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Interfacial Tension between Low Salinity Solutions of Sulfonate Surfactants and Crude and Model Oils

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ABSTRACT: Interfacial tensions (IFT) between low salinity surfactant solutions of sodium dodecylbenzenesulfonate (SDBS) and sodium dioctylsulfosuccinate (Aerosol OT or AOT) and different oil phases were measured using the spinning drop method. The oil phases were either n-heptane, a 1:1 mixture of n-heptane and toluene or crude oils. The IFT was strongly affected by variation of the salinity and especially by the presence of calcium. IFT values between SDBS solutions and heptane, as well as all four crude oils, decreased when adding sodium and calcium. IFTs down to 32 μN/m for crude oil were measured in the presence of AOT solutions with low salinity electrolyte. In the IFT region below 1 mN/m the presence of small amounts of calcium could lower the IFT by more than 1 order of magnitude compared to solutions containing only sodium chloride with the same ion strength.

■ INTRODUCTION

Surfactant and polymer injection are two enhanced oil recovery (EOR) methods that have successfully been applied on oil fields over the world for several decades.[1] Surfactants are capable of lowering the oil/water interfacial tension (IFT) and emulsifying oil in water.[2] Increased viscosity (η) gained by polymer injection, together with a low oil/water IFT (γ) can, at a given effective flow rate (ν), increase the capillary number (eq 1) in a reservoir. This is usually correlated with an increase of the total oil recovery.[3]

$$N_C = \frac{\nu\eta}{\gamma} \tag{1}$$

A further objective of surfactant injection in EOR is formation of oil in water (o/w) microemulsions, thermodynamically stable solutions of swollen micelles, for transporting mobilized oil within the reservoir. The connection between IFT and microemulsion formation has been described by eq 2,

$$\gamma = k\left(\frac{V_{surf}}{V_{diss}}\right)^2 \tag{2}$$

where V_{surf} and V_{diss} are the volumes of surfactant and either water or oil, respectively, dissolved in the microemulsion and k is a surfactant specific constant.[4]

IFT values close to 1 μN/m or lower, referred to as "ultralow IFT", are desired in EOR research as they often are linked to bicontinuous microemulsions.[5] The IFT of surfactant/brine/oil systems depends on the solubilization ratio of the surfactant between both phases and reaches minimum levels when the solubilization ratio approaches 1.[6,7]

While their amphiphilic nature enables surfactants to get dissolved in both aqueous and many nonaqueous phases, their structure determines which phase they prefer. The affinity of the surfactant monomers to the different phases is described by the hydrophilic–lipophilic balance (HLB). A value relating the structure of a surfactant, that is, volume (V_t) and length (l_t) of the hydrocarbon tail and its headgroup area (a_h), to the shape of its aggregates and to their preferred phase is known as the critical packing parameter (CPP, eq 3).[8]

$$CPP = \frac{V_t}{a_h l_t} \tag{3}$$

CPP values far below or above 1 describe a preference to form spherical or rod-like aggregates in the water or in the oil phase, respectively.

When the CPP is close to 1, that is, the tail forms a cylinder and allows a tight packing of surfactant molecules at the oil–water interface, the IFT reaches minimum values. The effective headgroup area of an ionic surfactant normally decreases drastically at addition of electrolyte as its charge is shielded, leading to a higher CPP.[9] Salt concentrations that minimize the IFT and lead to formation of microemulsions with equal amounts of dissolved oil and water are often referred to as the "optimal salinity" of a surfactant. While the optimal salinity for a surfactant system often is given by a certain amount of dissolved sodium chloride, bivalent metal ions have a special effect on the phase behavior. It has been observed that exchanging even small amounts of the sodium with calcium lowers the optimal salinity in surfactant solutions disproportionate to both ionic strength and molarity of the electrolyte.[1] Because the degree of protonation of the surfactant headgroup also alters its effective area (low pH, high CPP), IFT and phase behavior are strongly dependent on the solutions pH.[10]

