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Influence of pH on Oil-Water Interfacial Tension and Mass Transfer for Asphaltenes Model Oils. Comparison with Crude Oil Behavior

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Abstract — Asphaltenes are shown to be amphoteric, containing acidic and basic species that can ionize at low and high pH respectively when they come in contact with water. We have used a mass transfer model in order to determine the partition coefficients of asphaltenes between oil and water. We have compared the influence of type of asphaltenes on interfacial tension and on mass transfer between oil and water and analysed the influence of an added surfactant. We have also compared the behavior of asphaltenes dissolved in model solvents with that of diluted heavy crude oils. Although asphaltenes qualitatively reproduce the behavior of crude oil components at the oil-water interface, differences were observed, either in interfacial tensions at low pH, or in partition coefficients at high pH. These differences are due to other molecules present in crude oil, which are either more interfacially active or more soluble in water.

INTRODUCTION

Asphaltenes are the highest molecular weight components of crude oils [1]. They are also the most polar and they form aggregates in the bulk crude oil [2] and adsorb at interfaces between oil and water [3]. The asphaltene concentration in crude oils is especially large in heavy or extra heavy crude oils or bitumen, and they are responsible for their high viscosities. The behavior of asphaltenes at oil-water interfaces has been extensively studied in order to better understand the stability of crude oil-water emulsions. These emulsions are formed during water injection in petroleum wells or when surfactants are added for oil transport [4, 5]. They can be very stable when the concentration of asphaltenes is large, hence posing problems in oil-water separation methods.

It has been remarked that oil species are transferred into water after contact between the two liquids, as evidenced by water pH changes [6]. This transfer likely concerns ionizable oil species. It is known that crude oils indeed contain such species in a concentration usually characterized by the TAN (Total Acid Number) and the TBN (Total Base Number). Naphthenic acids are among the most abundant in crude oils. Asphaltenes also possess acidic and basic groups which were identified by Dutta and Holland by using different potentiometric titration methods in non-aqueous polar solvents [7]. They found weak quantities of strong acids (pKa < 4) and strong bases (pKa > 12), representing about 10-20% of the total amount of acids and bases in asphaltenes. Studies of the evolution of oil-water zeta potential as a function of pH were consistent with an average pKa of 4.5 and a pKb of 1 [8, 9]. These results suggest that asphaltenes contain usually more acidic species than basic ones.

Asphaltene adsorption at oil-water interfaces results in a decrease of InterFacial Tension (IFT). A large number of adsorption studies were performed with solutions of asphaltenes in organic solvents, usually mixtures of heptane and toluene (see Ref. [3] for a recent review). The acidic or basic groups of asphaltenes can ionize at oil-water interfaces at high and low pH respectively, increasing their hydrophilic character and their affinity for the interface. Poteau and coworkers used toluene solutions of asphaltenes as model oils to evidence the amphoteric properties of asphaltenes [10]. Asphaltene adsorption at the oil-water interface is stronger at basic pH, above 10, confirming that surface active asphaltenes wear more acidic functions than basic ones.

In addition to the interactions at the interface, it was shown that mass transfer of natural amphiphilic species from oil to water is responsible for variations of the water pH [11–18]. We have recently used the pH changes after oil-water contact to derive the partition coefficient of oil species between oil and water [19]. We have also studied the influence of added surfactants, used to stabilize crude oil-in-water emulsions (while in the absence of surfactant, water-in-oil emulsions are formed). We found that the oil-water interfacial tension is decreased by the addition of surfactant, especially if it is ionic and contains aromatic groups such as SDBS (Sodium Dodecyl Benzene Sulfonate). Ionic surfactants with an alkane chain or nonionic surfactants with aromatic groups do not lower the tension in comparable amounts [20, 21]. We have shown that SDBS also enhances the transfer of oil species in water and again from pH data analysis, we were able to estimate the ratio n of transferred surfactant and oil molecules. Although it is usually assumed that oil species are transferred to water into surfactant micelles, we found that n was close to one, suggesting that the transfer is rather performed with ion pairs [22].

