

## Effect of Heavy Crude Oil Polar Components on the Wettability of Pipeline Surfaces

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**Abstract.** *In contribution to the development of core-flow processes for the transportation of heavy oils, a study on the wettability of pipeline surfaces by heavy oil in the presence of an aqueous phase is carried out. The polar fractions (asphaltenes and naphthenic acids) are extracted from the crude and their individual effects on the wetting behavior of pipeline surfaces are determined by measurement of contact angles in crude oil/water/solid surface systems. Commercial and galvanized steel surfaces are used as the solid surfaces. Contact angles values are related to the wettability of surfaces in order to determine the tendency of the crude oil to spread on the steel surfaces in the presence of an aqueous solution. The results show that the wettability of the steel surfaces is dependent on the crude oil composition with the presence of asphaltenes and acids in the crude oil having the most important effects. Result also indicates that the use of sodium metasilicate diluted solutions as the aqueous phase appears to be effective in the prevention of the accumulation of oil on the surfaces. It is hoped that the results obtained in this work can contribute to the viable implementation of the core-flow technology as an alternative method for the transport of heavy oil.*

**Keywords:** *asphaltenes, naphthenic acids, contact angle, wettability, steel surface.*

## 1. Introduction

Petroleum is by far the source of the most commonly used liquid fuels (Speight, 1991). Its commercial importance is due to its position in the energy supply market and thereby strong influence on the world economy. Because of their simpler production process, light conventional oils are preferred to heavy oils. In fact, there are many technological problems that need to be overcome in the production, transportation and refining of heavy oil to become it an established energy source. The dwindling reserves of conventional oil and the abundant estimates of ultraviscous and heavy oil (densities lower than 20° API and viscosities larger than 400 cP) reserves worldwide have created new incentives for the development of new technologies that would make the exploration, production, transportation and refining of heavy oils possible. These high densities and viscosities of heavy oils elevate the inherent cost of the recovery and transportation of these oils. Most of the technologies suggested and investigated in the literature focus on the reduction of the viscosity of the crude oil through by heating or mixing with light oils, which could be convenient for certain reservoirs and reservoir conditions. Technologies based on the flow of oil lubricated by an aqueous film formed between the internal pipe wall and the oil flowing in the annular section of the pipeline, commonly known as *Core-Flow* represent a viable alternative for the transport of these oils (Beretta *et al.*, 1997). In *Core-Flow* systems, the frictional pressure drop generated by the high viscosity of heavy oils is reduced to a value comparable to the single-phase flow of water alone, making it possible to use conventional pipelines to deliver these oils at low energy consumption. Moreover, the increase in the flow rate and the reduction of the production cost in the core flow are important and attractive characteristics of this process. In principle, nothing hinders the application of the core flow for the production of heavy and ultraviscous oil, inclusively from offshore reservoirs, being possible the use of the seawater or production water as lubricating fluid (Vanegas Pradas, 1999). The presence of a lubricating fluid film can produce a significant reduction in the pressure drop, so that it reach values of the magnitude of the monophasic aqueous flow. However, the possibility of gradual accumulation of oil on the walls of the pipeline during the process could present a serious limitation for the implementation of core flow processes with the loss of the stability of the aqueous lubricating film due to the alteration of the wetting behavior of the inner pipeline surface from water-wet to oil-wet. Oil accumulation would increase the pressure drop due to reduction of flow diameter, maintenance cost for cleaning and could even lead, if not treated, to the total clogging of the pipeline. The dynamic fluid stability of the system isn't

sufficient to prevent the accumulation of the oil. The adherence of oil to inner pipeline surfaces and possible accumulation of this oil is related to interfacial activity of crude oil polar components and other effects of thermodynamic nature (Joseph, 1997).

The contact of the oil with the surface allows the potential adsorption of polar oil components onto the solid surface and has been pointed out as an important factor in the inversion of the wetting behavior of the solid surface. Asphaltenes, polar components of crude oil defined through their solubility behavior in low molecular weight n-alkenes, are the main components involved in the adsorption onto the solid surface and the alteration of the wettability due to their strong polar interaction with mineral surfaces (Kaminsky e Radke, 1997). Naphthenic acids and others crude oil components having carboxyl groups, mainly phenols and alkyl acids, are likewise indicated as agents that could have a strong impact on the wettability of the solid surfaces. Hoeiland *et al.* (2001) have demonstrated the influence of these components on the wettability of silica surfaces. Acid-base interactions also represent a proposed mechanism for which components of a crude oil can alter the surface wetting behavior (Buckley *et al.*, 1998).

