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Challenges and New Approaches in EOR
Défis et nouvelles approches en EOR

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Effect of Added Surfactants on the Dynamic Interfacial Tension Behaviour of Alkaline/Diluted Heavy Crude Oil System

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Résumé — Effet de l’ajout de tensioactifs sur le comportement dynamique de la tension interfaciale du système solution alcaline/brut dilué — Cette étude a été réalisée pour mieux comprendre les interactions entre les tensioactifs utilisés pour la récupération assistée de pétrole et les tensioactifs in situ présents dans le brut. Nous expérimentons le comportement dynamique des tensions interfaciales (mesurées par les méthodes de goutte pendante et goutte tournante) entre le brut lourd dilué et les solutions alcalines avec ajout de tensioactif. La tension interfaciale dynamique entre le brut dilué et une solution alcaline (pH 11) sans ajout de tensioactif croît fortement au cours du temps, cette augmentation est attribuée au transfert des tensioactifs in situ (produits par saponification des fonctions acides présent dans le brut) au travers de l’interface brut/eau. L’ajout de sulfonate de sodium dodécyl benzène (SDBS), à une concentration supérieure à la concentration micellaire critique (CMC ~ 0.002 %), change complètement le comportement dynamique de la tension interfaciale, elle diminue fortement pour atteindre finalement une valeur plateau de 1.5 × 10⁻³ mN/m. L’efficacité du SDBS est attribuée à l’interaction entre les tensioactifs in situ et les tensioactifs ajoutés qui forment une couche interfaciale mixte qui permet d’obtenir des tensions interfaciales ultra basses et de s’opposer au transfert de masse à l’interface brut/eau.

Abstract — Effect of Added Surfactants on the Dynamic Interfacial Tension Behaviour of Alkaline/Diluted Heavy Crude Oil System — This study has been undertaken to get a better understanding of the interactions between Enhanced Oil Recovery (EOR) surfactants used in chemical flooding and in situ surfactants present in an heavy oil. We report an experimental study of dynamic Interfacial Tension (IFT) behaviour of diluted heavy oils/surfactant enhanced-alkaline systems. The dynamic IFT was measured using pendant drop and spinning drop tensiometers. The dynamic IFT between diluted heavy oil and alkaline solution (pH 11) with no added surfactant increased sharply with time, which was attributed to the transfer of the in situ surfactant (produced by saponification of the acids groups present in the crude oil) across the oil/water interface. The addition of Sodium Dodecyl Benzene Sulfonate (SDBS) above the Critical Micellar Concentration (CMC ~ 0.002 %), changed completely the dynamic IFT behaviour of the diluted heavy oil as the IFT strongly decreased and finally reached a plateau, of about 1.5 × 10⁻³ mN/m at a concentration of only 0.02 %. We attributed the efficiency of SDBS to a synergistic effect between the in situ surfactant and the added surfactant that form a mixed interfacial monolayer, which is very efficient in decreasing the IFT to ultra low values and in resisting mass transfer across the oil/water interface.
INTRODUCTION

Worldwide average oil recovery rate is around 33%. Increasing this figure by 10% corresponds to an extension of the reserves of 30 years. This constitutes a very important challenge that would leave time to enable the development of new renewable energy sources and allow an efficient energetic transition. Among EOR technologies, surfactant flooding is a particularly attractive technique because one can expect an important incremental oil recovery rate related to a strong decrease of the residual oil saturation. Crude oils contain amphiphilic molecules (in particular asphaltenes and naphtenic acids), that can be in large amount in acidic or asphaltic crudes. Depending on pH and salinity, these natural surfactants will interact with the added synthetic surfactants in order to enhance the oil recovery.

Alkaline-enhanced oil recovery has been widely addressed [1-3]. It has already been established that the Interfacial Tension (IFT) is lowered between the acidic crude oil and the alkaline aqueous phase. The dynamic IFT occurring in these systems was firstly reported by McCaffery [1] in 1976, when the measurements of ultra low IFT as function of time were made possible by spinning drop technique. McCaffery found that the initial low values of IFT, measured when the acidic oil is brought in contact with the alkaline aqueous phase, can increase with time up to three orders of magnitude. In fact, the acidic species present in the crude oil will react with the added alkali to generate interfacially active species (called in situ surfactant) which accumulate at the oil/water interface and temporarily reduce the IFT. These species may either adsorb at the oil/water interface, or diffuse to the bulk aqueous or oil phases. The dynamic IFT behaviour is a function of these interfacial active species concentration, which depends on their rates of adsorption and desorption from the interface [4-6]. Rudin and Wasan [7] have found that the IFT goes through an ultra low minimum in certain pH ranges. They attributed this minimum to the simultaneous adsorption of unionized and ionized acid species upon the interface.

