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**Surfactant Loss Control In Chemical Flooding: Spectroscopic and
Calorimetric Study of Adsorption and Precipitation On Reservoir Minerals**

**Annual Report for the Reporting Period
September 30, 1992 to September 30, 1993**

**by
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ABSTRACT

The aim of this research project is to investigate mechanisms underlying adsorption and surface precipitation of flooding surfactants on reservoir minerals. Effects of surfactant structure, surfactant combinations, various inorganic and polymeric species, and solids mineralogy will be determined. A multi-pronged approach consisting of micro & nano spectroscopy, microcalorimetry, electrokinetics, surface tension and wettability is used in this study. The results obtained should help in controlling surfactant loss in chemical flooding and in developing optimum structures and conditions for efficient chemical flooding processes.

During the first year of this three year contract, adsorption of single surfactants and select surfactant mixtures was studied at the solid-liquid and gas-liquid interfaces. Surfactants studied include alkyl xylene sulfonates, polyethoxylated alkyl phenols, octaethylene glycol mono n-decyl ether, and tetradecyl trimethyl ammonium chloride. Adsorption of surfactant mixtures of varying composition was also investigated. The microstructure of the adsorbed layer was characterized using fluorescence spectroscopy. Changes in interfacial properties such as wettability, electrokinetics and stability of reservoir minerals were correlated with the amount of reagent adsorbed. Strong effects of the structure of the surfactant and position of functional groups were revealed.

EXECUTIVE SUMMARY

Adsorption of selected individual surfactants on oxide minerals was studied. The aim was to determine the effect of structure on surfactant adsorption at the solid-liquid as well as at the liquid-gas interface and to characterize the microstructure of the adsorbed layers. Electrokinetic behavior was also monitored along with adsorption in order to establish the role of electrostatic forces in determining the adsorption. Adsorption of surfactants at the solid-liquid interface was correlated with changes in interfacial behavior such as wettability and zeta potential. Nonionic polyethoxylated alkyl phenols, anionic xylene sulfonates and cationic tetradecyl trimethyl ammonium chloride (TTAC) were the surfactants studied. Effect of pH was studied both because it is a parameter with first order effect and because pH effects can help in developing mechanisms.

The position of the sulfonate and methyl groups on the benzene ring of the MXS was varied and its effect on the adsorption on alumina was determined. It was observed that the position of the sulfonate group was more critical than that of the methyl groups. Electrostatic attraction is a key force, and shielding of the charged sulfonate groups by the alkyl chain controls adsorption.

The effect of the number of ethylene oxide groups on the adsorption of polyethoxylated alkyl phenols on silica and changes in silica-water interfacial properties was determined since the ethoxyl groups offer a unique opportunity to control the adsorption as well as the hydrophilicity of the surfactant. Wettability of silica after adsorption of nonyl

phenyl polyethoxylated alcohols (with number of polyethylene oxide groups varying from 10-40) was measured using flotation technique to determine the orientation of the adsorbed layer. Interestingly, the amount of silica floated after the nonionic surfactant adsorption was found to be independent of the ethylene oxide chain length within the range tested.

Interactions between surfactants in their mixtures was also studied by determining surface tension of such mixtures and critical micelle concentrations. Mixed micellization of sodium dodecyl sulfate and dodecyl phenoxy polyethoxylated alcohol was found to be non-ideal and regular solution theory was found to adequately describe their interactions. The adsorption of sodium dodecyl sulfate (SDS) and octaethylene glycol mono n-decyl ether ($C_{12}EO_8$) on kaolinite was found to be higher from their mixtures than as single components. This enhanced adsorption was attributed to the hydrophobic chain-chain interactions. The effect of pH on the adsorption of single and surfactant mixtures on kaolinite was elucidated.

