

Regarding the effect that different twin-tailed surfactant have on a solid stabilized petroleum emulsion

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Abstract An industrial petroleum emulsion stabilized by colloidal silica particles was treated with four different twin-tailed surfactants: sodium bis-2-(ethylhexyl) sulfosuccinate (AOT), didodecylammonium bromide (DDAB), calcium oleate ($\text{Ca}(\text{OL})_2$), and dioctadecyldimethylammonium bromide (DODAB). Fourier transform infrared (FT-IR) spectroscopy, optical microscopy, centrifuge test, and conductivity measurement were employed to determine the effect of the amphiphile molecules on the crude oil emulsion. AOT and DDAB produce emulsion breakdown, while $\text{Ca}(\text{OL})_2$ does not alter the emulsion stability and DODAB produces an extra stabilization of it. The AOT adsorption at the oil–water droplet interface is a spontaneous process ($\Delta H^{\text{ads}} < 0$), which promoted the emulsion breakdown through an inter-droplet interaction mechanism. DDAB needs extra energy (via centrifugation) to destabilize the emulsion. $\text{Ca}(\text{OL})_2$ dissolves in oil phase and remains there without altering the emulsion strength, while DODAB increases the emulsion stability.

Keywords Solid stabilized emulsion · AOT · Twin-tailed surfactants · Demulsification · Inter-droplet interaction mechanisms

Introduction

Emulsions can be found in almost every part of the petroleum production and recovery process: in reservoirs, produced at well heads, in many parts of the refining process, and in

transportation pipelines. An emulsion that may be desirable to assist one stage of an oil production process and then must be carefully stabilized may be undesirable in another stage and necessitates a demulsification strategy. Considering the extraction of bitumen from oil sands as an example, the diluted recovered from bitumen froth contains $\approx 0.5\%$ of fine solids and 3% of emulsified water droplets $< 3 \mu\text{m}$ in diameter. The emulsified water in diluted bitumen causes serious corrosion problems in the downstream upgrading units due to the chlorides dissolved in water. By using an aliphatic diluent in recovering the bitumen, the amount of water in the settler product could be reduced from 3 to 0.3% by weight with a corresponding reduction in chlorides [1]. Hence, the amount of water carrying through to upgrading process could be reduced by a factor of 10. Unfortunately, the hydrocarbon recovery in the settler also dropped from 98 to 84%. It has been found that the non-polar solvent causes the dispersed water droplets to flocculate, partially coalesce, and settle out of the oil phase as a concentrated secondary emulsion between oil and water phases. Such secondary emulsions, which are generally produced after a demulsification process, are common in the crude oil dewatering and in hydrometallurgical industries. Hence, it is critical to determine in each case the presence and nature of the emulsions to find both the economic and technical success of the industrial process concerned.

Crude oils consist of at least a mixture of hydrocarbons (alkanes, alkenes, naphthenes, and aromatic compounds), as well as phenols, carboxylic acids, and metals. A significant fraction of sulfur and nitrogen compounds may be present as well. The carbon numbers of all these components range from 1 (methane) through 50 or more (asphaltenes). Some of these compounds can form films at the oil surfaces, and others are surface active. The tendency to form stable or unstable emulsions of different kinds is then not surprising.

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Emulsions may contain not just oil and water but also solid particles and even gas.

All of the petroleum emulsion applications or problems have in common the same principles that govern the nature, stability, and properties of colloidal emulsions. We have recently focused our research on the interactions between twin-tailed surfactants and petroleum emulsions [2].

At present, the effect of hydrophobic tails branching is not yet fully understood, despite the fact that many of the surfactants used in industrial applications are prepared with branched hydrocarbon tails. The effect of branching on the surface was investigated by self-consistent field calculations [3] and molecular-dynamic simulations on model surfactants [4, 5]. These studies agree on the fact that surfactants with two hydrophobic tails are less efficient in reducing the interfacial tension compared with their single-tail isomers. Experimentally, however, more, equal, or less efficient branched surfactants are reported [3–8]. Although it is assumed that branched molecules pack differently at the interface compared with linear ones [9, 10], a molecular description of their properties applied to emulsion knowledge is, to the best of our knowledge, still missing.

For this purpose, in this work, we have chosen an industrial petroleum emulsion and four double-chained surfactants: sodium bis-2-(ethylhexyl) sulfosuccinate (AOT), didodecyltrimethylammonium bromide (DDAB), calcium oleate ($\text{Ca}(\text{OL})_2$), and dioctadecyldimethylammonium bromide (DODAB), with the aim to understanding the mechanism responsible for the formulation or destruction of such emulsions and improve their treatment by such surfactant.

Experimental section

Materials

Emulsion The crude emulsion (water droplet of 2.5 to 5 μm in diameter) was kindly supplied by Petrobras, Argentina refinery at Bahía Blanca, and it was an undesirable result of the crude (35° API, American petroleum institute denomination for the sulfurs and solids present, $\delta_{\text{oil}}=0.8734 \text{ g cm}^{-1}$) manufacturing.