Asphaltenes tend to form deposits because of their tendency to aggregate. Changing in the temperature, pressure and composition conditions during production and transportation operations may compromise asphaltene stability in the crude oil and lead to their precipitation out of solution. There are several studies that show the effect of asphaltenes on the wettability of reservoir porous media. Denekas *et al.* (1959) showed that only petroleum fractions containing asphaltenes could produce oil-wet behavior of the reservoir. Collins and Melrose (1983) and Gonzalez and Middea (1987) showed that large variation in wettability is caused by asphaltene adsorption on mineral surfaces. Lord and Buckley (2002) verified that the properties of adsorbed asphaltene films are dependent on the oil composition. Acid fractions can be present in the both asphaltenic and deasphaltened fractions of the crude oil (Hoeiland *et al.*, 2001).

This work reports on the results of an experimental investigation on the wetting behavior of pipeline surfaces by petroleum polar components – asphaltenes and naphthenic acids – in the presence of an aqueous phase. The comparative study of the wettability is based on measured contact angles obtained in the oil phase/aqueous phase/solid surface systems, with oil phases being crude oil, crude oil without asphaltenes and crude oil without acids. The effect of the soluble salts in the aqueous phase is evaluated similarly.

## 2. Materials

N-pentane P.A. (99,0% in purity), n-heptane (99,8% in purity) and Toluene P.A. (99,5% in purity) were obtained from Merck and from Carlo Erba Reagent, respectively, and they were used in the extraction of asphaltenes from crude oil. Sodium hydroxide P.A. obtained from Merck, Ethanol 99.5%, from Lafan and n-Hexane 99,0% from Carlo Erba were utilized in the extraction of naphthenic acids. Chloride acid (Synth) and Dichloromethane 99,5% (Merck) were used. Sodium metasilicate and chloride were obtained from Chemco and Synth, respectively.

The crude oil tested is a heavy Brazilian petroleum, which were obtained from the Campos Basin. Its properties are summarized in Tab. (1). This oil was chosen because of its large reserves and because of the fouling observed when oil was transported via core-annular-flow in our laboratory installations.

Table 1. Properties of the original crude oil

Property	Value
Density (kg/m <sup>3</sup> )	925,5
Viscosity (mPa.s)	741,94
Surface Tension (mN/m)	29,05

In this study, the crude oil and its fractions used were classified as: (1) original crude oil, (2) deasphalted oil (original crude oil without asphaltenes) and (3) deacidified oil (original crude oil without naphthenic acids).

## 3. Experimental methods

### 3.1. Asphaltene extraction

The modified IP 143/89 Method (Standard Methods for Analysis and Testing of Petroleum and Related Products, 1989) was used for the recovery of asphaltenes as shown in Fig. (1). Using this method 20 g of crude oil were mixed with 800 mL of flocculant (n-pentane or n-heptane) for approximately 4 hours with reflux. The solid precipitated was filtrated under vacuum using Whatman 42 filter paper and the soluble phase (deasphalted oil) was collected. The flocculant, n-pentane or n-heptane is subsequently removed by placing the soluble phase under vacuum. The asphaltenes (undissolved fraction) were removed from the solid precipitate in the Soxhlet apparatus with toluene, which is subsequently removed from the toluene soluble fraction under vacuum using rotary evaporator. The solid material is the asphaltene fraction, n-pentane insoluble (C5I) or n-heptane insoluble (C7I), depending on the solvent used. When using different dilution ratios other than the 40:1 (milliliters of flocculant/milligrams of crude oil) suggested in the standard method, different asphaltene fractions can be obtained. In this work, fractions at 30:1, 40:1 and 50:1 dilution ratios were obtained with each solvent, n-pentane and n-heptane.

