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Hydrocarbon and alcohol effects on sulfonate adsorption on alumina

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COLLOIDS AND SURFACES

A: PHYSICOCHEMICAL AND ENGINEERING ASPECTS

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Abstract

Adsorbed surfactant aggregates are finding applications in areas such as soil washing and ultrafiltration. In order to optimize these processes it is imperative to fully elucidate the effects of the solubilizates and additives on surfactant adsorption and aggregation. The effect of alcohol and hydrocarbon additives on the equilibrium adsorption of isomerically pure *n*-decylbenzene sulfonate on alumina is studied here. Dodecane increased sulfonate adsorption by more than one order of magnitude at concentrations of $<10^{-4}$ mol l^{-1} sulfonate. At higher sulfonate concentrations the adsorption change was much less marked. The effects of varying the dodecane levels between 1 and 16.7 vol.% were surprisingly small. In contrast, addition of propanol decreased sulfonate adsorption under all conditions because the alcohol increased the power of the solvent towards the surfactant. Medium and long chain alcohols were found to interact synergistically with the surfactant, decreasing the onset of both hemimicellization and micellization. Sulfonate adsorption increased in pre-micellar solutions but decreased in micellar solutions. In addition, adsorption of sulfonate was found to be identical at low levels of decanol, both of which were well above the aqueous solubility limit. This suggested that the effect of the additive is limited by its solubility in the phase from which adsorption takes place.

Keywords: Alcohols; Alumina; Hydrocarbons; Sulfonate adsorption

1. Introduction

Adsorption and aggregation of surfactants on solids can occur with marked effects on interfacial and colloidal behavior [1] and drastically alter the solid/liquid interface. Indeed many industrial products/processes such as flotation, flocculation, dewatering, enhanced oil recovery, lubrication, paints, coatings, adhesion, cosmetics, pharmaceuticals and detergency derive their efficacy via surface modification [2,3]. Adsorption of ionic and nonionic surfactants as single components has been the subject matter of several studies using classical techniques to determine adsorption density, zeta potential, hydrophobicity and wettability in conjunction with relatively new techniques such as emission, magnetic and vibrational spectroscopies [4–6]. These investigations are usually carried out with a single pure surfactant dissolved in aqueous solution, with a single pure adsorbent suspended in it. In contrast, there has been limited work with mixed surfactant systems containing, for example, oil and alcohol in addition to the surfactant. Such systems are of both theoretical and practical impor-

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tance because of their capacity to form microemulsions and their applicability to industrial situations such as enhanced oil recovery and detergency. In addition to emulsification, adsorbed surfactant aggregates can solubilize oil or alcohol as in the incorporation of such molecules into micelles. Increased attention is being paid currently to the solubilization of hydrocarbons and alcohols in adsorbed surfactant aggregates primarily because of the projected applications in soil washing, filtration, thin films, separations, catalysis, etc. [7,8]. Partitioning of model hydrophobic solutes such as naphthol to the silica–water interface in the presence of long chain cationic surfactants has been widely studied by Monticone et al. [9]. It has been reported that the adsorbed surfactant aggregates are capable of solubilizing the insoluble or non-adsorbing solutes to a greater extent than simple micelles. Substrate porosity has little effect on the uptake of the solute but pH and other solution parameters alter solubilization primarily due to changes in solute dissociation characteristics.

The literature indicates that the behavior of adsorbed aggregates is similar to that of micelles in the presence of alkanes [10]. Atypical behavior was observed for alcohols primarily because of the availability of increased solubilization sites (the core and the hydrophobic perimeter), whereas alkanes are solubilized only in the hydrocarbon core. The presence of alcohol increased the adsorption of surfactant (sodium dodecylsulfate) on alumina, and with an increase in alcohol chain length surfactant adsorption was further enhanced. In a similar study, Esumi et al. [11] reported that the effect of alcohol on surfactant adsorption depends upon the nature of the alcohol. For example, hexanol reduces the polarity of adsorbed lithium dodecylsulfate (LiDS) or lithium perfluorooctane sulfonate (LiFOS) layers significantly but incorporation of heptafluorobutanol into the LiFOS bilayer alters the polarity only slightly. Interestingly, there was little effect of either alcohol on the surfactant adsorption itself. These contrasting effects of alcohols on surfactant adsorption suggest that the operating mechanisms are complex and need to be probed further. Adsorption from complex systems such as microemulsions can only be studied and the results interpreted, if there is an understanding of the interactions that occur in more basic systems. In this work, adsorption of an isomerically pure surfactant, *n*-decylbenzene sulfonate, on alumina was studied in the presence of oil and alcohol additives. This surfactant has a relatively simple structure and is resistant to the hydrolysis common for fatty acids and amines. Mixtures of sulfonated surfactants are potential oil flooding surfactants because of their high oil/water interfacial activity.