The adsorption isotherm of the cationic surfactant, tetradecyl trimethyl ammonium chloride (TTAC), on alumina was determined at two pH values. Changes in the settling rate of alumina suspensions after TTAC adsorption were also followed to describe the evolution of the adsorbed layer. At high surface coverage the alumina was observed to become hydrophilic suggesting the formation of a TTAC bilayer at the surface. Desorption of cationic tetradecyl trimethyl ammonium chloride (TTAC) studied at the alumina-water interface indicated that adsorption was reversible. Electrokinetic measurements supported this observation.

MATERIALS & METHODS

Materials

Surfactants: Anionic, cationic and nonionic surfactants were studied. Sodium dodecyl sulfate (SDS) of greater than 99% purity purchased from Fluka chemicals was used as received. The nonionic surfactants covered a wide range of hydrophobic and hydrophilic chain lengths and were purchased from Nikko Chemicals. The ethoxylated alcohols were of the general structure $C_nH_{2n+1}(CH_2CH_2O)_mH$ or C_nEO_m . The homologues studied were $C_{10}EO_8$, $C_{12}EO_8$, $C_{14}EO_8$, and $C_{16}EO_8$ thus providing an opportunity for studying the effect of surfactant structure on mixture adsorption. In addition to the alcohols, nonyl phenols obtained from Barnett Products, New Jersey with varying ethylene oxide groups were also studied. Cationic tetradecyl trimethyl ammonium chloride (TTAC) of greater than 99% purity purchased from TCI Chemicals, Japan was used as received.

Minerals

Mineral	Surface area (m ² /g)	Supplier	Particle size (μm)
Kaolinite	8.2	Univ. of Missouri	--
Alumina	15.0	Linde (Union Carbide)	0.3
Silica	25.0	Spherosil	40 - 100

Other Chemicals: Pyrene was obtained from Aldrich Chemicals and recrystallized from ethanol. NaCl, HCl and NaOH used were of ACS reagent grade. All solutions were prepared in triply distilled water and at constant ionic strength as indicated in later sections.

Methods

Analytical Techniques: Sodium dodecyl sulfate (SDS) concentration was determined using a two-phase titration method¹. Tetradecyl trimethyl ammonium chloride (TTAC)

concentration was determined by complexing the surfactant with excess SDS and measuring the non-complexed SDS using the two-phase titration. The concentration of ethoxylated alcohol (C_nEO_m) was determined using high pressure liquid chromatography (HPLC) with a C_{18} bonded silica column and a refractive index detector. The solvent used was a 90:10 mixture of acetonitrile and water. Polyethoxylated nonyl phenol concentration was determined by UV absorption at 223 nm.

Adsorption: Adsorption experiments were conducted in 25 cc Teflon capped scintillation vials. One gram of the solid was brought in contact with 5 cc of solution of desired ionic strength for 2 h. Next, 5 cc of salt solution containing surfactant or surfactant mixture of desired concentration was added. The system was conditioned on a wrist action shaker 15 h in the case of silica, 24 h in the case of alumina and 72 h in the case of kaolinite. The suspensions were then centrifuged at 3000-4000 rpm and the supernatant analyzed for residual concentration. Adsorption was calculated based upon surfactant depleted from solution.

Surface tension: Surface tension of surfactant solutions was measured using a Wilhelmy plate or a du Nuoy ring tensiometer.

Zeta potential: Zeta potential of mineral particles before and after adsorption was measured using a Zeta Meter Model D system.

Fluorescence spectroscopy: A Photon Technology International PTI LS-100 was used for fluorescence experiments. The samples containing pyrene dissolved to its maximum solubility in water ($\approx 2 \times 10^{-7}$ kmol/m³) were excited at 335 nm and emission between 365 and 500 nm was recorded.