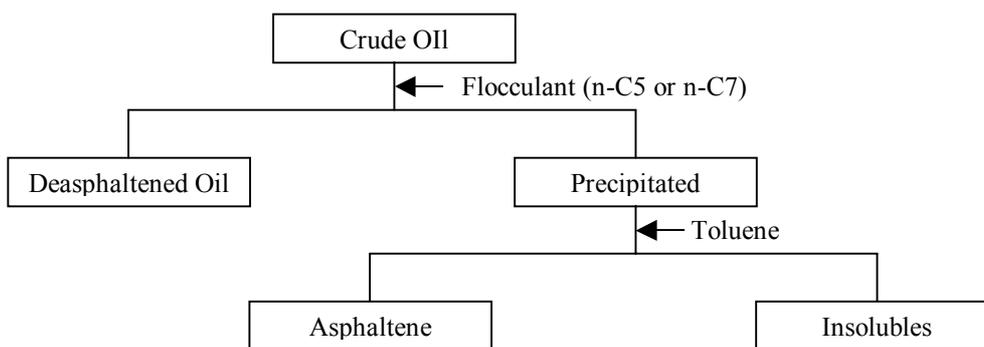


Figure 1. Schematic illustration of the asphaltene fractionation procedure.

### 3.2. Naphthenic acids extraction

The naphthenic acids fraction of crude oil was extracted from the oil with an alkali solution and back-extracted following the acidification of the aqueous extract with a mineral acid. Briefly, the crude oil sample (about 200g) was mixed with 200 mL n-hexane and then treated with 5x100 mL 1M NaOH solution in the 1:1 EtOH/H<sub>2</sub>O ratio. The extraction divided the system in the two phases. The phases were separated and the alkali phase was treated with 3x100 mL n-hexane to remove any traces of oil. The acids were recovered from the carboxilates by the addition of an HCl concentrated solution for the alkali phase until a pH 2 is reached. The recovered acids were extracted from the solution with 5x100 mL dichloromethane. The DCM was eliminated under vacuum using rotary evaporator and the acids were weighted. Figure 2 present a simplified illustration of the experimental extraction procedure.

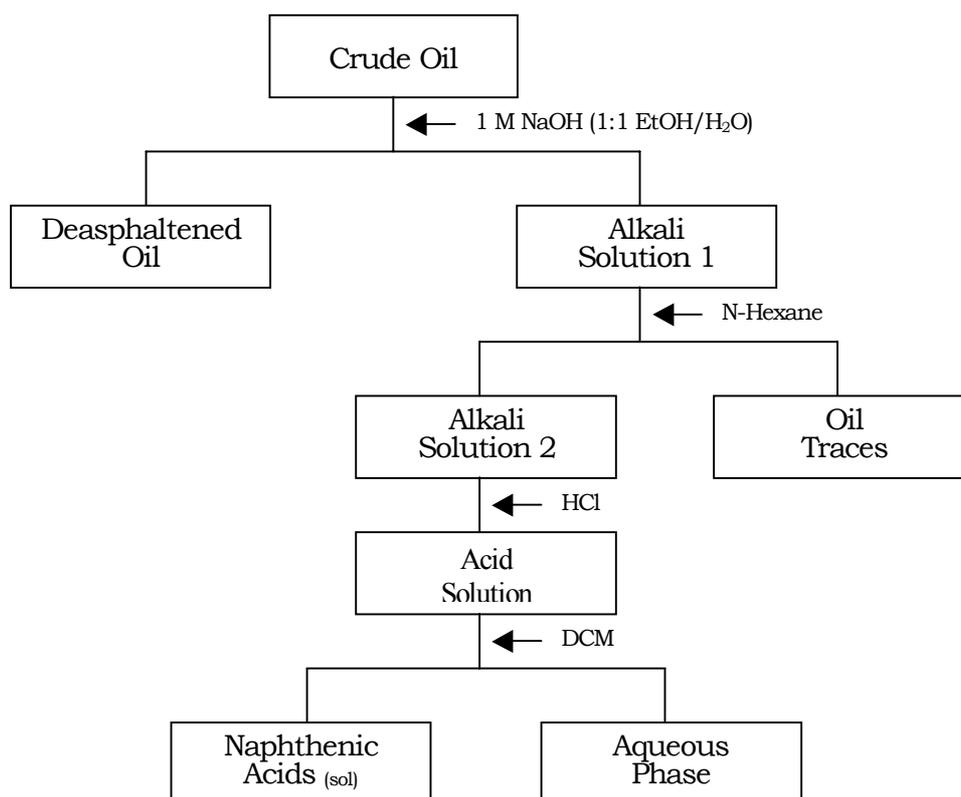


Figure 2. Schematic illustration of the acid fractionation procedure.