For surfactant-enhanced alkaline crude oil, it has been shown that there is a beneficial synergistic effect of combining alkali with surfactant in achieving ultra low IFT and consequently improving oil recovery [8, 9]. Dynamic IFT of surfactant-enhanced alkaline/crude oil system has been largely studied in literature [10-12]. The oil recovered through surfactant-enhanced alkaline flooding of Berea sandstone cores correlates better with minimum IFT values than with equilibrium IFT [13].

Nasr-El-Din and Taylor [14] studied the dynamic IFT of surfactants (Neodol 25-3s and Triton X-100)/enhanced alkaline/ Lloydminster crude oil. They found that the addition of synthetic surfactants with high salt tolerance did not always lower the IFT of the system. Nasr-El-Din and Taylor [15] examined in detail the effect of partially hydrolyzed polyacrylamide on dynamic IFT in the David crude oil/Sodium carbonate system. They were the first to show that IFT versus \( t^{1/2} \) (t is the interfacial age), displayed a linear relationship, suggesting that adsorption of the surface active species is controlled by diffusion. In order to study surfactant-enhanced alkaline/crude oil, Taylor et al. [13] used a modified spinning drop technique which enables accessing short interfacial ages as two seconds range. They showed that for such systems, the dynamic IFT behaviour included minima which vary in both magnitude and interfacial age at which they occur. These minima were followed by a sharp increase of the IFT. Rudin et al. [2] examined in details the dynamic IFT behaviour of surfactant enhanced alkaline/acidic oils. They showed that the formation of mixed micelles with the ionized acids of the crude oil is the dominant mechanism by which added surfactant reduced the IFT to ultra low values. The addition of surfactant also caused a higher interfacial resistance to mass transfer across the oil/water interface and reduced the rate of acid ionization, resulting in a longer time of low dynamic IFT.

Touhami et al. [16] studied the effect of adding surfactant (Sodium Dodecyl Sulfate: SDS) on the dynamic IFT between a model acidic oil and various alkalines (NaOH). The IFT of the acidic oil without added surfactant initially decreased with time, reaching a minimum and then finally increasing sharply with time. They showed that below the Critical Micellar Concentration (CMC), the surfactant didn’t change the dynamic IFT behaviour of the acidic oil/alkaline system but contributes significantly to the reduction of the IFT, whereas after the CMC the added surfactant plays an important role in damping the dynamic trends observed without added surfactant (the IFT initially decreased then becomes constant after a period of time and finally increases slightly with time). Zhao et al. [12] also showed that dynamic IFT between flooding system and acidic oil can reach and maintain ultra low values at low surfactant concentration for optimal alkalinity and salinity. The added salt has an important influence on the adsorption onto the interface and the partition between the oil and water phase of these surfactant active species.

In our previous work [9], we have only reported transient IFT measurements of surfactant-enhanced alkaline/diluted heavy crude oil system. We showed that the addition of small amount of any of the three surfactants tested (Triton X-405, Sodium Dodecyl Benzene Sulfonate (SDBS) and Sodium Dodecyl Sulfate (SDS)) induces a further decrease of the IFT. Notably, SDS was by far the most efficient surfactant in reducing the IFT to ultra low values ~ 4 x 10^4 mN/m at a concentration of only 0.05% and a pH of 11. We have also reported that observing ultra low IFT implies not only a suitable choice of surfactant type and concentration but also optimization of salinity and pH. For a better understanding of our system, we decided to further investigate its dynamic IFT behaviour by analyzing the effect of pH, added surfactant concentration and type on this dynamic interfacial behaviour.
1 MATERIALS AND METHODS

Samples were prepared from a 9°API Venezuelan heavy crude oil. The SARA (Saturates Aromatics Resins Asphaltenes) analysis gives 12% saturates, 37% aromatics, 33% resins and 17% asphaltenes (obtained with pentane). This heavy oil is acidic, TAN (Total Acid Number) is 4.2. The diluted heavy oil has been prepared by dilution of the Venezuelan heavy oil in toluene (3.4 weight dilution, i.e. 2.4 of toluene per g of heavy oil) in order to obtain a crude oil containing 5% asphaltenes. Asphaltenic extraction from the heavy oil was performed using the ASTM 863-69 standard: the crude oil was first stirred with an excess of n-pentane (1 g of oil and 30 mL of pentane). The precipitated fraction was filtered, dried and ground. We evaporate pentane from the remaining solution to recover maltenes (oil without asphaltenes). Rectapur toluene (99.9%) was used as a solvent, both for diluting the heavy oil and the maltenes and solubilizing the extracted asphaltenes. The extracted asphaltenes were simply solubilized with toluene to obtain the model oil.