DISCUSSION

Effect of surfactant structure on adsorption of xylene sulfonates

The position of the functional groups has a significant effect on the adsorption of alkyl xylene sulfonates: when the sulfonate was in the meta position with respect to the methyl groups (124 MXS), surfactant adsorption on alumina was lower than with the sulfonate in the para position (135 PXS - Para 1). But when the position of the methyl group was changed yet maintaining the sulfonate in the para position (125 paraxylene sulfonate - para2), the adsorption isotherm was identical to that of the para1². This suggested that the position of the methyl groups does not play as important a role as the position of the sulfonate. The structure of the surfactants studied is shown below:

Figure 1 4C11 2,4 Meta xylene sulfonate (Meta)

Figure 2 4C11 3,5 Paraxylene sulfonate (Para1)

Figure 3 4C11 2,5 Paraxylene sulfonate (Para2)

Figure 4 4C11 4,5 Orthoxylene sulfonate (OXS)

The adsorption behavior of these xylene sulfonates on alumina is shown in figure 5. The adsorption isotherm of OXS is different from that of meta and para xylene sulfonates.

Figure 5 Adsorption of xylene sulfonates on alumina

The results in figure 5 indicate that the adsorption density of OXS on alumina increases above a certain concentration ($\approx 2 \times 10^{-5}$ kmol/m³). The concentration of OXS was determined by two phase titration and this technique is not sensitive below 10⁻⁵ kmol/m³. At higher concentrations the adsorption of OXS is consistently lower than that of MXS, Para1 as well as Para2. Lower electrostatic attraction because of the shielding of the sulfonate group could be a possible reason for the lower adsorption. This aspect has to be investigated further.

Interfacial Behavior of Nonionic Surfactants

The effect of the number of ethylene oxide (EO) groups on the adsorption behavior of polyethoxylated alkyl phenols on silica was studied. The number of EO groups on the surfactants, 10, 15, 20 and 40, offered a wide range. Pure reagents with 10, 15 and 20 EO groups obtained from Nikko Chemicals, Japan. In addition a commercial grade NP-40 was also used. The generic structure of the surfactants is shown below:

Figure 6 Polyethoxylated nonyl phenol (NP) surfactant (n: 10, 15, 20, 40).

The purity of the surfactants used is evident from the surface tension behavior of the surfactants shown in figure 7; these measurements were performed on the Fisher du Nuoy ring tensiometer. The surface tension of the commercial grade polyethoxylated nonyl phenol with 40 ethylene oxide groups (NP-40) is also shown for comparison. The minimum in surface tension which is indicative of impurities is detected only for the commercial NP-40.

It can be concluded from the results in figure 7 that as the number of ethylene oxide groups are increased the surface activity is decreased and the critical micellization concentration (CMC) is also increased. These agree with our earlier results on the behavior of the nonionic surfactants³.

The adsorption isotherms for some polyethoxylated nonyl phenols (NP) on silica are shown in figure 8. With an increase in the number of ethylene oxide groups on the

Figure 7 Surface tension of polyethoxylated nonyl phenols with 10, 15, 20 & 40 ethylene oxide groups surfactant the adsorption density at the silica water interface is decreased.

The slope of the curve in the pre-adsorption maximum region, which is an indication of cooperative association behavior of the hydrocarbon chains at the solid-liquid interface, decreases as the number of EO groups increases. An increase in the number of EO groups on the surfactant causes the molecule to become bulky. This will provide steric hindrance to the packing of the molecules into aggregates and as a result the adsorption density will be lower. Future work will focus on characterizing the microstructure of the adsorbed layer in terms of size and mobility of aggregates formed at the interface using fluorescence and

Figure 8 Effect of change in number of ethylene oxide groups on the adsorption of polyethoxylated nonyl phenols on silica

electron spin resonance spectroscopic techniques.

The effect of pH on the adsorption of polyethoxylated nonyl phenol with 10 ethylene oxide groups (NP-10) was determined and the results are shown in figure 9. Three different concentrations were studied and the pH was varied from 2.5 to 11.

Interestingly, there was no effect of pH on the adsorption of NP-10 on silica in the ranges studied. The mechanism of adsorption of ethoxylated surfactants on silica is considered to be hydrogen bonding between the ether oxygen of the ethylene oxide group

Figure 9 Effect of pH on the adsorption of polyethoxylated nonyl phenol (NP-10) on silica

and the surface silanol groups⁴. As the pH is raised, the number of silanol groups on the silica surface will decrease and the adsorption of NP-10 could have decreased if the mechanism of adsorption was via hydrogen bonding. To explain this behavior the electrokinetic behavior of silica was determined and the results are given in figure 10.