Surfactants Sodium bis-2-(ethylhexyl) sulfosuccinate (AOT), didodecyltrimethylammonium bromide (DDAB), and dioctadecyldimethylammonium bromide (DODAB) were from Sigma and were of analytical grade (99%).

Calcium oleate [$\text{Ca}(\text{OL})_2$] was prepared by mixing the appropriate amounts of sodium oleate (Sigma, 99%) and calcium chloride water solutions. The resulting precipitate was washed several times to eliminate NaCl excess and dried under vacuum until constant weight.

Experimental

Centrifuge Test Emulsion characterization was made using a modification of the centrifuge test [11–14] in which sedimentation force is artificially increased to effect separation. The rate of separation can be enhanced by replacing the gravitational driving force by a centrifugal field. Centrifugal force, like gravity, is proportional to the mass, but the proportionality constant is not “g” but ω^2x , where ω is the angular velocity (equal to $2\pi \times$ revolutions per second) and x is the distance of the particle from the axis of rotation. Therefore, the driving force for sedimentation becomes $(\delta_2 - \delta_1) \omega^2x$, where δ_2 and δ_1 are the droplet and the external fluid densities, respectively. Basically, the test consist in diluting the emulsion with a known amount of solvent (Toluene, Sintorgan 99%) and centrifuging (an ALC Centrifuge PK 120 was used) for fixed time (20 min) and centrifuge speed (6,000 rpm).

For the second part of the work a fixed emulsion quantity (30 ml) was mixed with 10 ml of (0.005–0.05) mol dm^{-3} surfactant aqueous solution. Different forms of surfactant addition were essayed. The solid incorporation and the dispersion in water phase of all tested surfactants were evaluated. The surfactant effect was similar in both experiments. Therefore, we decided to incorporate them to the emulsion in the simple manner for each case, trying to simplify the emulsion treatment thinking in the possible industrial application of this investigation. In the case of $\text{Ca}(\text{OL})_2$ and DODAB, which are water insoluble, surfactant (solid) and water (10 ml) were added to the emulsion separately. The mixture was sonicated in a laboratory ultrasound generator (MADA n° 6000) during 5 min and left to equilibrate at room temperature for approximately 24 h before experimental measurements. The samples were centrifuged during 10 min varying the accelerator at 6,000 rpm to evaluate the surfactant effect on the emulsion system.

FT-IR spectroscopy and optical microscopy The emulsion separated phases were collected with a syringe and analyzed with an Infrared Spectrophotometer (Nicolet FT-IR, Model Nexus 470) and by an Optical Microscope (Ernst-Leitz Wetzlar). Before recording the IR spectra, the oil sample was recorded using a capillary film; the gel like phase sample was dried under vacuum to eliminate the remaining water and diluted with KBr. All determinations were made at 25 ± 0.1 °C.

Conductivity measurements Conductivity of emulsion treated with AOT and DDAB was measured as a function of temperature or surfactant concentration with a CRIBABB-Selected CON-04 conductivimeter, an ORION conduc-

tivimeter cell and a CRIBABB-Selected CT-16 probe. Conductivity cell was calibrated with KCl solution as usual. The test tube with the sample (prepared as mentioned above) was placed in an Edmund Bühler thermostated bath with a CRIBABB-Selected CT-47 heating head ($T \pm 0.02$ °C). The sample was equilibrated for at least 10 min after any each temperature change and before measuring the conductivity.

To determine the conductivity variation vs surfactant/oil ratio 30 ml of the emulsion was titrated with a concentrated (0.05 mol dm^{-3}) surfactant solution.

Gravimetical analysis The aqueous phase obtained by emulsion destabilization was studied by weighing an aliquot. Then, the aliquot was dried to constant weight. The residue (composed by surfactant and silica) was calcinated to determine the silica content and, by difference, that of surfactant content. Corrections were made by the ash produced by surfactant calcinations.

Result and discussion

The emulsion analysis

Emulsion characterization often involves three phases: the water phase, the oil phase, and the stabilizing agent. The centrifugation in the presence of toluene separated the emulsion in two phases: water, oil, and a third layer between the oil and the water phases. The two phases and the third intermediate layer were analyzed by IR-spectroscopy and optical microscopy.

Optical microscopy revealed that, after separation, both oil and water phases did not present droplets or particles in

suspension. The intermediate layer was formed by a complex gel-like structure composed of oil and water mutually dispersed and other components. The water region showed dispersed particles, while the oil regions had water droplets containing dispersed particles, as it can be seen in Fig. 1.

This “third layer” is what is called in petroleum emulsion chemistry as “rag layer.” Rag layer is a mixture of oil, water, salts, and solids in emulsion, which is located between the oil and water phases [15].