2. Experimental

2. *Materials*

2.1.1. Surfactant

The surfactant, *n*-sodium decylbenzene sulfonate, was synthesized in our laboratories and the details are provided elsewhere [12]. Characterization by ^{1}H- and ^{13}C-NMR, mass spectrometry and high performance liquid chromatography (HPLC) showed the surfactant to be at least 98% isomerically pure.

2.1.2. Inorganics

Sodium chloride, used to control ionic strength, was of ultrapure grade (99.999%) and was used as received from Aldrich Chemicals.

2.1.3. Hydrocarbons

n-Dodecane (99% pure) from Aldrich Chemicals was used as received. The alkane was utilized as a model for oil in this study.

2.1.4. Alcohols

n-Propanol, *n*-pentanol and *n*-decanol were purchased from Fisher Scientific, and were of certified reagent grade.

2.1.5. Alumina

Linde A high purity alumina (90% alpha and 10% gamma) was purchased from Union Carbide. The specific surface area as measured using a Quantasorb apparatus by the BET method was 15 $m^2\ g^{-1}$. Electron micrographs of the samples showed them to be irregularly shaped and to have rough surfaces.

2.1.6. Water

All water used in the experiments was distilled three times in a glass still, and then deaerated with nitrogen to remove carbon dioxide.

2.2. Methods

2.2.1. Adsorption

0.5 g samples of alumina were transferred to 25 ml flasks and the desired amounts of NaCl solution added to wet the mineral. The flasks were sealed and the suspension equilibrated for 1.5 h on a wrist-action shaker located inside an incubator. The surfactant and any additives were then pipetted into the flask. If oil was to be used in the experiments, it was first dispersed in the surfactant solution by ultrasonication (Labline Ultratip 9100 system, 30 W power for 1 min) and the resultant emulsions were then pipetted into the flasks. Alcohol, when used, was pipetted directly into the flasks since it was more difficult to keep it dispersed in dilute sulfonate solutions. The suspensions containing the surfactant and the mineral were further equilibrated for 4 h on a wrist-action shaker. Following this, solids were separated by centrifugation at 4500 rev min^{-1} in an incubator. Aliquots of the supernatant were then removed for analysis.

2.2.2. Analyses

Sulfonate concentrations above $\approx 2 \times 10^{-4}$ mol l^{-1} were determined using a two-phase titration technique with dimidium bromide–disulphine blue as the indicator [13]. Sulfonate concentrations below 2×10^{-4} mol l^{-1} were measured by UV absorbance at 223 nm. For measurements of alcohol (decanol only), the components were separated using HPLC (the mobile phase was a 70:30 mixture of acetonitrile and 0.01 M tetrabutylammonium phosphate solution, refractive index detector, C_{18} bonded silica column).

2.3. Conditions

All experiments were carried out at 75°C to ensure complete solubility of the surfactant over the entire concentration range studied. The pH of the system was not adjusted and was allowed to attain its equilibrium value of ≈ 8.2. Ionic strength was maintained at 0.1 M NaCl. It must be mentioned that, with the exception of propanol, the initial levels of alcohols studied were above the solubility limits for each of the additives. This resulted in the formation of two-phase liquid systems and stable emulsions at high surfactant levels. The aqueous volume was maintained at 10 ml for all experiments and thus the initial fluid volumes of the samples varied with the level of oil or alcohol added. From partitioning experiments it was found that sulfonate did not partition into the oil phase.