Silica is negatively charged in the entire pH range studied. By extrapolation, the isoelectric point (IEP) is < 2 . Above pH 4.5 the zeta potential of silica is constant suggesting that there is no change in the charged surface groups above this pH value for this sample. On the basis of this, pH will be expected to have no effect on adsorption of NP-10 on silica above pH 4.5. But from figure 9, it can be seen that the adsorption of NP-10 is constant

Figure 10 Zeta potential of silica

even down to a pH value of 3. We propose that at pH values higher than the IEP the number of silanol groups ($-\text{SiOH}$) on the surface are very few and there is no significant change in their number to affect adsorption drastically. However, this interesting effect merits further investigation using spectroscopic techniques to probe the interfacial region.

Changes in the electrokinetic properties of silica after adsorption of NP-10 and NP-15 are shown in figures 11 and 12 along with the adsorption isotherms. In both cases, adsorption of the nonionic surfactant decreases the surface charge of silica.

It is proposed that the adsorbed layers of NP-10 and NP-15 cause a shift in the shear

Figure 11 Effect of NP-10 adsorption on the zeta potential of silica (pH=6)

Figure 12 Effect of NP-15 adsorption on the zeta potential of silica (pH ≈ 6)

plane resulting in a decrease in the magnitude of the zeta potential. There seems to be no significant difference in the adsorbed layer thickness for NP-10 and NP-15 since their effect

on the surface charge of silica is identical.

The wettability of silica after adsorption of nonionic surfactant was measured by determining flotation using a modified Hallimond tube and the results are shown in figures 13 and 14. The surfactants chosen were nonyl phenols with 10 and 40 ethylene oxide groups. Based on adsorption results it was proposed that the NP-10 formed aggregates at the silica-water interface whereas the bulky NP-40 did not.

Figure 13 Wettability of silica after NP-10 adsorption

hydrogen bonding between the ether oxygens of the EO group and surface silanol groups will expose a hydrocarbon chain to the aqueous phase which renders the silica surface hydrophobic thereby increasing the floatability. Interestingly, the maximum hydrophobicity achieved in the presence of each adsorbed surfactant is identical. It is to be noted that the flotation results in figure 13 and 14 are plotted as a function of initial surfactant concentration. Since the adsorption of NP-10 is significantly higher than NP-40 it is likely that the adsorbed layers for similar initial

Presence and absence of aggregates at the interface can be expected to affect the wettability to different extent. From figures 13 and 14 it is seen that in the absence of surfactant, silica is hydrophilic and floats very little.

Surfactant adsorption via

concentrations will be very different. The residual concentrations could not be measured at the time of flotation. Nevertheless, it is interesting that the flotation recovery reaches a maximum and does not decrease above a certain surfactant concentration.

This suggests that these **Figure 14 Wettability of silica after NP-40 adsorption** surfactants do not form a bilayer at the interface: formation of a bilayer at the interface would create a hydrophilic surface and reduce flotation.

Fluorescence spectroscopy was used to determine the nature of the adsorbed layer in terms of micropolarity. Pyrene monomer fluorescence is used for determining the polarity of unknown environments. The ratio of intensities of the third to the first peaks on the pyrene emission spectrum is sensitive to the polarity of the medium in which the pyrene resides⁵. In polar solvents such as water the value of this ratio (I_3/I_1) is ~ 0.6 but in nonpolar solvents and hydrocarbons it varies from 1-1.7; in sodium dodecylsulfate micelles I_3/I_1 is ~ 1.0. The value of the polarity parameter when pyrene is solubilized in NP-40 micelles is around 0.8. Since this ratio characterizes the polarity it is termed here as the *polarity parameter*.