Figures 2 and 3 show the oil phase and the gel-like layer IR spectra. Only paraffinic hydrocarbons were present in both phases ($-\text{CH}_3$; $-\text{CH}_2-$ stretching vibrations at $3,000$ – $2,850 \text{ cm}^{-1}$ and $-\text{CH}_3$; $-\text{CH}_2-$ bending vibrations at $1,480$ – $1,350 \text{ cm}^{-1}$). As there were not peaks appertaining to aromatic hydrocarbons or others organic compounds, it was concluded that no asphaltenes, resinous substances, oil-soluble organic acids (such as naphtenic acid), sulfates, sulfides, or chemical additives were present. Consequently, we discarded the presence of these chemical substances (which are commonly found in petroleum emulsions) as emulsifier agents. Nevertheless, three bands at $1,110$, $1,000$, and 920 cm^{-1} , corresponding to Si–O stretching vibrations [16], appeared in the gel like phase spectrum. It follows that the emulsion stabilization was due to silica particles.

The presence of asphaltenes was investigated by addition of heptane to the emulsion. Asphaltenes are insoluble in heptane [17–19]. This test was performed, and no one precipitate was obtained. This fact confirmed that asphaltenes were not present, so it follows that the emulsion stabilization was due to silica particles.

Solid-stabilized emulsions are often encountered during the bitumen extraction from oily sands, crude-oil dewatering, separation fines from shale oil, and separation of oil from wastewater. In some extent, the stability of an emulsion depends on the partitioning and positioning of the particles at

Fig. 1 Optical micrographs of the intermediate layer (formed by a complex gel-like structure composed of oil and water mutually dispersed and other components). **a** Water region; **b** oil region with water cavities and eventually particles dispersed in such water

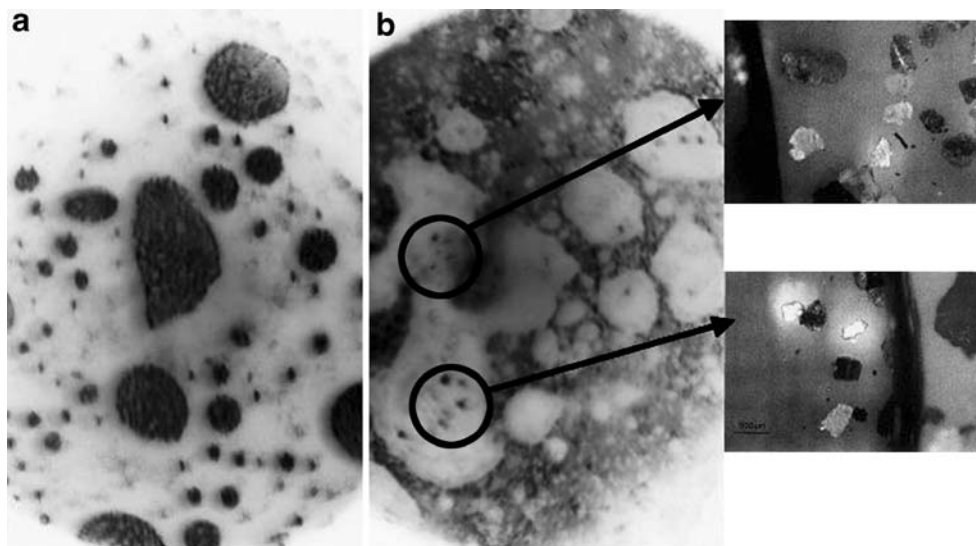
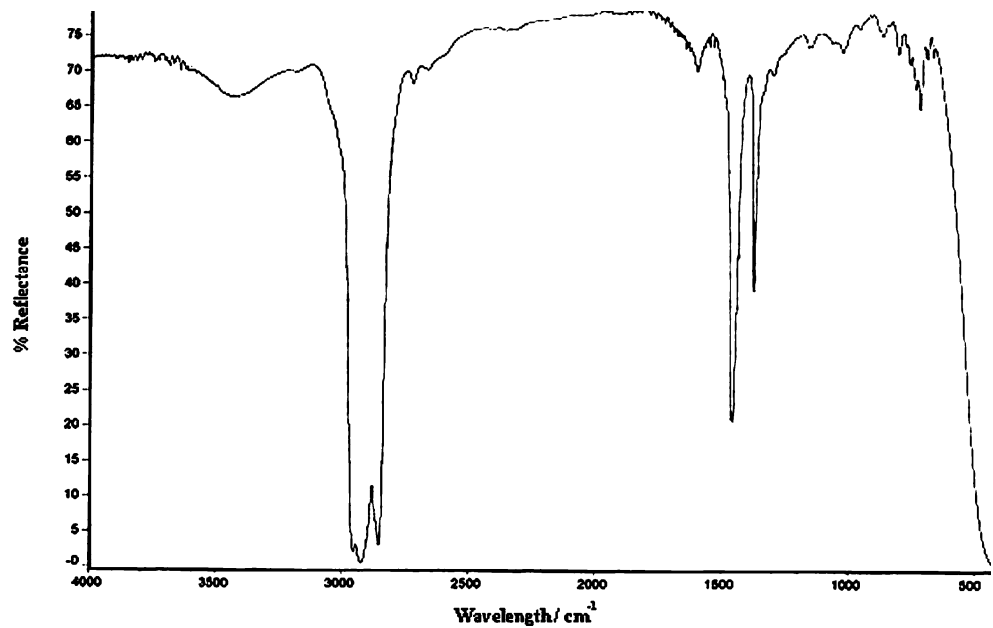