### 3.3. Contact angle measurement

First, the oil and the aqueous phases were equilibrated at the 1:4 oil-to-aqueous phase volume ratio at room temperature for 5 days, before being separated.

Commercial steel and galvanized steel flat plates (1.5 x 3.0 cm<sup>2</sup>) were used. Before use, the flats were treated with toluene for 24 hours to remove any oil residues and, then, treated with n-hexane to remove the toluene. The clean surfaces were equilibrated with the aqueous phase for 24 hours before the test for the measurement of contact angles begins.

To measure the contact angles in oil/water/solid systems, oil drops (about 20  $\mu\text{L}$ ) were carefully deposited on the solid surface, which was immersed in the aqueous phase. The contact angle values, measured in the aqueous phase, were obtained by analyzing projected drop images. The image was photographed with a digital camera and, then, the contact angle was determined using the Image Tool 3.0 software.

## 4. Results and discussion

### 4.1. Asphaltenes in the crude oil

The quantities of asphaltene removed from the crude oil for the three flocculant/crude oil ratios are presented in Table 2. The results show larger amounts of C5I than C7I and that the difference between the C5I asphaltene and C7I asphaltene is about 6-wt%. The values reveal the influence of the nature of the flocculant nature on the asphaltene yield, which is in agreement with literature (Mohamed *et al.*, 1999; Speight, 1991 and Speight, 1999) for n-alkane with different chain length. The results also show that the 40:1 ratio is adequate to precipitate the maximum amount of the asphaltene in the crude oil.

Table 2. Quantity of asphaltene extracted from the crude oil through the precipitation with low molecular weight n-alkane: n-pentane and n-heptane.

Flocculant Quantity (mL/g crude oil)	Asphaltene Quantity (wt% )	
	C5I	C7I
30	8,8	2,8
40	8,5	3,3
50	9,7	3,1

Experiments were carried out in triplicates with the deviations from the average values being  $\pm 0.3$  wt% for the C5I asphaltene and  $\pm 0.2$  wt% for the C7I asphaltene.

### 4.2. Naphthenic acids in the crude oil

Acid extraction from the crude oil yielded 0.94 g of the naphthenic acids from the 200g oil sample. This amount is equivalent to 4.82 milligrams of acids per gram of crude oil, and thus represents 0.48-wt% of acids in the crude. This value is in the range of 1.7-8.7 milligrams acid/grams crude oil reported by Standal *et al.*, (1999).

Using solvent extraction, according to the procedure described in the section 3.1, a larger amount of the asphaltene in the deacidified oil (about 10 wt%) was identified.

### 4.3. Contact angle measurement

In this work, the surface wettability is evaluated through contact angle measurements. By convention, the contact angle is measured through the aqueous phase, as illustrated in Fig. (3). Hence, the reported values indicate that an increase in the contact angle implies an increase in the surface oil-wet behavior, or a decrease in the surface water-wet behavior.

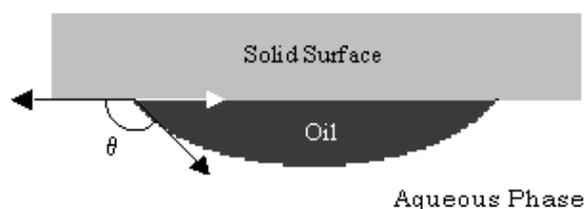


Figure 3. Illustration of the phase arrangement in the contact angle measurements.

In order to save space, the following abbreviations were adopted and used in the rest of the manuscript: Original crude oil (OCR), Deasphalted oil (DAO), Deacidified oil (DAC), Commercial steel surface (ACB), Galvanized steel surface (AGV), Pure water *mili-Q* quality (WATER), 1 wt% Sodium metasilicate aqueous solution (MS1%) and 1 wt% Sodium chloride aqueous solution (CL1%). The measurements of contact angles were made in triplicate. The measurements were within 6° from the average value. Based in the wettability literature data and in our sense, the wetting behavior was defined within the following range of contact angles: (i) water-wet -  $0^\circ < \theta < 70^\circ$ , (ii) neutral-wet -  $70^\circ < \theta < 110^\circ$  and (iii) oil-wet -  $110^\circ < \theta < 180^\circ$ .