3. Results and discussion

The aim of the present study was to determine changes in sulfonate adsorption on alumina in the presence of oil and alcohol additives. The adsorption of *n*-decyl benzenesulfonate (*n*-DBS) on alumina in the presence of varying amounts of *n*-dodecane is shown in Fig. 1. The adsorption of *n*-DBS alone on alumina is characteristic of ionic surfactant adsorption on oxide minerals with four well-defined regions. Models to account for this behavior were previously proposed based upon electrostatic and hydrophobic interactions [14,15] and confirmed by several spectroscopic and calorimetric studies [16–19]. Surfactant aggregation on particles (solloid formation, hemimicellization) occurs at a residual concentration of $\approx 9 \times 10^{-5}$ mol l^{-1}. In the presence of dodecane the adsorption in the lower concentration region (region I) is enhanced, with a slight increase in adsorption also occurring in the micellar region (region IV). Neither the hemimicellization concentration nor the critical micelle concentration (CMC) seem to be affected by the presence of the hydrocarbon although the adsorption density at the onset of hemimicellization is about 15 times higher. Test supernatants in the premicellar range were clear, without a visible oil phase, while more concentrated systems exhibited increasing turbidity with increasing sulfonate concentration. Turbidity is an indication of emulsification with more residual oil in micellar systems. Interestingly, increasing the

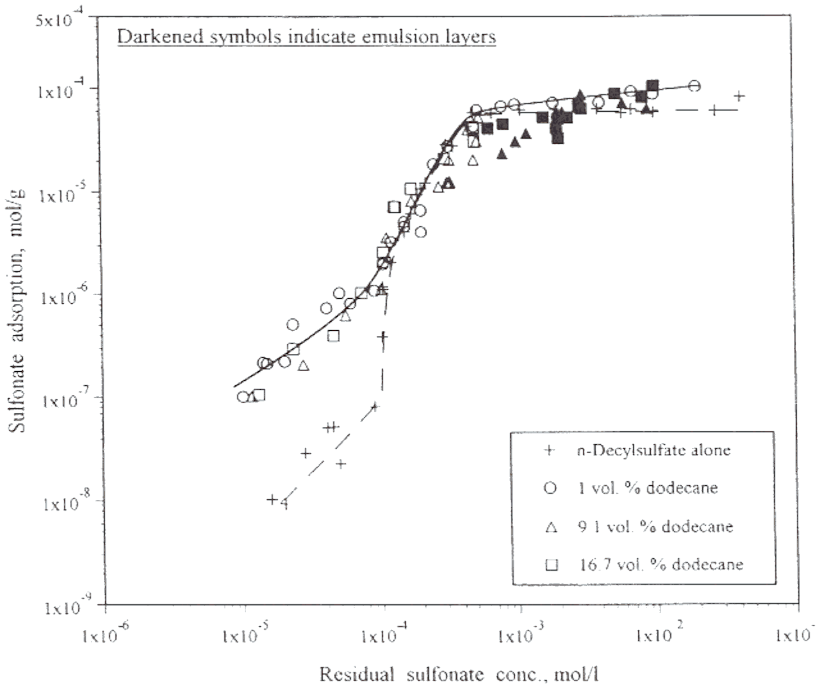

Fig. Adsorption behavior of *n*-DBS on alumina in the presence of varying dodecane levels (1, 9.1 and 16.7%).