Because crude oils contain ionic species other than asphaltenes, we have undergone a study of the transfer across oil-water interfaces, using model oils containing only asphaltenes. It has been established that the IFT between these model oils and water is close to the IFT between the original crude oil and water [20, 21, 23]. The experiments have been performed with and without SDBS, with different type of asphaltenes and at different concentrations. The results are presented in this paper and are compared with the crude oil results in order to estimate the relative importance of asphaltenes in the transfer process.

1 MATERIAL AND METHODS

1.1 Crude Oil and Model Oil

The oil samples were prepared using a 9° API Venezuelan heavy crude oil. The oil acidity is given by the Total Acid Number (TAN). TAN is determined by the ASTM D664-01 method revisited by Fan and Buckley [24] and corresponds to the amount of potassium hydroxide (KOH) that is needed to neutralize the acids in the oil. The heavy oil has a TAN of 4.2 ± 0.2 mg KOH/g. The basicity of the oil is given by the Total Base Number (TBN). TBN is measured by the Dubey and Doe method [25] and corresponds to the amount of perchloric acid expressed in terms of the equivalent number of milligrams of KOH that is required to neutralize the bases in oil. The TBN of the oil is 2.7 ± 0.4 mg KOH/g.

The asphaltenes were precipitated from the heavy oil by addition of an alkane, n-pentane (Rathburn, HPLC grade) and n-heptane (BDH VWR Prolabo). The corresponding asphaltenes will be denominated as C5 and C7 asphaltenes. The ASTM 893-69 method was used: the oil was mixed with an excess of alkane (1 g of oil and 30 mL of alkane) and
refluxed for 30 min. Before addition of the alkane, the heavy oil was heated during 30 min at 60 °C to ensure homogenization. The mixture was then left to cool for 2 h in the dark. The precipitated fraction was filtered using a sintered glass crucible and washed several times with the hot corresponding alkane until the filtrate was clear. The crucible was then dried at 100 °C until there is no more mass loss. The precipitated asphaltenes were ground and the maltenes (C5 and C7 maltenes) were separated from the alkane using a rotary evaporator at 50 °C under vacuum. The SARA (Saturates, Aromatics, Resins and Asphaltenes) analysis is given in Table 1. The model oils are asphaltene solutions in xylene (Rectapure 99.9%). Xylene was used instead of toluene because of new hazard regulations. It is known that the solubility of asphaltenes in toluene and xylene are similar [26]. The gyration radii \( R_g \) of C5 asphaltene aggregates were measured in the two solvents at the same concentration, 0.3 wt% asphaltenes from the same crude oil [27, 28]. The \( R_g \) values are the same within experimental error (2-3%): 6.8 nm in toluene and 6.6 nm in xylene. This means that using xylene instead of toluene will not affect our results. Unless stated otherwise, in the following the name model oil will be used for xylene solutions of 5 wt% C5 asphaltenes.

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The oil used in the previous work [19, 22] has been prepared by dilution of the Venezuelan heavy crude oil in toluene (3.4 weight dilution, i.e. 2.4 g of toluene per gram of crude oil). In this way, we obtained a diluted crude oil containing the equivalent of 5 wt% C5 asphaltenes with a TAN of 1.25 mg KOH/g and a TBN of 0.8 mg KOH/g. The different TAN and TBN are recapitulated in Table 2.

One sees in Table 2 that the TAN of the model oil is smaller than that of the diluted crude oil containing the same amount of asphaltenes. This is due to the presence of other molecules bearing acid groups (such as naphthenic acids, essentially present in the resins) in the crude oil.

### 1.2 Water Phase

Ultrapure water from a Millipore Milli-Q UV system (resistivity 18.2 MΩ cm) was used. The pH of the aqueous phase was adjusted to the desired value by adding aqueous solutions of sodium hydroxide 0.1 mol/L (VWR Prolabo) or of hydrochloric acid 0.1 mol/L (Titripur Merck). We also added 5 g/L of NaCl (Fisher scientific) to increase the ionic strength of the aqueous phase. An anionic surfactant, Sodium Dodecyl Benzene Sulfonate (SDBS) from TCI (>95%), was added to study the influence of synthetic surfactant on mass transfers. We fixed the surfactant concentration to 0.1 wt%, well above its critical micellar concentration (0.005 wt%) [20].