Figure (4) shows the contact angles measured in systems formed by commercial steel/pure water and original crude oil, deasphalted oil, or deacidified oil.

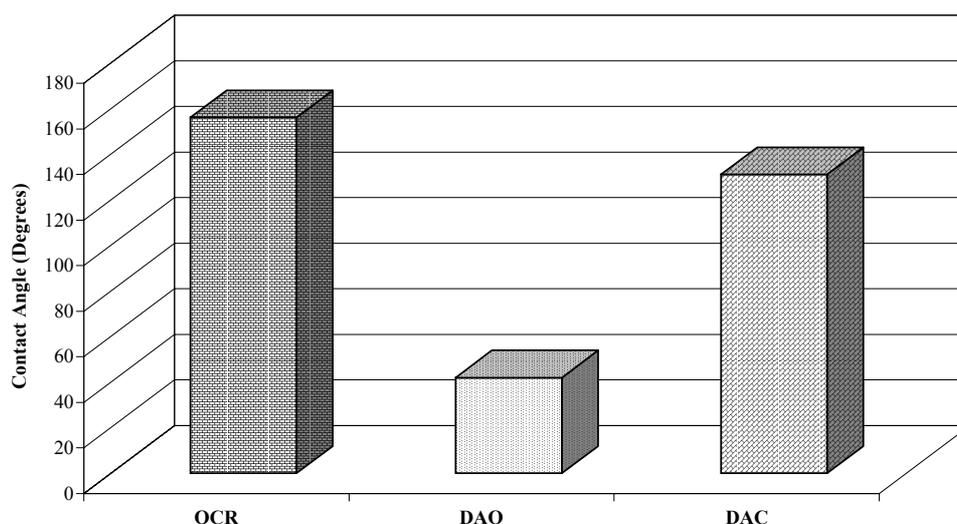


Figure 4. Contact angle measurements for oil drops of OCR, DAO and DAC on commercial steel surface immersed in the water.

The results in the Fig. (4) show low angles ( $\theta < 45^\circ$ ) for systems containing DAO, while angles are notably larger ( $\theta > 130^\circ$ ) for those containing OCR or DAC. These contact angle values imply an oil-wet behavior for the original crude oil and DAC and water-wet behavior for DAO. This shows that the absence of asphaltene in the crude can make commercial steel surface have a wet-water behavior, but the absence of the naphthenic acids cannot make it.

Figure (5) presents the results of contact angles measured for oil drops on galvanized steel surface immersed in pure water. Qualitatively, the results are similar to those obtained on commercial steel, as seen comparing Fig. (4) and (5).

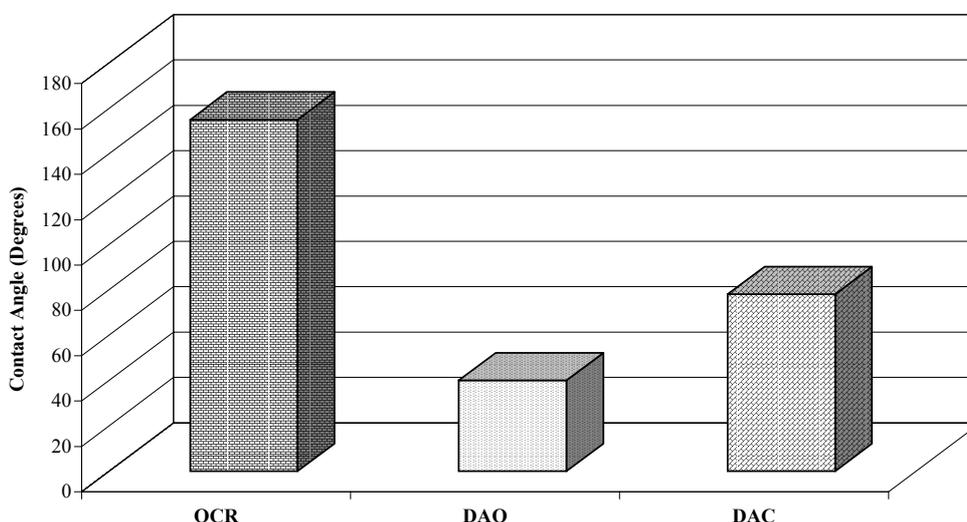


Figure 5. Contact angle measurements for oil drops of OCR, DAO and DAC on galvanized steel surface immersed in the water.