The adsorption of NP-40 on silica was determined in the presence of low

concentrations of pyrene. There was no effect of the pyrene on the amount of surfactant adsorbed. Fluorescence emission spectra were recorded from the suspension as well as the supernatant to determine the presence of hydrophobic aggregates. The results are shown in figure 15.

Figure 15 Adsorption of NP-40 on silica and characterization of the adsorbed layer using pyrene

At low values of adsorption density (low residual concentration) the value of the I_3/I_1 ratio is ~ 0.6 indicating an aqueous environment. Only above 10^{-3} kmol/m^3 surfactant does the value of the I_3/I_1 ratio increase to ~ 0.8 . At this concentration there are micelles in the supernatant, and they are detected by pyrene. Since the emissions from the suspension and the supernatant are similar it is proposed that there are no hydrophobic aggregates at the

solid-liquid interface in this case. The long ethylene oxide chain prevents aggregation between the hydrocarbon chains. Similar experiments are being conducted with NP-5 and NP-10 surfactants to determine the microstructure of the adsorbed layer.

Interfacial and Solution Behavior of Anionic - Nonionic Surfactant Mixtures

Mixtures of anionic and nonionic surfactants offer improved solution and interfacial properties as compared to that of the individual components. The interactions between two commonly used surfactants, anionic sodium dodecyl sulfate (SDS) and nonionic dodecyl phenoxy polyethoxylated alcohol with some polydispersity in the number of ethylene oxide groups (TRITON X-100) were studied using surface tension, and the interactions were modelled using regular mixing theory. Understanding the activity of the surfactants at the air-water interface will help to explain the differences in the behavior of the surfactants at the solid-liquid interface. The surface tension of mixtures of SDS and TRITON X-100 of varying compositions are shown in figure 16. The measurements were made with a Wilhelmy Plate tensiometer using a sand-blasted platinum plate as the sensor. With an increase in the concentration of the nonionic surfactant, the surface tension of the mixture is drastically reduced.

Table I lists the results obtained for critical micellization concentration (CMC) at different mole fractions (α) of the nonionic surfactant, TRITON X-100.

Figure 16 Surface tension of mixtures of sodium dodecyl sulfate (SDS) and polyethoxylated dodecyl phenol (TRITON)

Table I: Mixed CMC (C^*) at different mole fractions of TRITON X-100

α	0	0.125	0.25	0.50	1.00
C^* (kmol/m ³)	1.6×10^{-3}	4×10^{-4}	3.4×10^{-4}	2.0×10^{-4}	1.8×10^{-4}

Regular mixing theory is based on the assumption that the excess Gibbs free energy of mixing is given by:

$$\Delta G_{mix} = X_1 X_2 W R T \quad (1)$$

where X_1 and X_2 are the mole fractions of the two surfactants in the mixed micelle, W the interaction parameter, R the gas constant and T the temperature. Regular solution also assumes that the excess entropy and volume of mixing are zero and hence the excess enthalpy of mixing is given by:

$$\Delta H_{mix} = X_1 X_2 W R T \quad (2)$$

The interaction parameter W can be evaluated as an experimental parameter from CMC measurements and used to interpret subsequent experiments. If C_1 and C_2 are the CMC values of the pure surfactants and C^* that of the mixed system, the following relationships⁶ permit solution for W in terms of C_1 , C_2 and C^* :

$$\frac{X_1^2 \ln \left(\frac{C^* \alpha}{C_1 X_1} \right)}{(1-X_1)^2 \ln \left[\frac{C^*(1-\alpha)}{C_2 (1-X_1)} \right]} = 1 \quad (3)$$

$$W = \frac{\ln \left(\frac{C^* \alpha}{C_1 X_1} \right)}{(1-X_1)^2} \quad (4)$$

where X_1 is the mole fraction of surfactant 1 in the mixed micelle and α is the mole fraction of surfactant 1 in the total mixed solute. Equation (3) must be solved iteratively for X_1 ,

whereupon substitution of this X_1 into equation (4) results in immediate solution for W . C_1 and C_2 in this case are 1.8×10^{-4} and 1.6×10^{-3} respectively and using values of -3.5 and -4.0 for W , results obtained are shown in Table II.