In recent years, several groups have studied the effect of low salinity water injection, normally performed after the secondary seawater flood, on total oil recovery.[11] In core flood experiments a lowering of the electrolyte concentration inside the formation generally increased the oil recovery while the wettability of the rock was altered from oil wet or mixed wet to more water wet.[12] Oil desorption, observed during flooding

with pure sodium brine or soft water, has been proposed to be caused by Multicomponent Ion Exchange (MIE). Here, negatively charged crude oil components like naphthenic acid and fatty acid anions are released from their complexes with multivalent ions on the rock surface, therewith destabilizing the adsorbed oil layer.[11] A low salinity EOR mechanism suggested by *Austad* (2010), in which acid/base reactions at the surface of the reservoir rock cause desorption of polar oil components, takes both acidic and basic compounds into consideration. It is believed that at low salinity water injection multivalent cations such as calcium are desorbed from the rock surface and replaced by protons from the water. The resulting local pH increase causes dissociation of adsorbed acids and protonated nitrogen compounds, which leads to their desorption from the surface.[13] According to studies on acidic and basic crude oils by Farooq (2011), both acidic and basic oil components have an affinity to silica surfaces and show desorption from these under injection of low salinity water.[14] Farooq also observed a strong desorption of adsorbed asphaltene layers from silica surfaces at injection of diluted brines and seawater, which in general was most pronounced in the absence of calcium ions. An explanation was the expansion of the electrical double layer at the rock surface, which in the presence of calcium was counteracted by complex formation with polar groups of the asphaltene.[15]

Alagic and Skauge (2010, 2011) studied the combination of low salinity water and surfactant flooding and observed a pronounced improvement of the absolute oil recovery. While the low salinity water improves oil desorption, the surfactant forms o/w microemulsions for transporting the oil. By keeping the salinity far below the optimal salinity of the surfactant, phase transitions from o/w to w/o emulsions, related with loss of surfactant and changes in the systems viscosity, can be avoided.[16,17] Simultaneously the loss of surfactant by adsorption at the rock surface is lowered as its CPP stays low at low salinity.[9]

The main focus of this work was to see whether, and under what conditions, ultralow IFTs could be reached between oil and aqueous surfactant solutions at low salinity and without addition of cosurfactants. Interfacial tensions between crude oils or hydrocarbons and low salinity solutions of two anionic surfactants, were measured with a spinning drop tensiometer. Results were discussed in context of surfactant and ion type, pH, and composition of the oil phase.

■ MATERIALS AND EXPERIMENTAL METHODS

Surfactant Solutions. Two commercial surfactants, SDBS (techn., Sigma Aldrich) and AOT (96%, VWR International AS), were used as received. The structures of the surfactants are shown in Figure 1. The critical micellar concentrations (CMC) were determined by surface tension measurements with the DuNoüy ring method, using a Sigma 70 Tensiometer (KSV Instruments Ltd., Finland). The measured CMC were 1.69 mmol/L for SDBS and 2.55 mmol/L for Aerosol OT and were in agreement with literature values.[18−21] The surfactant

Figure 1. Chemical structures of SDBS (upper) and AOT (lower).

concentrations in the sample solutions used for spinning drop measurements were 1.25 mmol/L for SDBS and 2.47 mmol/L for AOT. Stock solutions of double these concentrations were prepared in deionized water (mQ-water).

Brines. Two brines, one containing 40 mmol/L sodium chloride (p.a., Merck KGaA, Darmstadt, Germany) only and the other containing 37.55 mmol/L sodium chloride and 0.82 mmol/L calcium chloride (calcium chloride dihydrate, p.a., Sigma-Aldrich) in the molar ratio 45:1, were prepared. Both brines had an ionic strength of 40 mmol/L.

Sample Solutions. The surfactant solutions and brines described were mixed to give the low salinity (LS) water phases for the IFT measurements. The ionic strength of these were 20 mmol/L. Additional salt free (SF) solutions were prepared by mixing the surfactant stock solution with an equivalent volume of mQ water. The nomenclature of the sample solutions is described in Table 1. The densities of all solutions used for the IFT measurements were measured with a DMA-5000 density meter (Anton Paar GmbH).