For the AGV surface, the contact angles measured indicate different wetting behaviors depending on the oil component in the system: OCR presents an oil-wet behavior ( $\theta > 150^\circ$ ), DAC a neutral-wet behavior ( $70 < \theta < 110$ ), with DAO presenting a water-wet behavior (about  $40^\circ$ ). In this case, isn't only the absence of asphaltene that could alter the wettability surface from oil-wet to water-wet, but the absence of naphthenic acids could also take the surface from the water-behavior to neutral-wet behavior.

The difference between the wetting behavior on commercial and galvanized steel, according the Fig. (4) and the Fig. (5), respectively, is the larger affinity of the galvanized steel surface for petroleum acids. This means that for

galvanized steel surfaces, the acids are capable to maintain the surface as oil-wet, which is not the case for commercial steel. The presence of asphaltenes alters the wetting behavior from water-wet to oil-wet for both steel surfaces.

Figure (6) presents the contact angle values for oil drops obtained from the measurements carried out using commercial steel surface immersed in the sodium metasilicate solution at a concentration of 1 wt%.

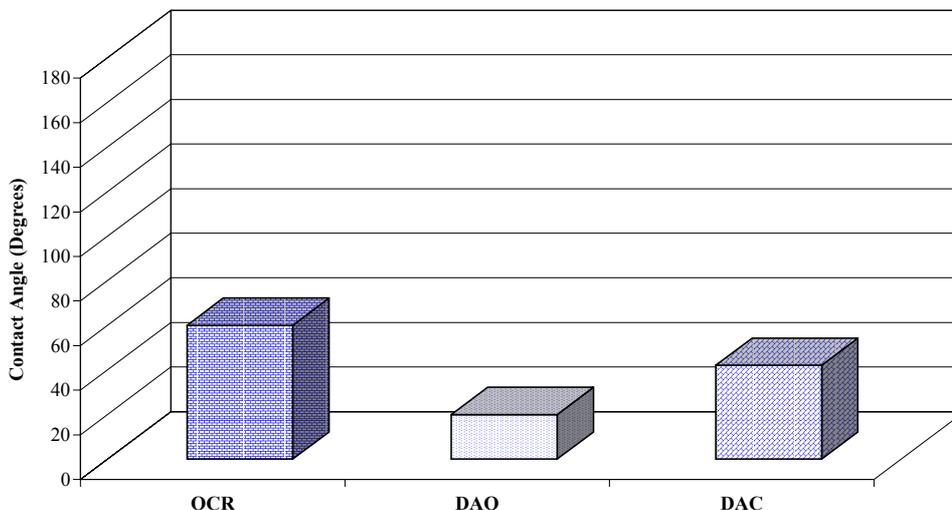


Figure 6. Contact angle measurements of OCR, DAO and DAC droplets on commercial steel surface immersed in the 1 wt% sodium metasilicate solution.

Contact angles in Fig. (6) display water-wet behavior, once that all angle values are lower than  $60^\circ$ . This observation indicates that the sodium metasilicate solution guarantees water-wet behavior for the ACB surface, despite the presence of both asphaltenes and the naphthenic acids. Comparing Figures (4) and Fig. (6), one can also note that the metasilicate solution reduces the contact angles and, consequently, increases the water-wet tendency.

Contact angle data for measurements on galvanized steel in the MS1% are presented in the Fig. (7).