dodecane concentration from 1 to 16.7 vol. % does not cause any further increase in the sulfonate adsorption. Emulsions were observed for the 9.1 and 16.7 vol. % dodecane systems at high sulfonate concentrations and the data show a large degree of scatter in these cases, making comparison with the reference isotherm difficult. For both the 9.1 and 16.7 vol. % dodecane cases, there was excess oil at the end of each experiment and observations of agglomeration and floc extraction into the oil phase were made. As mentioned earlier, there was no measurable partitioning of the sulfonate into the oil phase, possibly due to the ionic character of the functional group. As a result, adsorption determinations were direct when aqueous and oil phases were separate as was observed in the presence of 1 and 9.1 vol. % dodecane. For tests done at 16.7 vol. % dodecane there was a significant volume of emulsion which could be measured easily. In this case, measurements were made assuming the emulsion to be a separate phase. The results are summarized in Table 1 for the system containing 16.7 vol. % dodecane and it is evident that the emulsion layer contains the highest surfactant concentration. A clear trend that develops from the volume readings is the increase in emulsion at the expense of free hydrocarbon as surfactant levels are raised. Both observations are consistent with the fact that emulsions are stabilized by surfactants. Nevertheless, the three sulfonate adsorption isotherms obtained in the presence of dodecane are similar and there is no significant difference below a DBS concentration of 2×10^{-4} mol l^{-1}. At higher sulfonate concentrations, the adsorptions at 9.1 and 16.7 vol. % dodecane differ from that at 1%. Adsorption at the two high levels seems to follow a similar trend in that the slopes of the isotherms decrease at 2×10^{-4} mol l^{-1}, and do not reach a plateau like the isotherms at 0 and 1% dodecane. Before attempting to interpret this behavior it should be noted that very stable emulsions form at the high sulfonate and dodecane concentrations. There will be some errors associated with the surfactant analyses under these conditions and the data will be less reliable.

It is interesting that sulfonate adsorption is

Table 1
Concentration and phase volume measurements of supernatants from *n*-DBS adsorption tests on alumina. Initial dodecane concentration = 1.67% by volume

Initial conc. (mol l^{-1})	Volume (ml)			Concentration (mol l^{-1})			Res. conc. (mol l^{-1})	Adsorption (mol g^{-1})
		Emulsion	Oil	Aqueous	Emulsion	Oil		
3.0×10^{-3}	9.0	0.3	1.1	7.8×10^{-4}	1.6×10^{-3}	≈ 0	8.2×10^{-4}	4.4×10^{-5}
4.1×10^{-3}	8.7	1.1	0.9	1.3×10^{-3}	6.7×10^{-3}	≈ 0	1.9×10^{-3}	4.4×10^{-5}
4.1×10^{-3}	8.6	1.7	1.0	1.2×10^{-3}	5.4×10^{-3}	≈ 0	1.6×10^{-3}	5.1×10^{-5}
4.9×10^{-3}	9.2	1.2	0.4	1.4×10^{-3}	7.6×10^{-3}	≈ 0	2.4×10^{-3}	5.0×10^{-5}
5.3×10^{-3}	9.2	1.2	0.5	1.6×10^{-3}	7.8×10^{-3}	≈ 0	2.6×10^{-3}	5.4×10^{-5}
6.1×10^{-3}	9.1	1.4	0.5	2.2×10^{-3}	6.7×10^{-3}	≈ 0	3.0×10^{-3}	6.2×10^{-5}
6.2×10^{-3}	9.0	1.3	0.4	2.2×10^{-3}	5.8×10^{-3}	≈ 0	2.9×10^{-3}	6.6×10^{-5}
9.6×10^{-3}	8.2	2.1	0.1	4.0×10^{-3}	7.6×10^{-3}		5.3×10^{-3}	8.6×10^{-5}
1.2×10^{-2}	7.7	2.3	0.1	6.2×10^{-3}	9.9×10^{-3}		8.0×10^{-3}	8.0×10^{-5}
1.6×10^{-2}	7.9	2.4	0.1	8.6×10^{-3}	1.1×10^{-2}		1.0×10^{-2}	1.2×10^{-4}

increased only in region I wherein the predominant adsorption mechanism is electrostatic interaction between the sulfonate ion and the alumina surface. It is unlikely that dodecane enhances electrostatic attraction forces between the sulfonate species and alumina sites but it is possible that sulfonate aggregation is enhanced at the interface resulting in enhanced adsorption. The slopes of the isotherms in region I in the absence and presence of dodecane are however very similar, suggesting that the electrostatic driving force is not altered. Below the hemimicellization concentration, the surfactant will adsorb as individual molecules or as dimers. This will increase the hydrophobicity of the surface locally creating sites where the alkane can coadsorb. Coadsorbed dodecane can enhance sulfonate aggregation at the interface, resulting in increased surfactant adsorption. Once sulfonate forms hemimicelles and bilayers at the solid–liquid interface, the oil will be solubilized into these aggregates and the effect on adsorption is reduced. Similarly, the oil will preferentially solubilize into micelles in the bulk at higher sulfonate concentrations, resulting in minimal effects on adsorption. Similar results have been reported in a study of dodecane adsorption/abstraction on alumina [20].