Fig. 2 Oil phase IR spectrum. Only paraffinic hydrocarbons peaks are presents

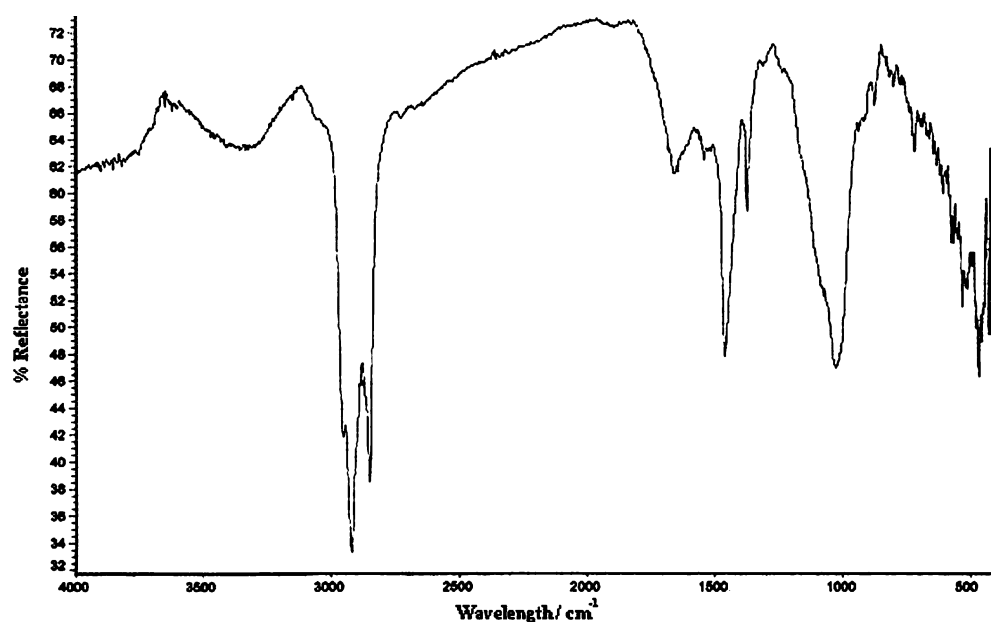


the oil–water interface [20], which are in turn related to the particles hydrophobicity. If particles are very hydrophilic, a large fraction of their volume resides in the water phase, and they cannot provide an effective mechanical barrier to prevent the coalescence of water droplets. On the other hand, if the particles are very hydrophobic, the majority of them will be immersed in the oil phase and cannot protect the water droplets against coalescence. Particles having some intermediate hydrophobicity locate at the oil–water droplet interface providing an adequate protection against coalescence and resulting in a stable without emulsion [20] as in the industrial emulsion sample here studied. Thus, changing the lyophilicity of the solid particles can alter stability of the emulsion.

The stability analysis

Centrifugation was used to investigated emulsion stability and the effect on it by the four tested twin-tailed surfactants. An emulsion sample (30 ml) plus 10 ml of added water was centrifuged during 10 min at 6,000 rpm producing 2-ml water separation. Then, the samples of emulsion with different concentration of added surfactant were centrifuged at the same conditions; the obtained results were summarized in Fig. 4, which shows the separated water volume/total emulsion volume ratio variation vs surfactant concentration [S]. It can be seen that both AOT and DDAB molecules caused the emulsion breakdown. In contrast $\text{Ca}(\text{OL})_2$ did not

Fig. 3 Emulsion gel like layer (separated during centrifuge test) IR spectrum



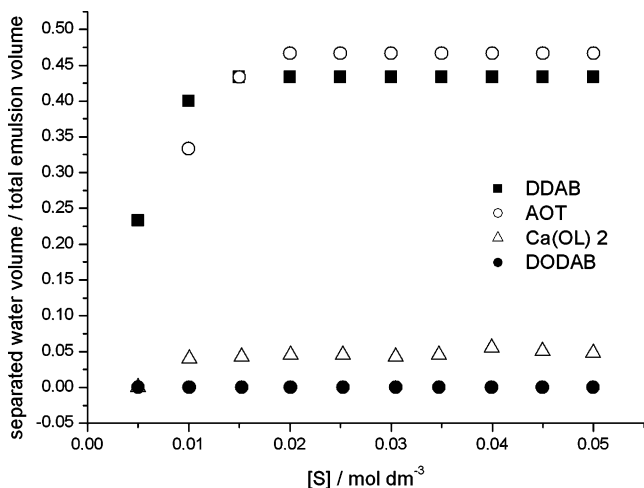


Fig. 4 Separated water volume/total emulsion volume ratio variation vs surfactant concentration, [S]

affect the original emulsion stability, i.e., water separation was approximately the same as in the emulsion without surfactant addition (5%). DODAB increased the emulsion stability (not phase separation was observed).