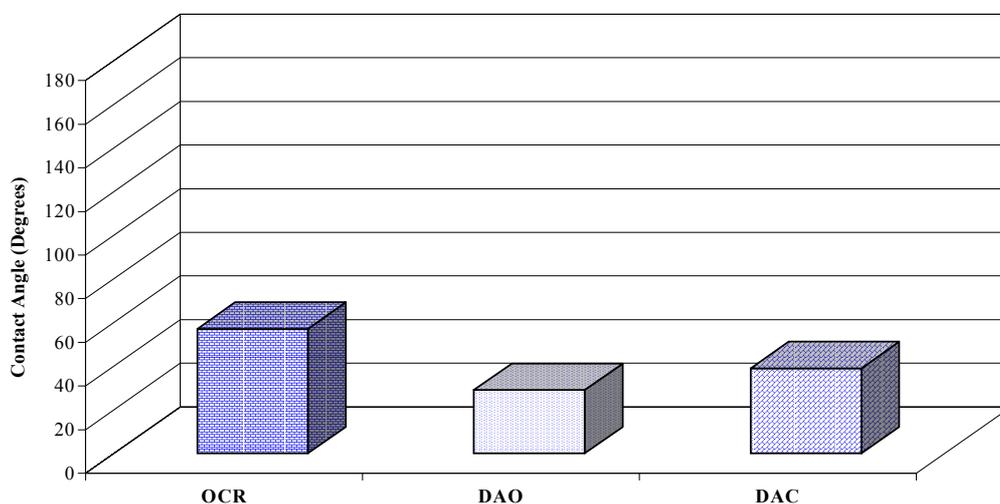


Figure 7. Contact angle measurements of OCR, DAO and DAC on the galvanized steel surface immersed in the 1-wt% sodium metasilicate solution.

The presence of the metasilicate when galvanized steel surfaces are used has similar effects to those observed for commercial steel surfaces. For both surfaces, contact angles are lower than  $60^\circ$  indicating water-wet behavior in the presence of MS1% (Figures 6 and 7).

Wettability tests were also carried out on surfaces immersed in the 1-wt% sodium chloride solution. Figure (8) shows the results of the measured contact angles on the ACB immersed in this aqueous sodium chloride solutions.

The behavior exhibited in Fig. (8) illustrates qualitative and quantitative differences relative to the behavior in water as the aqueous phase - Fig. (4) - and to that in the MS1% as the aqueous phase - Fig. (6). In Fig. (8), the water-wet behavior is observed for the OCR ( $\theta < 60^\circ$ ) and for the DAC ( $\theta < 35^\circ$ ), while oil-wet is observed for the DAO ( $\theta$  about  $120^\circ$ ).

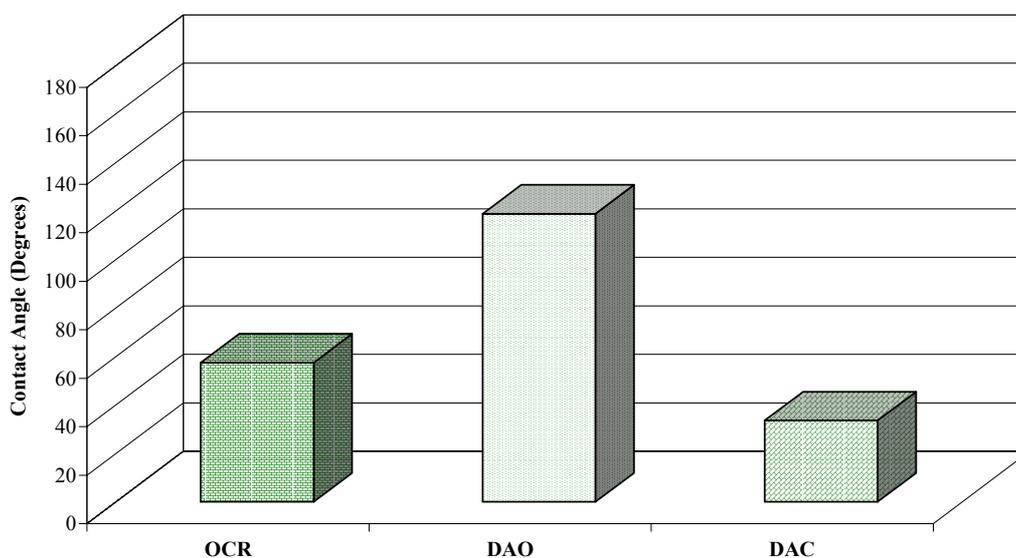


Figure 8. Contact angle measurements of OCR, DAO and DAC on the commercial steel surface immersed in the 1 wt% sodium chloride solution.

The contact angles for the OCR and for DAC in the CL1% (Fig. (8)) are statistically comparable to contact angles for these oil phases in the MS1% (Fig. (6)). For the DAO, however, the values obtained in the CL1% are much larger than the respective values measured in the water (Fig. (4)) and in the MS1% (Fig. (6)), where the contact angles for DAO did not exceed 45 °.

For the galvanized surface the results of the measurements of contact angles in the CL1% are contained in Fig. (9).