Table II: Calculated results of X_1 and C^* by regular solution theory

α	$\alpha/(1-\alpha)$	$W = -3.5$		$W = -4.0$	
		X_1	$C^* (10^{-4})$	X_1	$C^* (10^{-4})$
0.05	0.053	0.538	9.16	0.538	8.09
0.10	0.111	0.605	6.31	0.597	5.60
0.125	0.143	0.628	5.56	0.617	4.94
0.20	0.25	0.677	4.22	0.662	3.78
0.25	0.333	0.701	3.69	0.685	3.32
0.30	0.428	0.722	3.31	0.705	2.99
0.40	0.67	0.759	2.78	0.739	2.53
0.50	1	0.791	2.44	0.769	2.24
0.60	1.5	0.821	2.2	0.799	2.04
0.80	4	0.886	1.9	0.863	1.8
0.90	9	0.928	1.82	0.908	1.76
0.95	19	0.957	1.8	0.941	1.76

Experimental data and calculated results are plotted in figure 17. It can be seen that the experimental data show negative deviation from ideal mixing predictions. The effectiveness of regular solution theory can be seen from the fit using $W = -4.0$. The negative values of W results in CMC and monomer concentration values which are less than that predicted by the ideal solution theory. When the two surfactants with dissimilar polar heads form micelles, electrostatic repulsion between the SDS molecules is reduced by the presence of TRITON X-100 molecules.

Figure 17 Correlation of CMC of a mixture of SDS and TRITON with mole fraction of TRITON

Adsorption of Surfactant Mixtures at Solid-Liquid Interfaces

The adsorption of ionic-nonionic surfactant mixtures at the kaolinite-water interface was systematically studied. The system studied was a 1:1 mixture of anionic sodium dodecyl sulfate (SDS) and nonionic octaethylene glycol mono-n-decyl ether ($C_{12}EO_8$). Isotherms obtained for the adsorption of anionic sodium dodecyl sulfate (SDS) on kaolinite are shown in figure 18 (a). The adsorption of SDS decreases as the pH is increased from 5 to 10. Both positive and negative sites coexist on the kaolinite surface and the number of positive sites will decrease with increasing pH. As a result it can be stated that the adsorption

mechanism prevalent here is purely electrostatic. At pH 5, the saturation adsorption is $\approx 1.6 \times 10^{-6} \text{ mol/m}^2$: using a cross-sectional area of $53 \text{ \AA}^2$ for an SDS molecule, this translates into a surface coverage of roughly 56% which suggests that roughly half the surface is covered by positive sites.

Figure 18 Effect of pH on the adsorption on kaolinite of (a) SDS and (b) $C_{12}EO_8$ from SDS/ $C_{12}EO_8$ mixtures.

As in the case for the adsorption of sodium dodecyl sulfate (SDS), $C_{12}EO_8$ adsorption on kaolinite decreases with an increase in pH (figure 18b). A hydrogen bonding mechanism has been proposed for the adsorption of ethylene oxide (EO) groups on oxide surfaces and it can be expected that a similar effect predominates here. Reduced adsorption at higher pH values can be attributed to the deprotonation of the surface hydroxyl groups which will

result in a decrease in the number of hydrogen bonding sites available for $C_{12}EO_8$ adsorption. Using a molecular cross-sectional area of $65 \text{ \AA}^2$ for $C_{12}EO_8$ in the adsorbed state, the surface coverage at saturation can be estimated to be 12% at pH 5.

Unlike alumina which does not adsorb ethoxylated alcohols and silica which adsorbs ethoxylated alcohols but not sodium dodecyl sulfate (SDS), kaolinite adsorbs both SDS and $C_{12}EO_8$ to about the same order of magnitude suggesting that the kaolinite surface exhibits the characteristics of both alumina and silica with respect to the adsorption of these two surfactants.