### 1.3 Oil in Water Emulsions

Oil and water at an initial pH (pHi) were mixed with a magnetic stirrer for at least 2 h. After this period, the pH reaches an equilibrium value pHf. The pH measurements were made with an Inlab®Science electrode connected to a pH meter (Seven Easy, Mettler Toledo). When large amounts of oil were used, we separated the oil and water phases before measuring the pHf. For this purpose, we waited for 10 min to let the oil droplets cream before measuring the pH in the water phase. In most cases, only 5% or less oil was dispersed in water, and the pH measurements were done in the emulsion thanks to the Inlab®Science electrode which was insensitive to the presence of oil. The electrode was cleaned between each measurement and re-calibrated after 10 measurements. All pH measurements were performed at room temperature (24 ± 1 °C).

Water was degassed prior to measurements, in order to remove CO₂ molecules, which influence the water pH. For this purpose, the water was heated at 60 °C to facilitate the extraction of gases by a vacuum pump for at least 3 h.

### 1.4 Interfacial Tensions

The IFT was measured with an automated drop tensiometer (Tracker, Teclis) and a spinning drop tensiometer (SITE 100,
We used the drop tensiometer for IFT larger than 2 mN/m and the spinning drop tensiometer for IFT smaller than 2 mN/m. Aqueous solutions and oils were not equilibrated together before the measurements, which started immediately after contacting them. Note that the use of the spinning drop technique does not allow for the measurement of the IFT at times less than 1 min. All IFT measurements were performed at room temperature, 24 ± 1 °C.

2 RESULTS AND DISCUSSIONS

2.1 Comparison between Model Oil and Diluted Crude Oil

We first compared the pH variation of the equilibrium interfacial tension between water and either the model oil or the diluted crude oil (Fig. 1). For the IFT measurements, a drop of oil is contacted with a large volume of aqueous phase, so very few hydroxide groups OH− and hydronium H3O+ were consumed to ionize endogenous surfactants and the pH did not change during the equilibrium phase. The equilibrium values of IFT were obtained after a few minutes. We also show for comparison measurements made with the same crude oil diluted with toluene. One sees that the IFT does not depend on the solvent used to dilute the crude oil, within experimental uncertainty.

The interfacial tensions for the model oil are somewhat lower than for the diluted crude oil at pH < 10, but become the same at pH 10 and 11. Similar results were obtained at pH 8.4 for diluted bitumen and model oil containing C5 asphaltenes extracted from this bitumen [29]. At high pH, the acidic functions of the species present in the oil are saponified and these species become negatively charged at the contact of water [19]. The sharp decrease in interfacial tension above pH 9 suggests that the acidic asphaltenes are strongly interfacially active. In turn, at low pH, the basic functions of oil species become positively charged but these cationic species are likely less surface active. Because the IFT is the same at pH 10 and 11, the interfacially active species in the crude oil are likely mostly C5 asphaltenes at these pHs.

The interfacial tensions vary slightly between pH 3 and 9, suggesting that the basic functions of C5 asphaltenes do not significantly affect the IFT in this range of pH and that the interfacially active species are mostly non ionizable species. The IFT is higher in the case of diluted crude oil in this pH range. It is well known that asphaltenes are co-solubilized by resins in crude oils and therefore they have less affinity for the interface, thus explaining the higher IFT with the diluted crude oil.