Table 1. Composition of Sample Solutions

name	composition	ion strength
surfactant/SF	surfactant + no electrolyte	0
surfactant/LS	surfactant + 20 mM NaCl	20 mM
surfactant/LS-Ca	surfactant + 18.78 mM NaCl + 0.41 mM CaCl₂	20 mM

Model Oils. The solvent *n*-heptane (p.a., Merck KGaA, Darmstadt, Germany) was used as purchased or mixed (v:v/1:1) with toluene (99.5%, VWR International AS) to give the model oil referred to as *mix* (42 mol % heptane, 58 mol % toluene), respectively.

Crude oils. The crude oils used in these experiments stem from offshore and onshore fields in the *North Sea* and Germany, respectively. The densities of the oils were measured in temperature scans from 15 to 60 °C with a DMA-5000 density meter. The viscosity of each oil was measured in temperature scans between (20 and 80) °C and at a shear rate around 10 s⁻¹ with a Physica MCR301 rheometer (Anton Paar GmbH). Acid and base content were measured by potentiometric titrations with an 809 Titrando (Metrohm, U.S.A.) as described by Farooq (2010).[22] The bulk composition of the oil was investigated by SARA (saturates/aromatics/resins/asphaltenes) fractionation as described by Hannisdal (2005).[23]

Spinning Drop Measurements. All IFT values between water and oil/hydrocarbon were measured with a Spinning Drop Video Tensiometer, SVT20 (DataPhysics Instruments GmbH, Germany). A Fast Exchange Capillary (FEC 622/400-HT) was filled with the aqueous solution by a syringe and thereafter closed with a screw lid with PTFE septum. The capillary was inserted into the tensiometer and a small amount of the oil or model oil, ideally a single drop, was injected into the center of the capillary with a syringe. Rotation of the capillary was started and increased to gain a free and elliptical or cylindrical bubble. The SVTS 20 IFT software was used to fit the profile of the bubble and to calculate the IFT according to the method of Cayias, Schechter, and Wade (CSW). As the o/w IFT is known to be strongly dependent on the equilibration and measurement time, the experiments were usually run for between 2 and 5 h. The IFT values used in this work are arithmetic mean values from regions at which the IFT appeared stable for between 30 min and 1 h. The deviation of the single measurement points normally lay between 0,1 and 2%. Prior to the measurements, equal volumes of oil and sample solution were shaken and allowed to equilibrate for about 72 h at the measurement temperature of 60 °C. Oil and water phases were separated by centrifugation and the densities of the pre-equilibrated brines at 60 °C were measured and used for calculating the IFT. Measurement times between 10 and 48 h were normal for achieving equilibrium values.
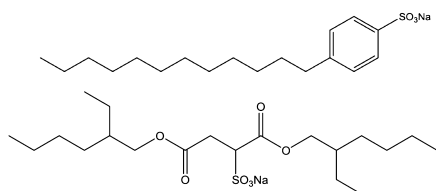
■ RESULTS AND DISCUSSION

Effect of Salinity and pH on the IFT between Surfactant Solutions and Model Oil. As seen in Figure 2,
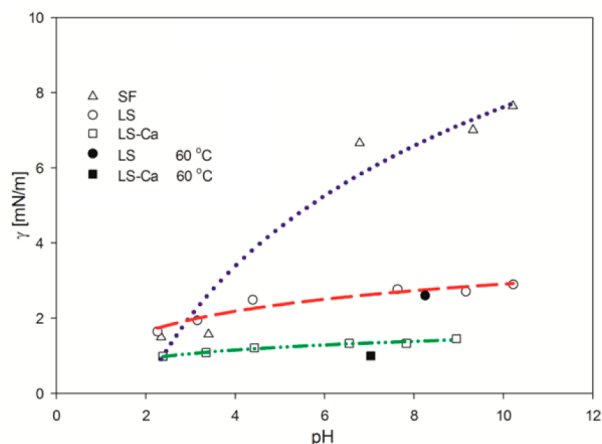