The emulsion separation (only in the case of AOT and DDAB) increased with surfactant concentration until a plateau was reached at $[S] \approx 0.02 \text{ mol dm}^{-3}$; further [S] increase did not augment the water separation. At this point, the separated AOT and DDAB was about 46 and 44%, respectively.

The separated oil and water phases were analyzed by Fourier transform infrared (FT-IR) and optical microscopy. The oil phase did not show water droplets, silica particles, or surfactant residues. Furthermore, the water phase gravimetric analysis showed that all added surfactant and silica particles remained in water after emulsion rupture.

Figure 5 shows the emulsion conductivity for emulsions treated with AOT and DDAB, measured at different temperatures, as a function of surfactant/oil ratio (X). The emulsion conductivity of the emulsion treated with AOT exhibited a characteristic sigmoidal behavior as the AOT concentration was increased (Fig. 5a). This effect would be attributed to enhanced inter-droplet interaction [21–24] due to the elimination of the silica particle steric barrier and to an interfacial increased fluidity because of the surfactant presence.

In the light of the concept of droplet association, the thermodynamic parameters of droplet clustering were calculated from standard equations [25, 26].

$$\Delta G_{\text{cl}}^0 = RT \ln X_p \quad (1)$$

where R is the gas constant, T is the absolute temperature, and X_p is the surfactant/oil ratio at the beginning of droplet association at temperature T . Another way of arriving at Eq. 1 is to assume equilibrium between individual droplets and droplet clusters [27]. Application of Gibbs–Helmholtz

equation allows the standard enthalpy of cluster formation, ΔH_{cl}^0 , to be expressed as:

$$\Delta H_{\text{cl}}^0 = -RT \left[\frac{\partial \ln(X_p)}{\partial T} \right] = R \left[\frac{\partial \ln(X_p)}{\partial (1/T)} \right] \quad (2)$$

Finally, the standard entropy of cluster formation per mole of droplets, ΔS_{cl}^0 , can be obtained from:

$$\Delta S_{\text{cl}}^0 = (\Delta H_{\text{cl}}^0 - \Delta G_{\text{cl}}^0) / T \quad (3)$$

It was been shown for surfactant micellization and block copolymers [27] that, within experimental error:

$$\frac{\partial \ln(X_p)}{\partial (1/T)} = \frac{\partial \ln(X)}{\partial (1/T_p)} \quad (4)$$

Equation (3) thus becomes.

$$\Delta H_{\text{cl}}^0 = R \left[\frac{\partial \ln(X)}{\partial (1/T_p)} \right] \quad (5)$$

Figure 6 shows the temperature effect on emulsion conductivity for a fixed AOT concentration. An increase in temperature would favor the surfactant ionization and the

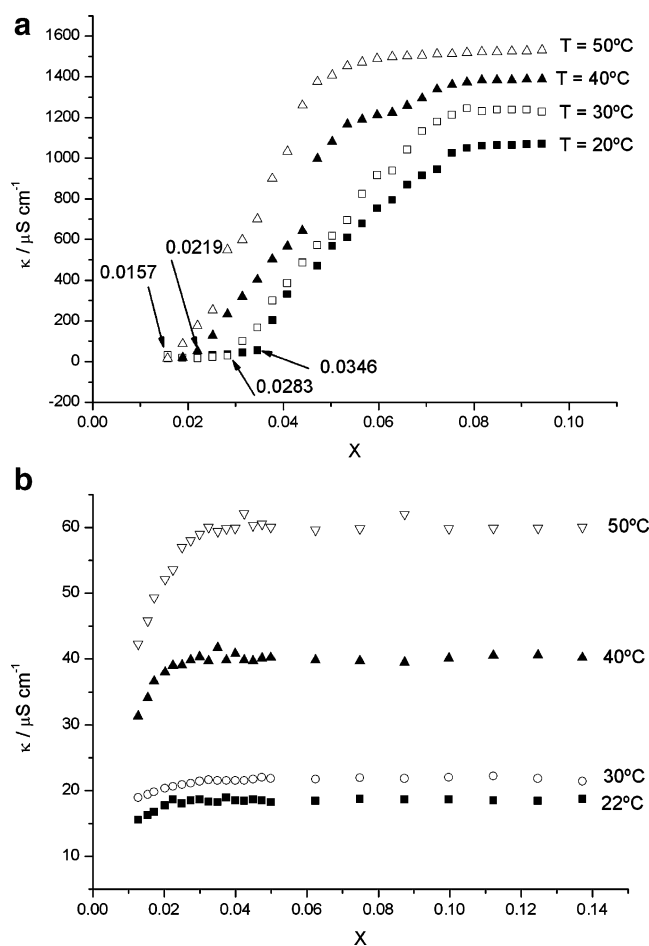


Fig. 5 Emulsion conductivity, measured at different temperatures, as a function of surfactant/oil ratio (X). Emulsion treated with **a** AOT (the numbers represent the surfactant/oil ratio at which percolation begins) and **b** DDAB