The results obtained for the effect of alcohols of varying chain length on the adsorption of *n*-DBS are given in Fig. 2. Addition of 1% propanol decreases the adsorption measurably below 6×10^{-5} mol l^{-1} and also through most of regions II and III. An increase in propanol concentration to 10 vol % decreased the adsorption further. There is no region I detected in the presence of alcohol. The tendency for propanol to reduce sulfonate adsorption is clearly shown in Fig. 3. The trend is evident as adsorption decreases from 6.2×10^{-5} mol g^{-1} in the absence of propanol to 4.4×10^{-7} mol g^{-1} at 50% propanol. This decrease is attributed to the increased solubility of sulfonate in water/propanol mixtures. It was observed that concentrated *n*-DBS solutions at room temperature formed precipitates as the solubility limit was exceeded; when propanol was added these precipitates dissolved. An increase in solvent power leads to reduced surface activity and hence reduced adsorption.

The sulfonate adsorption isotherms in the presence of 1% pentanol and decanol are also shown in Fig. 2. Both pentanol and decanol increase adsorption at lower sulfonate concentrations but reduce the plateau adsorption. Interestingly the shape of the isotherms in the presence of all three alcohols is similar.

The alcohol adsorption as a function of residual DBS concentration was also determined and the results are shown in Fig. 4. Uptake of decanol was determined to be very near 100% below 4×10^{-5} mol l^{-1} *n*-DBS. The residual alcohol was below the detection limit of HPLC. Assuming a parking area of 20 Å^2 for alcohol adsorbed in a vertical orientation to the surface, monolayer coverage is achieved

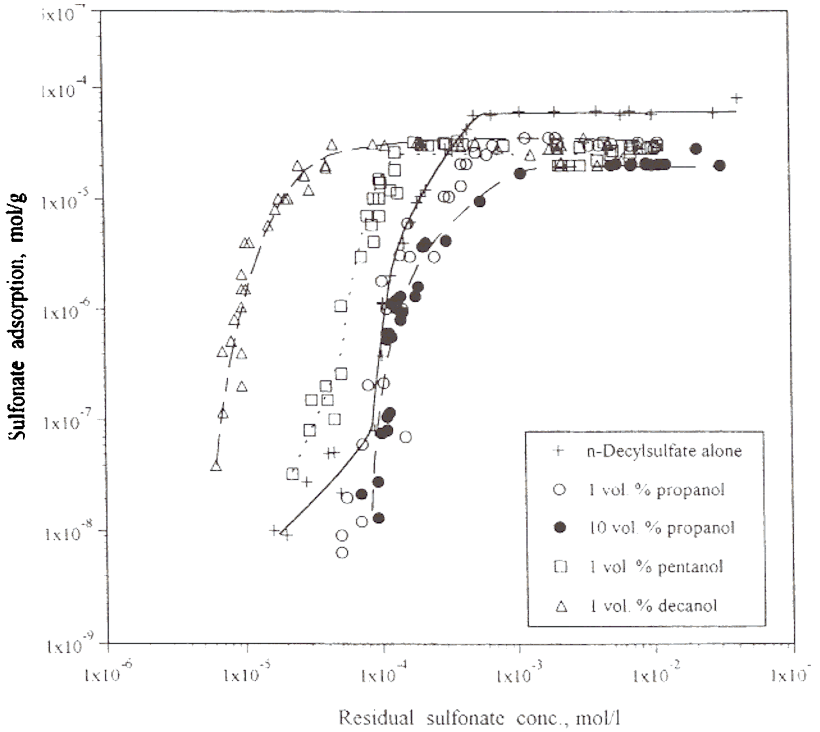

Fig. 2. Adsorption behavior of *n*-DBS on alumina in the presence of alcohols of chain length varying from propanol to decanol.