Figure 2. IFT values between *n*-heptane and SDBS solutions with different salinities (SF/I = 0; LS/NaCl, I = 20 mmol/L; LS-Ca/NaCl/CaCl$_2$, 45:1, I = 20 mmol/L) and different pH measured at 25 °C (hollow items) and 60 °C (filled items).

all SDBS solutions showed an increase of their IFTs to heptane when the pH was increased from 2 to 10. The IFT/pH-slope and also the absolute IFT values were strongly dependent on the salinity. The lowest IFT and the weakest increase with pH were observed for SDBS/LS-Ca with an overall increase of 0.5 mN/m. The IFT between heptane and SDBS/LS solution were slightly higher than those for LS-Ca and showed an increase of about 1.5 mN/m between pH 2 and 10. The by far strongest increase was observed between heptane and SDBS/SF. While the IFT at the lowest pH was nearly equal to that of LS, an increase of more than 7 mN/m was observed over the full pH range.

The IFT/pH-slopes in the model oil measurements are nearly logarithmic, while at low pH the IFT values of all three SDBS solutions to heptane show very similar values, almost independent of the salinity (Figure 2).

Since the variation of pH by addition of small amounts of acid and base to the solutions also causes small changes of the solutions ion strength, some reference samples were measured: Instead of adjusting the pH of the SDBS/SF solutions by addition of HCl or NaOH, respective amounts of NaCl were added. Therewith, the pH was the same as for the native solutions (pH 8.2−8.5), while the ion strength increased. The sample with 1.2 mmol/L NaCl, which simulated SDBS/SF pH 3.4 (IFT = 1,6 mN/m), gave an IFT of 4.0 mN/m. For the sample with 0.3 mmol/L NaCl, which simulated SDBS/LS pH 10.2 (IFT = 7.6), 6.8 mN/m were measured.

It can therefore be concluded that the effect of pH increase on IFT is strongest at low pH values. At higher pH values IFT changes seem to depend more on the ion strength of the added acid and base than on the presence and concentration of H$_3$O$^+$ and OH$^-$ ions. Also at initially higher ions strengths (i.e., LS and LS-Ca) the effect of pH is less pronounced than in salt free solutions (SF). Similar observations are known from studies on sodium dodecyl sulfate (pK_a = −0.09), where the CMC was low at low pH and both higher and independent of pH beyond pH 5.[24]

The observed changes are expected to result from a reduction of electrostatic repulsion between the surfactants head groups and therewith a closer packing of surfactant molecules at the interface as a combined effect of increasing salinity and partial protonation of surfactant molecules at the interface. Even though the pK_a values of sulfonic acids in aqueous bulk are far lower than the pH range studied in this work, the slight response of the surfactant properties might arise from a positive shift of the sulfonic acid's pK_a when located at an interface in the vicinity of other sulfonic acid molecules. This phenomenon has been observed for polyelectrolytes at interfaces[25] and for carboxylic surfactants where pK_a values can be up to five units higher at the interface than in bulk.[26] One reason for this is an increased oxonium ion concentration close to the interface compared to that of the bulk.[27]

Sein et al. (1995) explained the different effects of monovalent ions on the electrical double layers surrounding micelles and larger aggregates of SDBS. A high concentration of electrolyte in the bulk aqueous solution shields the overall surface charge of the aggregates. Further, the osmotic pressure, otherwise causing migration of the surfactants counterions to the bulk, decreases. Both mechanisms result in a compressed double layer, a larger number of surfactant molecules per interfacial area and therewith a lower CMC and IFT.[28] Further studies on different types of counterions showed that the strong binding between calcium ions and SDBS leads to an extra strong compression of the interfacial surfactant layer.[29]

The decreased effect of osmotic pressure by addition of electrolyte to the pure aqueous surfactant solution is clearly observed when comparing the IFT/pH-slopes of SDBS/SF and SDBS/LS (Figure 2). Additional double layer compression because of the 8-fold excess of counterions, compared to the SF SDBS concentration, should also play a large role. A stronger decrease of IFT when going to the SDBS/LS-Ca solution cannot be explained with the same effects because (a) the overall electrolyte concentration decreases slightly (from 20 mM for LS to 19.18 mM for LS-Ca), therewith increasing the osmotic pressure and (b) the ionic strength of the bulk solution stays unchanged (I = 20 mM for both solutions). It can therewith be assumed that the low IFT as well as the decrease of the IFT/pH slope are effects of the calcium only, that is, compression of the interfacial surfactant layer and increase of the surfactants CPP by decreasing its headgroup area (eq 3).