Adsorption of SDS/ $C_{12}EO_8$ mixtures on kaolinite was also conducted at different pH values. The adsorption of sodium dodecyl sulfate (SDS) from the mixtures is shown in figure 18 (a) and that for octaethylene glycol mono-n-decyl ether ($C_{12}EO_8$) in figure 18 (b). At pH 5, the adsorption of the nonionic $C_{12}EO_8$ is markedly enhanced by the presence of the anionic sodium dodecylsulfate (SDS) suggesting cooperative adsorption through hydrocarbon chain-chain interactions in the adsorbed layer. At pH 10, adsorption of the nonionic $C_{12}EO_8$ is suppressed by the presence of SDS, indicating competition between the anionic SDS and the nonionic $C_{12}EO_8$ for the limited number of common adsorption sites available.

The mechanisms of a pH effect on surfactant mixture adsorption are schematically presented in figure 19. While hydrocarbon chain-chain interaction between the adsorbed surfactant species is predominant at low pH it is not likely to be as predominant at high pH because the adsorbed surfactant species cannot be close to each other due to lack of adjacent adsorption sites for both surfactant species. Instead competition from the anionic

sodium dodecylsulfate (SDS) for limited common adsorption sites leads to suppression of $C_{12}EO_8$ adsorption.

Figure 19 Schematic representation of pH effect on the adsorption of SDS/ $C_{12}EO_8$ mixtures on kaolinite

Fluorescence Probing of Mixed-surfactant Adsorbed Layers

Fluorescence spectroscopy could not be conducted at the kaolinite-water interface since kaolinite quenched the fluorescence signal from pyrene. Therefore fluorescence probing of the adsorbed layer was performed for adsorption on alumina.

The adsorption of mixtures of sodium dodecyl sulfate (SDS) and octaethylene glycol mono-n-decyl ether ($C_{12}EO_8$) on alumina was studied. The I_3/I_1 values of pyrene obtained for the mixed adsorbed layers are given in figure 20 along the isotherms.

It is seen that the polarity parameter is nearly constant along each adsorption

Figure 20 Polarity parameter of pyrene in the adsorbed layer of 1:1 SDS/C₁₂EO₈ mixtures on alumina

aggregates at the alumina-water interface (figure 20). The aggregates at the solid-liquid interface are more compact than micelles so that water molecules are more effectively excluded from the hydrocarbon core.

Table III: Polarity parameter (I_3/I_1) values for surfactant micelles in aqueous solution

Surfactant	Concentration studied (kmol/m ³)	C.M.C. (kmol/m ³)	I_3/I_1
SDS	3×10^{-2}	1.5×10^{-3}	0.88
C ₁₂ EO ₈	1.0×10^{-3}	1.0×10^{-4}	0.80
1:1 SDS/C ₁₂ EO ₈	2.6×10^{-3}	1.1×10^{-4}	0.85

However, the values obtained for the mixed micelle of SDS and C₁₂EO₈ is close to

isotherm and has a value higher than that obtained for the NP-40 adsorbed layer on silica (figure 15). The former is explained if the increased adsorption is realized by self-replication of the surfactant aggregates with the overall structure of the aggregate remaining unaltered. The I_3/I_1 values for surfactant micelles are given in Table III. It is seen that the polarity parameter for SDS micelles is lower than that obtained for SDS

that obtained at the alumina-water interface suggesting that the presence of the ethoxyl chains of the nonionic $C_{12}EO_8$ could be a key factor in determining the polarity in mixed surfactant aggregates. Subsequent studies will be directed towards discerning the evolution of the adsorbed layer in greater detail.

Effect of hydrocarbon chain length of nonionic surfactant on its adsorption

Figure 21 shows the isotherms for the adsorption of the nonionic surfactants C_nEO_8 with different hydrocarbon chain length ($n=10, 12, 14, 16$) on kaolinite.