Ultrapure water from a Millipore Milli-Q UV system (resistivity 18.2 MΩ.cm) was used as the aqueous phase. The pH of the aqueous phase was adjusted to the desired value by adding an aqueous solution of sodium hydroxide 30% or by adding sodium carbonate 99% (VWR GPR Rectapur). NaCl (Fisher scientific) was added to increase the ionic strength of the aqueous phase. Except when noted, 5 g/L NaCl aqueous solutions were used. Three different surfactants, SDBS, SDS and Triton X-405 (ethoxylated nonylphenol) were tested. SDS (98%) and Triton X-405 (98%) were obtained from Sigma Aldrich. SDBS (>95%) was purchased from TCI Europe. SDBS solutions were heated during 10 minutes at 30°C to facilitate solubilization.

Before dilution, the heavy oil was also heated during 30 minutes at 60°C before each experiment to assure homogenization. Fresh surfactant and diluted heavy oil solutions were prepared daily. The interfacial tension was measured with a commercial pendant drop tensiometer (Tracker from Krüss SITE 100). We used the pendant drop tensiometer for IFT larger than 2 mN/m and the spinning drop tensiometer (Krüss SITE 100). For IFT smaller than 2 mN/m. In all cases aqueous solutions and diluted heavy oil were contacted before each experiment to minimize transfer across the crude oil/aqueous phase interface. More precisely a drop of crude oil was put in contact with a large volume of alkaline phase. IFT measurements were done at least one hour later. Thus, very few hydroxide groups were consumed in order to produce in situ surfactant, and the pH did not change. The use of spinning drop technique does not allow a complete representation of the IFT dynamic behaviour since it is not capable of IFT measurements which are conducted at less than 1 min range. In most of our measurements, we were not able to observe minima, due to the fact that sharp IFT reduction occurs as soon as the oil drop is in contact with the aqueous phase.

For all the IFT measurements, the initial time (T = 0 s) corresponds to the time at which the oil drop initially comes in contact with the aqueous phase. All IFT measurements were performed at room temperature, 23 ± 1°C.

2 RESULTS

Figure 1 shows the dynamic IFT between the crude oil and 5 g/L NaCl at pH 7 and 11. At pH 7, the IFT initially decreased in function of time and finally reached an equilibrium plateau of about 23 mN/m. At pH 11, representative of alkaline flooding, when a crude oil drop is injected inside the rotating capillary and at a low rotation velocity (1000 rpm), the drop was observed to fragment in smaller droplets. This fragmentation is due to very low IFT values. After the fragmentation of the initial drop, the IFT of the droplets was observed to increase as a function of time. The dynamic IFT behaviour shown in Figure 1 can be explained as follows: when the crude oil and the brine are brought in contact with each other, the acidic species present in the crude oil will migrate to the interface and react with the alkaline solution (pH 11) to produce interfacially active species that accumulate easily at the interface. The dynamic IFT is a function of the concentration of these species at the interface (rate of adsorption and desorption from the interface). Due to the low salinity of the alkaline aqueous phase (5 g/L NaCl), we therefore attributed the IFT increase to the transfer of these ionized species from the oil/water interface to the aqueous phase. Note that the transfer can be visualized by a brownish coloration of the water phase. For pH = 11, we were not able...
To pursue the IFT measurements above 600 seconds, the elongation of the oil drop inside the rotating capillary above this period of time was impossible (IFT > 2 mN/m).

In order to investigate the effect of added surfactant on the dynamic IFT between the diluted heavy oil and the alkaline aqueous phase, three surfactants were tested (Triton X-405, SDS and SDBS). Figure 2 shows the dynamic IFT between the crude oil and the alkaline solution when 0.3 wt% of Triton X-405, 0.1 wt% of SDS and 0.1 wt% of SDBS were added at pH 11. Whereas the IFT of the diluted heavy oil increases sharply as function of time with no added surfactant, the IFT with Triton X-405 and SDS increased during the first 400 seconds then reached an equilibrium plateau. The addition of either surfactant did not completely block the transfer across the oil/water interface but largely minimizes it. The addition of 0.1% of SDBS changes completely the dynamic IFT behaviour of the diluted heavy oil as the IFT strongly decreases during the first 200 seconds and finally reaches a plateau of about 1.5 × 10⁻³ mN/m. Note that in this case fragmentation of droplet can be observed and measurements become difficult. In our previous work, we also showed that SDBS was by far the most efficient surfactant used for the diluted heavy crude oil, reducing the IFT to ultralow values. We attributed the significant decrease of the IFT upon addition of SDBS to a synergistic effect between the in situ surfactant and the added surfactant while forming a mixed interfacial monolayer [9] which is very efficient in decreasing the IFT to ultra low values and resisting mass transfer across the oil/water interface.