In addition to the IFT values at equilibrium, some difference between the dynamic IFTs of SDBS samples without and with calcium was observed. While the IFT values of SF and LS samples always decreased logarithmically with time until the equilibrium was reached, the IFT values of LS-Ca samples normally increased, also with a logarithmic slope. The latter observation is most likely due to diffusion of surfactant molecules from the interface to the bulk oil phase as the surfactant forms lipophilic complexes with calcium ions.

As seen in Figure 2, an increase of the measurement temperature from (25 to 60) °C had only a small effect on the IFTs of SDBS/LS and SDBS/LS-Ca samples.

While all IFT values measured for SDBS containing solutions were around 1 mN/m or higher, relatively low values were obtained for solutions of AOT (Table 2). Here the IFT decreased from 0.14 mN/m to 29 μN/m by changing from AOT/LS to AOT/LS-Ca. By increasing the temperature from (25 to 60) °C the IFT of the AOT/LS-Ca sample decreased to 4 μN/m, a so-called "ultralow" IFT. Surprisingly the same

Table 2. IFT Data from Measurements between AOT Solutions and Heptane

AOT/LS/heptane		AOT/LS-Ca/heptane	
pH		pH	
T	γ(CSW) [mN/m]	T	γ(CSW) [mN/m]
6.2	0.14	6.2	29×10^{-3}
25 °C		25 °C	
6.5	1.1 ± 0.1 $(9\%)^a$	7.0	4.0×10^{-3}
60 °C		60 °C	

[a]Two parallels measured.

change in temperature increased the IFT of AOT/LS from 0.14 mN/m up to 1.1 mN/m.

In different works the IFTs of heptane and hexane, respectively, and water has been shown to decrease linearly with temperature.[30,30a] The same has been observed for dilute solutions of sodium dodecyl sulfate (SDS) and toluene at fixed concentration and fixed pH.[31] Recently, Ataev (2012) derived a relation between the surfactant concentration in a water/alkane system and the pH dependence of its IFT, where an inversion of the IFT/pH slope with increasing concentration of a simple surfactant was shown and the surface excess of the surfactant at the o/w interface was related to the surfactant concentration in the solution.[30a]

In our experiments, contrary to these described in literature, the surfactant concentrations were kept constant while the ion composition of the aqueous phase was changed. Changes of the IFT should therefore stem from electrolyte induced changes of the surfactants surface excess.

Inverse IFT Changes with pH and Salinity. One set of pH dependent IFT measurements for LS and LS-Ca solutions of both surfactants was also performed with the mixed model oil (n-heptane/toluene, v:v/1:1) at 25 °C. As seen in Figure 3, two completely opposite trends were observed for the IFT change. For the SDBS solution the IFT increased with pH and decreased at addition of calcium. This was also seen for the similar samples with pure heptane in the oil phase. For AOT solutions, however, the IFT decreased with increasing pH and was largest in the presence of calcium. In either case, the changes were rather small with $\Delta\gamma = 0.02 - 0.10$ mN/m over the entire pH range. Over all, the IFTs between the surfactant solutions and the mixed model oil were lower than those measured between the same solutions and heptane.