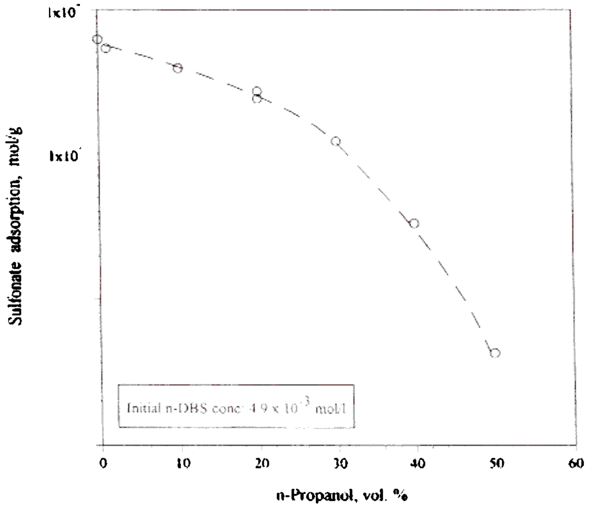

Fig. 3. Adsorption behavior of *n*-DBS on alumina as a function of *n*-propanol concentration.

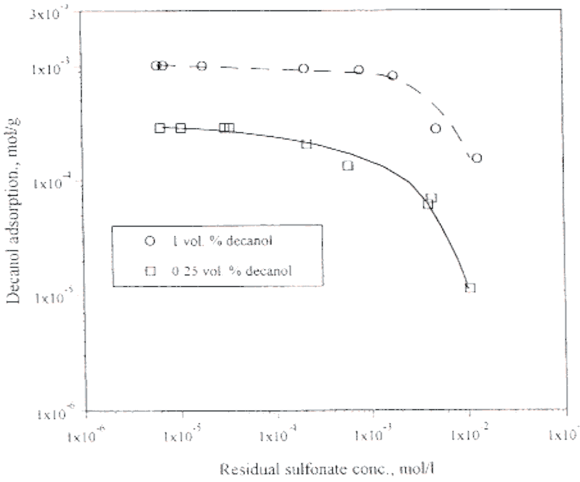

Fig. 4. Adsorption of *n*-decanol on alumina at initial *n*-decanol levels of 0.25 and 1% by volume.

at 1.2×10^{-4} mol g^{-1}. The measured adsorption is 1×10^{-3} mol g^{-1}, indicating that alcohol forms multilayers at the interface. So use of the term abstraction would be more precise to describe the loss of decanol. At higher surfactant levels, decanol abstraction begins to decrease. A reduction of the decanol concentration from 1 to 0.25% did not affect the sulfonate adsorption but the shape of the decanol abstraction curve was similar.

Adsorption at the solid/liquid interface is governed by: (i) electrostatic interactions between the sulfonate ions and charged surface sites; (ii) hydrophobic interactions between adsorbed sulfonate ions as well as between sulfonate and the additive in solution and at the interface; (iii) changes in solvent power stemming from the dissolution of the additive; and (iv) shielding of the ionic head groups by coadsorbed non-ionic heads. In bulk solution, alcohols reduce electrostatic repulsions at the micellar surface, enhance surfactant micellization and reduce the CMC. However, this trend was found to be reversed for short chain alcohols at high concentration levels because under these conditions the solvent power towards the surfactant was increased. Such increase in solvent power explains the reduction of sulfonate adsorption in the presence of propanol (Fig. 3). However, the increased level of molecular associations caused by higher alcohols will result in increased sulfonate adsorption when pentanol and decanol are present. The greater effect of decanol over pentanol reflects the chain length dependence of the alcohol/sulfonate interactions. An interesting observation is that the sulfonate adsorptions in the presence of 1 and 0.25% decanol were identical. This may appear puzzling considering the strong synergistic interactions that occur between the decanol and the sulfonate. It must be recalled, however, that decanol is present at levels above its miscibility with the aqueous solution and therefore its activity in solution is identical in both cases.