The interfacial tension between toluene and water in the presence of 0.1 wt% SDBS is about 1 mN/m, independent of time and pH [20]. When the crude oil or the model oil are used, the interfacial tension evolves over very long times and becomes very low. Equilibrium values cannot therefore be determined, excepted at neutral pHs. The time evolution of the interfacial tensions for the model oil is shown in Figure 2 for different initial pHs and follows the same trends as diluted crude oil [20]. At pH 3, the presence of SDBS promotes the transfer of bases into water, the IFT decreases and goes through a minimum. This time evolution is characteristic of transfer of species at liquid interfaces in the presence of a desorption barrier [30]. At pH 7, the interfacial tension varies less, there is less transfer than at the other pHs. At pH 11, the IFT decreases to ultra-low values as in the case of crude oil, below which the measurements are interrupted (the oil drops fraction into smaller drops) and it is not possible to follow the complete time evolution [20].

In the following, we will analyse the transfer of oil species across the oil-water interface using pH measurements. The evolution of pHf as a function of pHi was measured for the model oil and compared with the diluted crude oil (Fig. 3).

The variation of pHf is the same within experimental error for the crude oil and the model oil for pHi between 3 and 8. This means that the transferred basic species are the same for the two oils. However, for pHi above 8, the pHf is higher for the model oil suggesting that there is less transfer of acidic species than for the diluted crude oil. This is consistent with the fact that the TAN is larger for the diluted crude oil (Tab. 2): the model oil contains fewer acids than the diluted crude oil.
crude oil, explaining why there is less transfer of acidic species in water.

The same experiment was done with added SDBS. As seen before with the diluted crude oil, SDBS increases the transfer at low pH [22]. This was attributed to the complexation of the surfactant, which is anionic, with the oil basic species. Figure 3 reveals an increase of pHf at acidic pHi: the basic species transferred in water increase the pHf. Since this pHf is similar for the two oils, the transferred basic species in the diluted crude oil are probably present in the C5 asphaltenes. SDBS favors the transfer of the endogenous bases from oil to water in the same way for the two oils, again supporting the fact that these bases come from the C5 asphaltenes.

We have evaluated the mass transfer for the model oil with the model proposed in Reference [19]. The entry data are the pKas of the acid and basic species, the TAN and TBN and the volume fraction of water in the emulsion \( X_w \), this volume fraction being 95%. We have used the measured values of TAN and TBN (Tab. 2) and \( pK_{A_1} = 5 \), \( pK_{A_2} = 9 \), as for the diluted crude oil [19]. The adjustable parameters are the partition coefficients between oil and water, \( X_a \) for the acids and \( X_b \) for the bases:

\[
X_a = \frac{[A_{H_o}]}{[A_{H_w}]}
\]

\[
X_b = \frac{[B_o]}{[B_w]}
\]

where \([A_{H_o}], [B_o], [A_{H_w}] \) and \([B_w] \) are the acid and base concentration in the oil and water phase respectively.

In the absence of surfactant, the bases are transferred with difficulty in the water phase and the difference between pHf and pHi is very small at low pH. The fit leads to \( X_a \sim 10^5 \) and \( X_b \sim 10^7 \). The values of \( X_a \) and \( X_b \) are reported in Table 3, together with their values for the diluted crude oil taken from Reference [19]. The model oil and the diluted crude oil have a similar TBN (Tab. 2), \( X_b \) is also similar and very large in both cases. \( X_a \) is smaller, but higher than for the model oil, for which \( X_a \sim 10^4 \). This difference is consistent with the difference in TAN (Tab. 2). At high pH, crude oil contains other acidic species than asphaltenes that transfer into water, likely naphthenic acids. Interestingly, the differences between partition coefficients for crude and model oils do not mirror the IFT differences, which are the same at high pH and differ at low pH. This can be however rationalized: the partition coefficient relates to the transferred species, while the IFT relates to the adsorbed ones. Although the overall behavior of model and crude oils are similar, the results presented evidence differences between interfacially active species and water soluble species.

An example of pH fit in the presence of SDBS is shown in Figure 4. The transfer of bases being favored by SDBS, the partition coefficient \( X_b \) decreases from \( 10^7 \) to \( 10^5 \) while \( X_a \) remains equal to \( 10^5 \). This is to be compared with the crude oil for which \( X_a = X_b = 10^4 \) [22]. With surfactant, \( X_b \) is one order of magnitude higher for the model oil as compared to the crude oil. This means that at low pH, other oil species than asphaltenes transfer into water when surfactant is present. As discussed before, this is associated to the complexation of basic oil species and surfactant.