The mixed model oil has a higher polarity than pure heptane as it contains toluene. Most likely, this gives the water-soluble surfactant AOT, which because of its two tailed structure has a higher CPP than the one tailed SDBS, high affinity to the interface and leads to lower IFTs. When further increasing its CPP by compression of the headgroup area through pH lowering or addition of calcium, diffusion of the surfactant molecules to the bulk oil phase may result in increased IFTs. AOT is known to have strong microemulsifying properties and to readily form oil soluble reversed micelles due to its high CPP.[21,32]

Saien's (2006) observation of a similar IFT/pH slope in interfacial studies with SDS solutions and pure toluene,[31] supports the assumption that the IFT change with pH is directly related to the solubility of the surfactant in the respective oil phase. In this case the surfactant had a lower CPP than AOT due to its single tail structure, while the hydrocarbon phase consisted of toluene only and was therewith more polar.
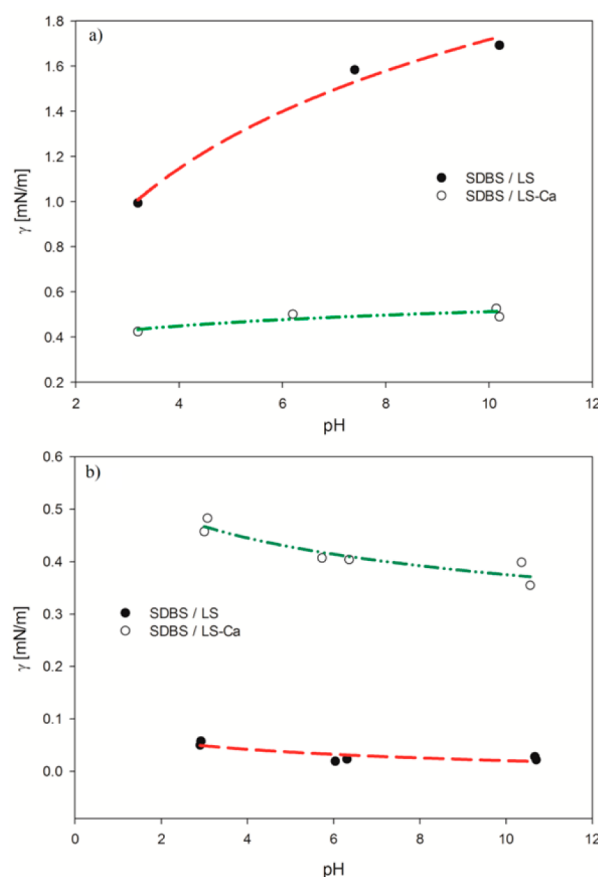
Figure 3. IFT values between n-heptane/toluene mix (v:v/1:1) and (a) SDBS solutions and (b) AOT solutions, respectively, with and without calcium ions (I = 20 mmol/L).

Effect of Salinity on the IFT between Surfactant Solutions and Crude Oil. The physicochemical properties of the investigated crude oils are listed in Table 3.

Comparing the physical properties of the oils it is seen that crude A and B have more or less similar densities and viscosities, while crude C is the heaviest and most viscous and crude D is the by far lightest and least viscous one of the four oils. Looking at acid and base content as well as resin and asphaltene contents, it is seen that the heavy crude C both has the highest TAN and the by far highest resin concentration, while the light crude D has a very low acid number and the lowest resin concentration of the oils.

Figure 4 shows IFT values between SDBS solutions and four different crude oils. All samples showed the same behavior at increasing salinity: IFT(SF) > IFT(LS) > IFT(LS-Ca). The same trend was seen with heptane as the oil phase.

The IFT values between surfactant solutions and crude A and D, respectively, were quite similar to those measured for samples containing heptane. For crude B the IFT of the SF sample was exceptionally low, while for crude C all IFT values were approximately 10 mN/m.