Figure 21 Effect of hydrocarbon chain length of nonionic surfactant on its adsorption on kaolinite

The isotherms are consistently shifted to the lower concentration region as the hydrocarbon chain length is increased from C_{10} to C_{16} . It can be noticed that the plateau adsorption tends to increase slightly with increase in hydrocarbon chain length. Using a parking area of $9.2 \text{ \AA}^2$ per $(-O-CH_2CH_2-)$ group based upon adsorption on silica, it can be

found that the kaolinite surface is only partly covered by the nonionic surfactant.

Table IV: Surface coverage of kaolinite by nonionic surfactant (C_nEO_8)

Surfactant	Plateau Adsorption mol/m ²	Surface Coverage θ
$C_{12}EO_8$	2.5×10^{-7}	0.11
$C_{14}EO_8$	3.1×10^{-7}	0.14
$C_{16}EO_8$	4.4×10^{-7}	0.19

Subsequent studies will focus on the effect of nonionic surfactant's hydrocarbon chain length on adsorption on kaolinite from 1:1 SDS/ C_nEO_8 mixtures.

Cationic surfactant adsorption on alumina

To determine the effect of surfactant charge on adsorption/desorption behavior, adsorption of a cationic surfactant, tetradecyl trimethyl ammonium chloride (TTAC) was studied at the alumina/water interface. The adsorption isotherms of TTAC on alumina at two different pH values are shown in figure 22. Alumina is positively charged at pH 8 but negatively charged at pH 10 and thus the adsorption of the cationic TTAC is higher when the alumina is negatively charged. There is a sharp increase in the adsorption at $\sim 5 \times 10^{-4}$ kmol/m³ TTAC only at pH 10 which can be attributed to surfactant aggregate formation at the alumina-water interface. At pH 8, negatively charged sites on the alumina surface are proposed to be few and far apart to induce any surfactant aggregation.

The settling rate of the alumina suspensions after TTAC adsorption at pH 10 was measured and the results are shown in figure 23. In the absence of and at low surfactant adsorption, the alumina suspension in water is dispersed and the settling rate is low. Once the surfactant forms aggregates at the interface, the alumina surface becomes hydrophobic

Figure 22 Adsorption of cationic TTAC on alumina at two values of pH.

Figure 23 Settling rate of alumina suspensions after TTAC adsorption at pH 10

and the settling rate is markedly increased. The settling rate decreases above 10^{-3} kmol/m^3 which is proposed to be the concentration at which the TTAC forms a bilayer at the

alumina-water interface exposing a polar surface towards the solution. This model will be tested by measuring the zeta potential of the alumina particles after TTAC adsorption.

Desorption of Cationic Surfactant at Alumina-water Interface

Desorption of TTAC from the alumina surface was studied. The procedure adopted was as follows: the adsorption isotherm of TTAC on alumina was first determined. Supernatant solutions of varying residual concentrations along the isotherm were diluted with water and the slurry conditioned for 15 h. This procedure was repeated several times depending upon the concentration. The results are shown in figure 24. The solid line

Figure 24 Desorption of TTAC from alumina: Dilutions from systems with different residual concentrations.

represents the initial adsorption isotherm.

It is observed that adsorption is reversible in most cases except at low concentrations. At low concentrations, it does appear that there is some hysteresis but these could result from experimental error due to loss of material during dilution.

Electrokinetic

measurements were also performed on the same samples and the results are seen in figure

25. It does appear that the adsorption of cationic TTAC on alumina is reversible. Further studies will concentrate on spectroscopic characterization of the adsorbed layer.

Figure 25 Electrokinetic measurements of TTAC/alumina system after adsorption and upon dilution from systems with different residual concentrations.

SUMMARY

Adsorption/desorption of single surfactants and surfactant mixtures were studied on solids relevant to reservoir minerals. A strong effect of the structure of surfactant on determining its adsorption as well as the microstructure of the adsorbed layer has been demonstrated. The adsorption of surfactants from mixtures is invariably higher than when the surfactant was used alone. This finding has important bearing especially because commercially used surfactants are always mixtures. The role of pH on the adsorption of surfactants was dependent upon the system studied. In ionic systems, increase in pH reduced the adsorption but in nonionic surfactants the effect was much less or insignificant.

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