![Figure 2](image1.png)

**Figure 2**

Evolution of IFT as a function of time at pHi of 3, 7 and 11. Interface between the model oil and an aqueous solution containing 0.1 wt% SDBS. The lines are guides to the eye.

![Figure 3](image2.png)

**Figure 3**

Variation of pHf versus pHi for both model oil (triangles) and diluted crude oil (squares), without (solid symbols) and with (open symbols) SDBS. The lines are guides to the eye.
In order to increase the amount of acids and bases coming from the asphaltenes, we increased the asphaltene concentration in the model oil. The variation of pHf versus pHi with 7 wt% of C5 asphaltenes dissolved in xylene is shown in Figure 5.

By comparing with Figure 3, one sees that the differences in pHf between the new model oil containing 7 wt% asphaltenes and the diluted crude oil are smaller than for the model oil containing 5 wt% asphaltenes in the presence or in the absence of SDBS. The increase of the amount of C5 asphaltenes from 5 to 7 wt% in the model oil corresponds to an increase of TAN from 0.31 to 0.43 mg KOH/g, consistent with an increase of acid concentration into the water phase and then a decrease of the pHf. The concentration of C5 asphaltenes can be therefore adjusted in the model oil to mimic the acido-basic behavior of heavy crude oil in the presence or absence of SDBS. The partition coefficients obtained in the fits are reported in Table 3.

### 2.2 Comparison between C5 and C7 Asphaltenes

The composition of asphaltenes changes with the extraction method. Parameters such as the nature of the precipitating solvent, the amount of solvent used, the contact time between oil and solvent and the temperature influence the composition of the extracted asphaltenes [1, 31, 32]. We therefore also studied the behavior of a model oil containing C7 asphaltenes. These C7 asphaltenes have a higher average molecular weight than the C5 asphaltenes, they are more polar and contain less resins than C5 asphaltenes. The variation of pHf versus pHi for a model oil containing 5 wt% C7 asphaltenes is shown in Figure 6.

The pHf of model oils containing 5% of either C5 or C7 asphaltenes appear to be independent of the presence of SDBS. This is at first sight surprising, because the TBN of C7 asphaltenes (~0.5 mg KOH/g) is smaller than the TBN of C5 asphaltenes (~0.9 mg KOH/g). It is possible that some
of the basic species of the C7 asphaltenes are not surface active or remain trapped at the oil-water interface. The surfactant appears unable to enhance their transfer.

**CONCLUSION**

Our work confirms that asphaltenes behave as amphoteric molecules. They contain both acidic and basic species that can ionize when they are in contact with water, adsorb at the interface and eventually transfer into the water phase. Negligible differences in the transferred species were seen for asphaltenes precipitated in pentane or heptane. The transfer of basic species is usually limited, but can be enhanced by adding a surfactant. We have used here an ionic surfactant possessing a benzene group, able to complex with asphaltene molecules. We have quantitatively analysed the transfer of basic species of the C7 asphaltenes are not surface active or remain trapped at the oil-water interface. The surfactant appears unable to enhance their transfer.

We have compared the behavior of a diluted crude oil with model oils being asphaltene solutions. We have shown that asphaltenes qualitatively reproduce the behavior of crude oil components at the oil-water interface: both the interfacial tensions and the partition coefficients between oil and water are similar. Quantitative differences were however observed, either in interfacial tensions at low pH, or in partition coefficients at high pH. These differences are due to other molecules present in crude oil, which are either more interfacially active or more soluble in water (such as naphthenic acids).

Contacting oil and water therefore allows extracting a certain class of asphaltene molecules, the extraction of basic species being greatly enhanced by the addition of surfactant. It would be interesting to investigate further the nature of these molecules. This could be also valuable for the understanding of water contamination by crude oils during oil recovery processes.

**REFERENCES**


