplets in water when the steel specimen is pre-wet with the oil phase, which consists of asphaltenes (Asph) with either toluene or heptol as the solvent.

CONCLUSIONS

- Asphaltenes, fully dissolved in toluene, significantly reduce the corrosion rate when added at a sufficient concentration. This effect seems to be rather persistent with time.
- Asphaltenes, when partially precipitated such as in a heptol solution, deposit more readily on the steel surface and reduce the corrosion rate even further. Consistent with other surface dependent phenomena, asphaltenes express their effect under conditions of incipient precipitation.
- In the presence of asphaltenes, the wettability of the steel surface depends on the wetting sequence. Surfaces pre-wetted with water tend to stay hydrophilic, while surfaces pre-wetted with oil tend to remain hydrophobic.

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