The effects of propanol observed here are contrary to that proposed using the two-site adsolubilization model of Lee et al. [10]. However, for the higher alcohols (pentanol and decanol) sulfonate adsorption is enhanced significantly at low surfactant adsorptions. It can be said that the two-site adsolubilization model will be valid above a critical alcohol chain length.

Hydrocarbons do not have a strong influence on the CMC of surfactants [21]. This much weaker effect, as compared to that of alcohols, has been attributed to their solubilization primarily in the hydrocarbon core of the micelle, while alcohols can also reside in the palisade layer and reduce the free energy of micellization. Solubilized hydrocarbons do not alter micellization and this is also seen in Fig. 1 as neither the onset of micellization nor hemimicellization is measurably affected. It was also seen that the sulfonate adsorption is not very sensitive to the amount of oil present in the system. The aqueous activity of an additive determines its effect on adsorption. Since the concentration of dodecane present was above its aqueous solubility limit and sulfonate did not partition into the oil phase the effect was minimal. Increasing the amount of oil, however, tends to increase the oil/water interfacial area. This would result in a reduction of surfactant activity in the aqueous phase (and therefore adsorption) as more surfactant molecules would adsorb at the oil/water interface. Comparison of the adsorption isotherms in Fig. 1 suggests that the curves are similar below a sulfonate concentration of 2×10^{-4} mol l^{-1}. Under these conditions, there is insufficient surfactant to prevent coalescence, and so the oil/water interfacial area is minimal. Above $\approx 2 \times 10^{-4}$ mol l^{-1} sulfonate, the emulsions become more stable and adsorption at the oil/water interface may be quite high. Emulsions that appear milky white typically have dispersed droplets in the size range 1–50 μm [22]. So for example, at an oil/water ratio of 0.1, assuming a parking area of 25 Å^2 for sulfonate and 10 μm spherical particles, sulfonate equivalent to 4×10^{-4} kmol m^{-3} can be accommodated at the interface. Under the same assumptions, 1 μm droplets can adsorb 10 times as much surfactant. Therefore, emulsions of moderate oil volume can affect the aqueous activity of sulfonate. The reduction in sulfonate adsorption observed in the two high oil systems between 2×10^{-4} and 3×10^{-3} mol l^{-1} is attributed to such effects. However, the adsorption decrease would have been expected to be the greatest for the 16.7% dodecane system, but this is not supported by the data in Fig. 1.

In highly concentrated surfactant systems, the total quantity of surfactant could far exceed the quantity that could be adsorbed at the oil/water interface and the fraction of surfactant depleted from the aqueous solution would then be quite low. From Fig. 1 it is indeed seen that above 3×10^{-3} mol l^{-1} there is no reduction in adsorption for the 9.1 and 16.7% dodecane systems.

4. Summary

Adsorption of sulfonate from mixtures with alcohols and alkanes was studied at the alumina–water interface. The aim was to identify the role of additives in the case of adsorption from microemulsions using dodecane as a model for oil. Dodecane tends to increase adsorption, particularly in region I of the isotherm, but sulfonate adsorption is not very sensitive to the initial level of the dodecane under the conditions tested. Short chain alcohols (propanol) decreased sulfonate adsorption due to their effect on surfactant solubility in the bulk. Medium and long chain alcohols increased the sulfonate adsorption in premicellar solutions and decreased it above the CMC. This effect is attributed to the decrease in the onset of hemimicellization and an even larger effect on the onset of micellization. Decanol abstraction was nearly 100% at low sulfonate concentrations, but decreased at higher sulfonate concentrations as alcohol became increasingly solubilized and emulsified.

This study clearly shows the important role that alcohol and hydrocarbon additives play on surfactant adsorption. While small additive molecules increase the solvent power for the surfactant and thus reduce adsorption, larger molecules coaggregate with the surfactant thus lowering the free energy of micellization and hemimicellization and enhancing adsorption. Adsorption of the surfactant in the presence of an additive is independent of the additive concentration if it is present above its aqueous solubility limit.

Acknowledgements

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