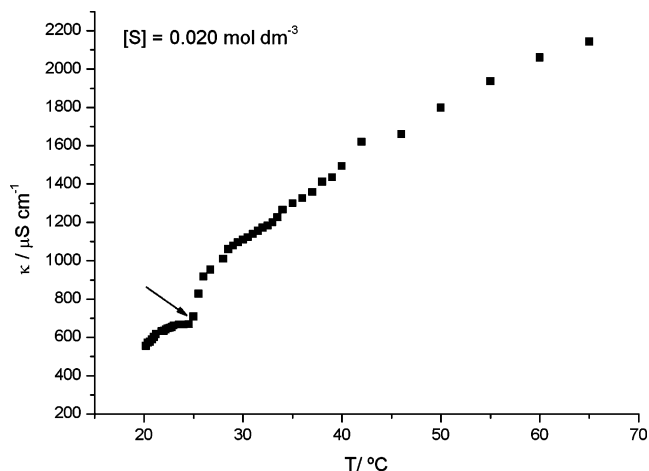


Fig. 6 Emulsion conductivity, for a fixed AOT concentration-emulsion system, as a function of temperature. Arrows indicate the percolation temperature

range of ion diffusion (charge-hopping percolation). The temperature at the beginning of droplet association, T_p (signed as an arrow in Fig. 6), is defined as the point at which a dramatic change in slope (break) in the conductivity vs temperature curve occurs. The thermodynamic obtained parameters are summarized in Table 1. The free energy, ΔG_{cl}^0 , is negative, as the droplet clusters were formed spontaneously. ΔH_{cl}^0 is positive indicating that the transfer of droplets from solution to the percolating cluster is an enthalpically disfavored process. It was therefore clear that the driving force for clustering during conductivity percolation is the positive entropy.

The surfactant adsorption at the oil–water droplet interface is described by (Figure 7):

$$\mu_s^{des} = \mu_s^{ads} \tag{6}$$

where s is the adsorbed surfactant. Considering the chemical potential dependence with temperature and the fact that droplet clusters associations is a phase transition [28], Eicke et.al. [29] deduced the following equation:

$$\frac{\partial T}{\partial x_s} = \frac{RT_p^2}{x_s \Delta H_s^{ads}} \tag{7}$$

where $\partial T / \partial x_s$ is the slope of the T_p vs x_s plot, R is the gas constant, x_s is the surfactant concentration and ΔH_s^{ads} is the surfactant adsorption enthalpy at the oil–water drop interface. The obtained negative ΔH_s^{ads} values (see Fig. 8) indi-

Table 1 Clustering thermodynamic parameters

T_p (K)	ΔS_{cl}^0 (kJ/mol)	ΔH_{cl}^0 (kJ/mol)	ΔG_{cl}^0 (kJ/mol)
293	0.449	123.57	-8.19
303	0.437	123.57	-8.98
313	0.426	123.57	-9.94
323	0.417	123.57	-11.15

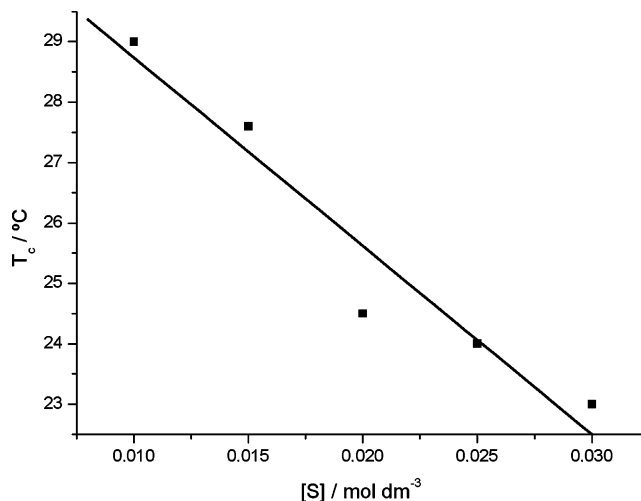


Fig. 7 T_p vs. surfactant concentration (X) for AOT treated water in oil emulsion

cated that the AOT molecules are spontaneously adsorbed at the droplet interface. ΔH_s^{ads} is augmented with surfactants concentration; this fact would be probably due to the surfactant molecules solubilization in oil phase with raising temperature. Similar results were obtained by Eicke et al. [30].