To have a better understanding of this synergistic phenomena, the IFT of SDBS alone was measured using a mixture of toluene and dodecane. The IFT between pure toluene and aqueous solution containing 0.1% SDBS and 5 g/L NaCl at pH 11 is close to 0.7 ± 0.1 mN/m, whereas for a mixture of 75:25 toluene/dodecane, the IFT decreases to 0.2 ± 0.1 mN/m, which is close to the value obtained with the diluted heavy oil with 0.1% SDBS [9]. As a reference this solvent will then be used to determine the CMC of SDBS. The IFT of pure SDBS was measured for different surfactant concentrations using 75:25 toluene/dodecane (Fig. 3). The CMC was found equal to 0.002%, lower than the CMC of pure SDBS using toluene (CMC ~0.005%), measured in our previous work [9].

Figure 4 shows the effect of SDBS concentrations on the dynamic IFT between the diluted crude oil and the aqueous phase at pH 11. For a concentration of SDBS equal to 0.001%, the IFT decreases upon SDBS adsorption from the value of the bare oil-water IFT down to a minimum where the interfacial surfactant concentration is momentarily large. This first step is too rapid to be observed in our measurements at low SDBS concentrations. The IFT increases afterwards due to the transfer of some oil molecules into the water phase, until the equilibrium IFT value is reached. When the concentration of SDBS was further increased up to 0.002% (CMC), the IFT decrease was slower (it can be observed during the first seconds) and an equilibrium plateau was reached without a subsequent increase. When the SDBS concentration is increased further, the IFT minimum can be observed. This behaviour could be due to the role of micelles on the oil transfer. Similar observations were made by Chiwetelu et al. [17] for mixed surfactant enhanced
alkaline/heavy crude oil. However in their case, the initial IFT values were considerably higher than those exhibited by the surfactant free system. It’s important to note that when SDBS was increased above 0.02%, the surface of the elongated drop became non-uniform and rough after 600 seconds inside the spinning drop tube, preventing IFT measurements at longer times. For an SDBS concentration of only 0.05%, the IFT was reduced to ultra low value ~4 × 10⁻⁴ mN/m after just 600 s.

For a better understanding of the origin of the transfer occurring across oil/water, we measured the IFT of toluene diluted heavy oil (5% asphaltenes), asphaltenes model oil (5 wt% pentane extracted asphaltenes dissolved in toluene) and maltenes model oil (toluene diluted maltenes with same dilution rate) with and without added SDBS at pH 11 (Fig. 5).

It is interesting to note that the IFT between the maltenes and the alkaline aqueous solution has the highest value among the other systems, meaning that the napthenic acids are not the only species responsible of reducing the IFT and that the contribution of asphaltenes to the IFT is very significant. Figure 5 shows also that the IFT increased sharply with time for the diluted heavy oil, asphaltenes and maltenes model oils, this being accompanied by coloration of the water phase. This is a clear indication that the mass transfer across the oil/water interface is not only induced by napthenic acids but also by asphaltenes. Note that we cannot completely exclude the fact that some napthenic acids may precipitate with asphaltenes during asphaltene extraction. When SDBS is added, the IFT of the 3 systems decreased to lower values and the transfer across the oil/water interface is slowed down, especially close to the CMC.

**CONCLUSION**

When crude oil and brine are brought into contact, the acidic species naturally present in the crude oil migrate to the interface and react with the alkaline solution (pH 11) to produce interfacially active species. The dynamic IFT behaviour is a function of these interfacial species concentration at the interface, which depends on their rates of adsorption and desorption from the interface. For the diluted crude oil used, the IFT first decreased when brought into contact of the alkaline solution at pH 11 (elongation of the crude oil drop followed by the fragmentation into smaller droplets). The IFT reduction is followed by an important increase as function of time. When SDBS is added, the dynamic IFTs show different behaviours depending on SDBS concentrations. For a concentration of SDBS below the CMC ~0.005%, the dynamic IFT behaviour remains similar to the one observed for the diluted heavy oil without added SDBS. However, upon further increase of SDBS, the dynamic IFT behaviour changes completely as the IFT strongly decreases and finally reaches a plateau. For concentrations of SDBS higher than 0.02%, the IFT decreases to ultra low IFT values and the surface of the elongated drop start to disintegrate preventing the extension of IFT measurements to longer times. We attributed this ultra low IFT to a synergistic effect between the *in situ* surfactant and the added surfactant while forming an interfacial mixed layer, which is very efficient in decreasing the IFT to ultra low values and resisting to mass transfer across the oil/water interface.

The dynamic IFT shows that maltenes and asphaltenes model oils exhibit the same interfacial behaviour than the
diluted heavy oil and the addition of SDBS was efficient in blocking the transfer across the model oil/water interfaces. The addition of either SDS or Triton X-405 to the diluted heavy oil did not block completely the transfer across the interface but largely minimize it. These results might have important applications in EOR of heavy crude oils: further work is currently underway to investigate this issue.

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