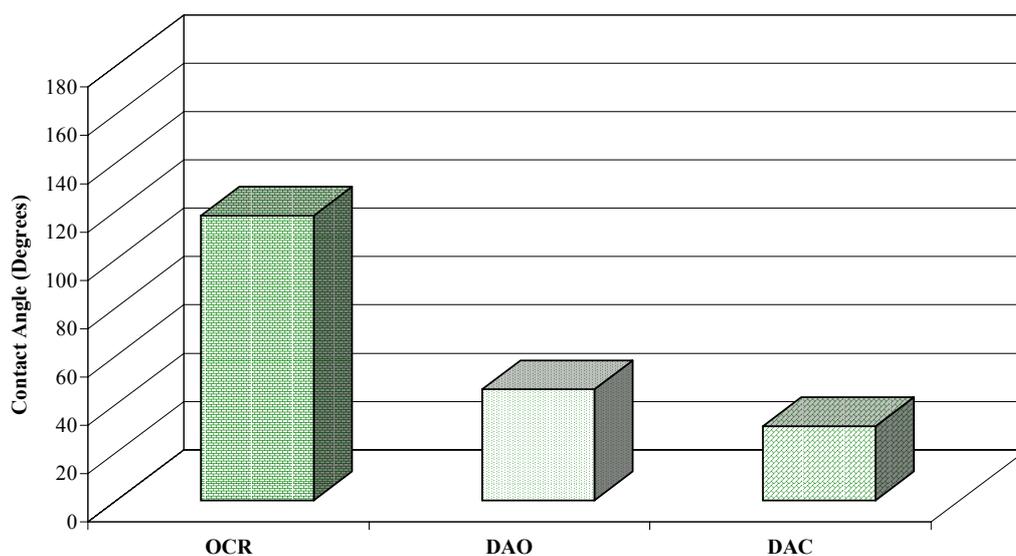


Figure 9. Contact angle measurements of OCR, DAO and DAC on the galvanized steel surface immersed in the 1-wt% sodium chloride solution.

Figure (9) shows that the AGV wettability in the CL1% is unlike that in the water and MS1% and it still different from that of the ACB in this same aqueous phase (Fig. (8)). The conclusion drawn on the basis of Fig. (9) is an oil-wet behavior for the OCR ( $\theta$  about 120 °), and the water-wet behavior for the DAO ( $\theta$  about 45 °) and for the DAC ( $\theta$  about 30 °).

Figures (8) and (9) show that the wettability behavior of the both commercial and galvanized surfaces in the chloride solution exhibit always water-wet behavior for the DAC, this can not be said for the behavior of the OCR and for the DAO. In the metasilicate solution, there is an agreement in relation to the behavior of all surfaces. The wetting behavior in metasilicate solution differs from that in the chloride solution and water for both surfaces. The different behavior of the surfaces when immersed in the chloride solution and it's the difference between these behaviors and those encountered in metasilicate solution may be related to the individual properties of the salts.

Sodium chloride aqueous solutions are very known for their corrosive action on metallic materials. In the petroleum industry, for example, above all in offshore operations and in water injection process, surface corrosion can lead to a change of the hydrophilic character of the surface and this can thus result in alterations in the wetting behavior. Sodium metasilicate, besides promoting surface corrosion because of the larger pH values in solutions, can adsorb on the surface, producing thin films that could act as a surface barrier.

## 5. Conclusions

The results show that crude oil polar components – asphaltenes and naphthenic acids were found to be present in the heavy crude oil under study in quantities comparable to those observed in the literature.

Commercial and galvanized steel surfaces, commonly utilized in pipeline construction for the petroleum industry, are susceptible to wettability alteration because of the presence of asphaltenes and naphthenic acids in the crude oils in crude oil/aqueous phase/solid. Asphaltenes appear to be the main contributors to this alteration from water-wet to oil-wet behavior. The use of 1-wt% sodium metasilicate aqueous solutions can satisfactorily overcome the wettability inconveniences generated by the presence of asphaltenes and acids in the crude oil. Sodium chloride solutions show lower efficiency in the alteration of the wettability to water-wet tendency than metasilicate solution. It is possible that both solutions have different and distinct mechanism in the alteration of surface wettability.

Some of the findings in this work are found in agreement with the experimental results obtained by Bannwart (2002).

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