No evidences of droplet association induced by surfactant concentration or temperature were shown by the emulsion treated with DDAB (Figs. 5b and 9). The low emulsion conductivity values indicated that the oil remained as the emulsion continuous phase. A weak conductivity increment was shown with the increase of T , probably due to the increase of droplet collisions and solubilizate exchange.

Similar results were obtained in the conductivity studies done over the emulsion treated with $Ca(OL)_2$ and DODAB.

In the light of the obtained results, it is possible to say that studied surfactants affect the emulsion in a diverse manner: both AOT and DDAB broke the emulsion under

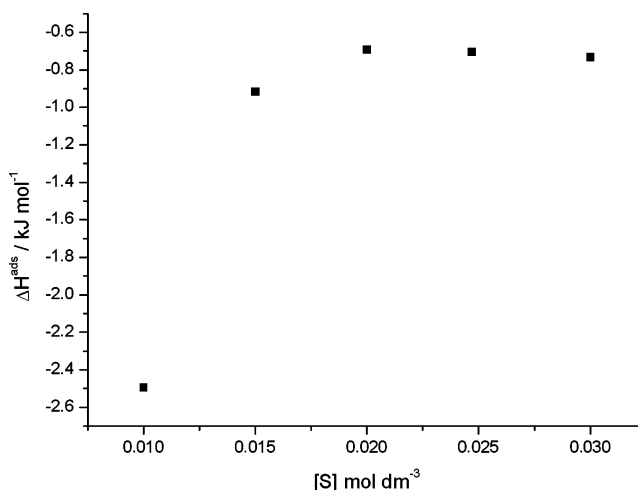


Fig. 8 AOT adsorption enthalpy (ΔH_s^{ads}) dependence on surfactant concentrations

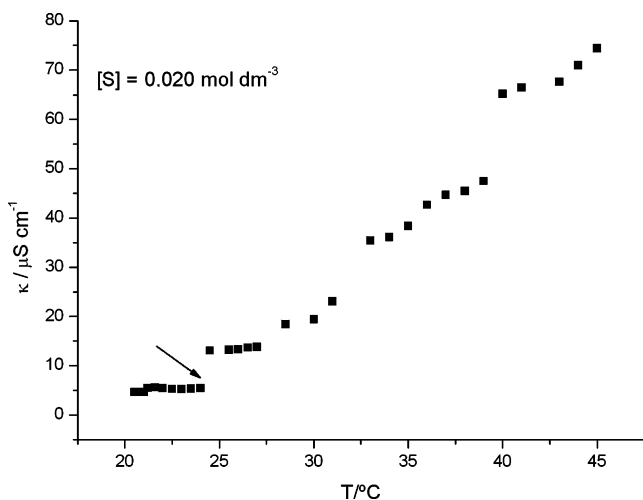


Fig. 9 Emulsion conductivity, for a fixed DDAB concentration-emulsion system, as a function of temperature. Arrows indicate a slight conductivity increment caused by droplet collisions

centrifugation, but only AOT induced inter-droplet interaction, indicating that different emulsion breakdown mechanisms are involved.

As previously said, the studied emulsion was stabilized by silica particles of intermediate hydrophobicity [31, 32].

In a solid-stabilized emulsion, one of the liquids wets the solid better than the other phase, the less wetting liquid becomes the disperse phase. The importance of the wettability of the particles at the oil–water interface can be quantified by the contact angle (θ). If θ (measured through the water phase) is slightly less than 90° , the particles will be held at the interface and tend to stabilize without emulsions. For conditions such that θ is slightly greater than 90° , the particles will still be held at the interface but will now stabilize without emulsion (as in our case). However, if the particles are either too hydrophilic (low θ) or too hydrophobic (high θ), they will tend to remain dispersed in either the aqueous or oil phase, respectively, giving rise to unstable emulsions [33]. Particles wettability may be altered by adsorption of suitable surfactants [34, 38].

We expected that twin-tailed surfactants would move through the oil phase (continuous phase) and would act at the oil–water interface removing the solid particles and favoring the inter-droplet interactions leading to the emulsion break.

Apparently, this was not the mechanism followed for the studied surfactant molecules because it appears that not all tested double-chained amphiphiles reached the drop interface even when all are oil soluble. Differences should be due to the dissimilarities that exist between the surfactant structures. It seems that the surfactant molecule possibilities to reach the droplet interface are related with more or less hydrophobicity. Rekvig et al. [39] used dissipative particle dynamic (DPD) simulations [40] to study the effect of branching on the interfacial properties of twin-tailed

surfactants. They found that if it was used with surfactants with sufficient hydrophilic head group, double-tail amphiphiles are more efficient than single-tail ones for a given interfacial concentration. The same investigations showed that they are less efficient for a given bulk solution. The reason is as follows: at a given interfacial concentration, the effective repulsion between the tails is higher compared to their single-tail isomer. Therefore, for double-tail surfactants, there are two opposite effects; the more efficient the surfactants are at the interface, the higher bulk concentration required to get them to the interface.