In Figure 5 the IFTs between AOT solutions and crude oil A−D are shown. While the absolute values in general are lower than for SDBS samples, the SF samples show exactly the same trend for both surfactants. Like for SDBS the IFTs are lower in the presence of electrolyte. Here, no similar trend can be observed for the IFT change between LS and LS-Ca samples. While the trend for crude A and crude D is the same as for all

Table 3. Composition and Properties of the Crude Oils[a]

	composition [wt%]			
	crude A	crude B	crude C	crude D
saturates	61.2	73.9	52.5	82.5
aromatics	32.4	22.7	34.6	16.7
resins	4.9	2.6	12.7	0.7
asphaltenes	1.5	0.9	0.2	0.1
Physical Properties				
TAN [mg KOH/g]	1.08	<0.1[b]	2.46	<0.1[b]
TBN [mg KOH/g]	1.16 ± 0.35	0.56 ± 0.14	[c]	0.18 ± 0.03
density [g/cm^3] at 15 °C	0.8582	0.8519	0.8909	0.8045
density [g/cm^3] at 60 °C	0.8252	0.8204	0.8593	0.7703
API gravity [°API]	33.4	34.5	27.3	44.3
viscosity [mPas] at 20 °C	19.90	19.00	133.00	3.85
viscosity [mPas] at 60 °C	4.07	3.48	23.10	1.52

[a]TAN/TBN = total acid/base number. [b]Value below detection limit of the method. [c]Not detectable because of resin precipitation on the electrode.
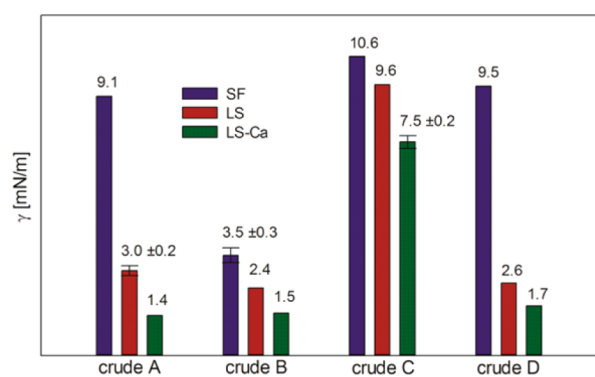

Figure 4. IFT values between SDBS solutions and four different crude oils at 60 °C. Natural pH of aqueous phase after pre-equilibration was between 7.1 and 8.3.
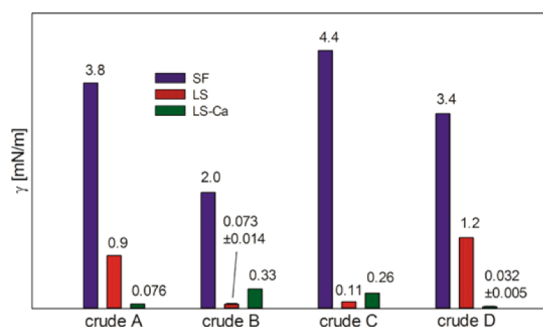

Figure 5. IFT values between AOT solutions and four different crude oils at 60 °C. Natural pH of aqueous phase after pre-equilibration was between 6.7 and 7.3.

SDBS samples, an increase of IFT when changing from LS to LS-Ca is observed for crude B and crude C. For LS-Ca and crude D an IFT as low as 27 μN/m was measured. During a measurement time of 12 h the value increased to 35 μN/m.

Like in the samples with heptane, the generally lower IFT values arise from the two tailed structure of AOT, which independent of electrolyte causes a higher CPP than that of SDBS.

The increase of IFT at addition of calcium to AOT/LS/ crude B and AOT/LS/crude C (Figure 5) might follow from partitioning of surfactant into the oil phase at conditions close to the optimal salinity. While this phenomenon already was discussed in context of the model oil measurements, the complex nature of the crude oils makes an explanation more difficult.

A direct relation of the experimental results to physical properties like density and viscosity or to the TAN and TBN values of the oils could not be found.