AOT, which is the more (comparing the four tested amphiphiles) hydrophilic surfactant (a combination of a big hydrophobic head group and a short branched hydrocarbon tail), would migrate to the droplet interface rapidly and cause the emulsion break spontaneously (bound to the hydrophobic parts of silica by hydrophobic bonds between their tails and making particles more hydrophilic); DDAB (less hydrophilic) needs an extra energy to crack the emulsion, so this surfactant can only provoke the emulsion rupture with centrifugation. $\text{Ca}(\text{OL})_2$ is water insoluble and dissolves in oil phase remaining there. Finally, DODAB is also insoluble but seemed to increase emulsion stability.

The two water soluble surfactants (AOT and DDAB) migrate to the original emulsion droplets and interact with silica particles at the oil–water interface, thus changing their lyophilicity. Silica particles have negative charges, so the interaction with AOT (negative) molecules is different from that with DDAB (positive) molecules. The adsorption of AOT molecules on the hydrophobic portions of silica particles by their hydrocarbon chains would increase the hydrophilicity of these particles. Then, increasing portions of the silica particles are immersed in the aqueous phase, and the interface cohesion and resistance are reduced causing destabilization of the emulsion. When emulsion breakdown occurs, both silica and surfactant remain in the aqueous phase.

As DDAB is also hydrophilic, it interacts with the emulsion water droplets in the same manner as AOT does, but because the surface active ion DDA^+ is positive, it can interact with the silica particles in two different ways: it may adsorb onto the hydrophobic regions of silica by its tails similar to AOT, giving a hydrophilic region, or it may adsorb by its cationic group facing a negative region of silica, then changing the hydrophilic character of this region to hydrophobic one. This changes the hydrophilic/hydrophobic ratio of the silica particles and alters emulsion stability. It also must be noticed that the adsorption packing of DDAB molecules at silica surface would be much more compact than that of AOT because DDAB chains are linear and those of AOT branched. The difference in interaction mechanism can explain the different emulsion destabilization behavior.

Because $\text{Ca}(\text{OL})_2$ is water insoluble, this amphiphile dissolves in oil phase and remains there. The almost unionized $(\text{COO})_2\text{Ca}$ headgroup and the two double bonds at the middle of the oleate chains are too weak hydrophiles to cause a strong adsorption at the oil–water interface and probably are displaced by silica particles. Moreover, adsorption of this molecule at the oil–water interface must satisfy the hydrophilicity of the mentioned groups, causing a conformation with the central $(\text{COO})_2\text{Ca}$ group and the two lateral $-\text{CH}=\text{CH}-$ groups in contact with water and the remaining hydrophobic tails forming loops in the oil interior, a conformation which cannot produce a stable interface. As a consequence, $\text{Ca}(\text{OL})_2$ probably forms small inverse micelles, which do not affect the stability of the original emulsion.

DODAB is almost water insoluble, but it has a strong hydrophilic group attached to two linear saturated hydrocarbon tails. It probably migrates to the interface and forms stable, elastic, and cohesive layers at the oil–water interface, which stabilized the emulsion better than silica does.

Conclusion

In this work, the effect of four twin-tailed surfactant, AOT, DDAB, $\text{Ca}(\text{OL})_2$, and DODAB over a real petroleum industrial emulsion was investigated.

In the light of the obtained results, it would be possible to say that the tested surfactants acted to the emulsion in a different way. Those different behaviors are explained on the basis of dissimilarities in the surfactants structure, solubility, and lyophilicity.

AOT with a combination of a big hydrophobic head group and a short branched hydrocarbon tails would migrate to the droplet interface rapidly and bound to the hydrophobic parts of silica particles by hydrophobic bonds between their tails, making them more hydrophilic and causing emulsion break. The positive ion DDA^+ , on the contrary, can interact with silica in two different ways: it may adsorb onto the hydrophobic regions of silica by its tails similarly to AOT, or it may adsorb by its cationic group. The packing of DDAB molecules at the droplet interface would be much more compact than AOT because DDAB chains are linear and those of AOT branched.

$\text{Ca}(\text{OL})_2$ with the almost unionized $-(\text{COO}^-)_2\text{Ca}$ headgroup and the two double bonds at the middle of the oleate chains, too weak to cause a strong adsorption at the oil–water interface, probably forms small inverse micelles, which do not affect the emulsion stability. Finally DODAB, which possesses a strong hydrophilic group attached to two linear saturated hydrocarbon tails, probably forms stable, elastic, and cohesive layers at the oil–water interface, which stabilized the emulsion better than silica does.

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