Another approach is considering the weight fractions of saturates, aromatics, resins and asphaltenes. Asphaltenes and resins are defined as polyaromatic hydrocarbons with large heteroatom content and therewith a high polarity. While resins are well soluble in saturated hydrocarbons, asphaltenes are defined as those components of the crude oil, which are nonsoluble in saturates but well soluble in aromatics.[33] Due to their large number of polar groups, both asphaltenes and resins show a strong tendency to film formation at air/water and oil/ water interfaces, respectively, while the resin fraction has a higher interfacial activity than the asphaltenes at air/water interfaces.[34,35]

In this work, all IFT measurements were performed at oil/ water interfaces. Here the main fraction of the resins is, because of their good solubility in both saturates and aromats, assumed to be dissolved in the bulk oil phase, while the conditionally stable asphaltenes might show a larger interfacial activity compared to air/water systems. The stability of the asphaltenic compounds in the bulk oil, which should be reciprocally related to their interfacial activity in oil/water systems, is highest at a high aromatic/saturate ratio and vice versa. As resins are known to stabilize asphaltenes in saturate rich oils by aggregate formation,[36,37] it is suggested that the asphaltene stability can be related to the ratio (aromatic × resin)/(saturate × asphaltene), where the amounts are given by their weight fraction (wt %) in bulk. A similar approach was done by Nazar (2008) using the ratio (aromatic + resin)/(saturate + asphaltene).[37] In case of crude C and D in our work, however, the very low asphaltene fractions of 0.1 and 0.2 wt %, respectively, seem to be neglected when using sums, as in the work of Naza. Multiplication gives values which are proportional to the IFT values measured between the SF solutions of both surfactants and the crude oils. In Figure 6, we plotted the IFT values from crude oil samples with SF solutions of both surfactants against the ratio (saturate × asphaltene)/(aromatic × resin). The same was done for one set of measurements with crude oils and mQ water in the absence of electrolyte and surfactants. While these three curves all show a linear relationship of IFT to that ratio, a certain tendency is still seen, though far from linear, for SDBS LS and SDBS LS-Ca samples. As crude C has the by far lowest ratio of 0.03, which in our experiments usually resembled a high IFT, also a connection to the exceptionally high IFT values of crude C with SDBS LS and SDBS LS-Ca, respectively, is thinkable. The crudes A and D, which have quite similar ratios of 0.56 and 0.49, respectively, show qualitatively the same IFT trends with both surfactants and the different salt solutions. Deviations from the linear trend should be due to competing effects of the surfactants' and native oil compounds' response to changes in
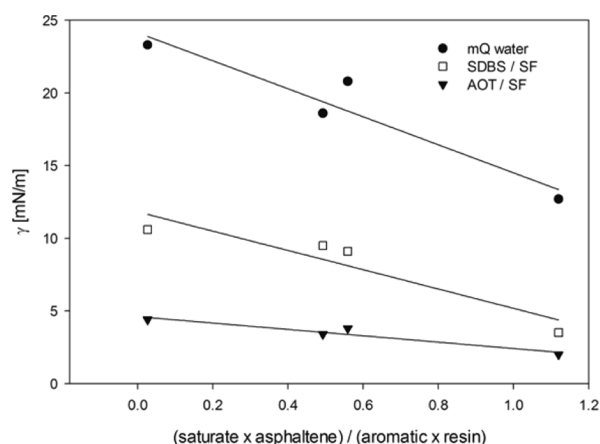
Figure 6. IFT values of electrolyte free aqueous solutions and crude oils, plotted against the weight ratios of native crude oil components (Order of oils from left to right: C, D, A, B).

salinity. As the IFT values reach low and ultralow levels in the presence of sodium and calcium ions, surfactant effects do obviously exceed those of interfacial adsorbed asphaltenes. This effect is strongest in case of AOT.

CONCLUSION

Even at low salinities and without using cosurfactants, low and ultralow values of IFT can be obtained between crude oils and solutions of the anionic surfactant AOT.

Interfacial properties of both surfactants (SDBS and AOT) depend strongly on the ionic composition of the water phase and under salt free conditions to some extent on pH. Even small amounts of calcium have as strong impact on the IFT between crude oils and surfactant solutions. At conditions leading to very low IFT values; however, no general trends related to the calcium concentration could be observed.

By comparing systems containing crude oils and different aqueous phases, a linear relation between IFT values and asphaltene stability, estimated from the composition of the bulk oil, was found. The trend is most obvious under salt free conditions at which some competition between the interfacial activity of asphaltenes and surfactant may be realistic.

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Notes
The authors declare no competing financial interest.

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