

Adsorption Behavior of Surfactant Mixtures at Solid-Liquid Interface

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Behavior of surfactant mixtures at solid-liquid interfaces was investigated using an-ionic-nonionic and cationic-nonionic surfactants of different structures. The results show that adsorption of nonionic surfactants on alumina was enhanced significantly by the coadsorption of ionic surfactants. The adsorption behavior of these binary surfactant mixtures was dependent upon the ratio of the two surfactants in the mixture. With an increase in the ionic surfactant content, the adsorption of nonionic surfactant increased and the isotherm shifted to lower surfactant concentrations. Synergism and competition between the ionic and nonionic surfactants were observed in different concentration ranges at different mixing ratios.

Key words: adsorption, surfactant mixtures, solid-liquid interface, surfactant aggregates

Adsorption of surfactants at the solid-liquid interface plays a crucial role in many important industrial processes such as detergency, flotation, and deinking. In many of these applications, the use of surfactant mixtures improves significantly the performance over those of single component systems. In processes such as enhanced oil recovery, on the other hand, surfactant adsorption on reservoir minerals has to be avoided, since it contributes to undesirable reagent loss. Mixed surfactant systems offer several advantages over single components since the adsorption of surfactants on reservoir minerals can be controlled using appropriate composition and solution conditions. As a result, studies on the adsorption and solution behavior of surfactant mixtures have increased significantly in the recent past [1–3].

Surfactant adsorption is related to the chemical potential of the surfactant molecules (monomers) in solution and the nature of the solid. In single surfactant system, the adsorption isotherm usually reaches a plateau when the surfactant equilibrium concentration reaches the CMC. This can be explained by the pseudophase separation model of micelle formation since the monomer concentration of surfactant will be constant above the CMC. When surfactants of different characteristics are present together, they will form mixed micelles with the critical micelle concentration (CMC) varying with the composition of the mixture. Under mixed micellization conditions the chemical potential of monomers will be lower than that for the single surfactant system and this in turn may reduce adsorption at the solid-liquid interface. But, on the other hand, the monomer concentrations and composition of surfactant mixtures

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do not remain constant above the CMC of mixtures. This can be predicted by either ideal solution theory or regular solution theory. This has important implications for the adsorption of surfactant mixtures since the adsorption will continue at the interface even above the mixture CMC. Besides, preferential adsorption may occur from the mixture, and this in turn can change the ratio of the surfactant components in the mixtures and makes the adsorption of mixed surfactants more complex than that in single surfactant systems. Interaction between surfactant mixtures in solutions has been studied for many systems [4–8]. Literature on solution behavior of surfactant mixtures suggests significant deviations in their behavior from ideal mixing. Generally, mixtures of surfactants with similar head groups behave more ideally in solution, whereas large deviations from ideality are observed for mixtures of dissimilar surfactants. In contrast to the case of solutions, there is very little information on interaction of surfactant mixtures at solid/liquid interfaces. In this paper, adsorption of binary mixtures of anionic-nonionic and cationic-nonionic surfactants at different solid-liquid interfaces is discussed. Synergism and competition between the two surfactants and the effects of surfactant structure are discussed. The relationships between the adsorption behavior and monomer concentration are also developed using the regular solution approximation.

MATERIALS AND METHODS

Alumina: Linde A alumina from Union Carbide specified to be 90% α - Al_2O_3 and 10% γ - Al_2O_3 with a mean diameter of 0.3 μm was used as the substrate for adsorption. The specific surface area as measured by the BET technique using nitrogen adsorption with a Quantasorb system was 15 m^2/g .

Kaolinite: Well-crystallized Georgia kaolinite was purchased from the clay repository at the University of Missouri and was converted to Na-kaolinite by ion-exchange [9]. Specific surface area of the sample obtained by nitrogen BET method was 8.2 m^2/g .

Surfactants: Anionic Sodium p-octylbenzenesulfonate, $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, or C_8PhS , was synthesized in our laboratory, and high-performance liquid chromatographic (HPLC) analysis of this compound showed it to be more than 97% isometrically pure. Sodium dodecyl sulfate ($\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$) of > 99% purity was purchased from Fluka Chemicals. The cationic surfactant n-tetradecyl trimethyl ammonium chloride (TTAC), $[\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3]\text{Cl}$, from American Tokyo Kasei, Inc., and the nonionic pentadecyl ethoxylated nonyl phenol (NP-15), $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{15}\text{Na}$ and ethoxylated alcohols ($\text{C}_n\text{H}_{2n+1}(\text{OCH}_2\text{CH}_2)_m\text{OH}$ or C_nEO_m , from Nikko Chemicals, Japan were used as received.

Reagents: Sodium chloride and sodium hydroxide from Fisher Scientific were of A.C.S. reagent grade.

Adsorption: Adsorption experiments were conducted in capped 20 ml vials. Two gram samples of alumina were mixed with 10 ml of 0.03 M NaCl solutions for 1 hour at the test temperature. The pH was adjusted as desired and the suspension allowed to equilibrate further for 1 hour. Then, 10 ml of 0.03 M NaCl solution containing the surfactant(s) at desired concentration was added and the samples were equilibrated for 15 hours. The pH was measured and, if necessary, adjusted using 0.1 M NaOH. The samples were allowed to equilibrate for about 3 more hours after the final pH adjustment and then centrifuged for 25 min. at 5000 rpm and about 20 ml of supernatant pipetted out for analysis.

Surfactant Concentration Analyses: Tetradecyl trimethyl ammonium chloride (TTAC), sodium p-octylbenzenesulfonate, and sodium dodecyl sulfate concentrations were measured using a two-phase titration technique [10]. Pentadecylethoxylated nonyl phenol (NP-15) concentration was analyzed by measuring UV absorbance at 223 or 275 nm using a Shimadzu 1201 W-Vis spectrophotometer.

Alcohol concentrations were measured by high-performance liquid chromatography (HPLC) with a C_{18} bonded silica column and a refractive index detector. The solvent used for HPLC analysis was a 90:10 mixture of acetonitrile and water.

have been studied using this procedure [4–8]. Literature values for the interaction parameter between ethoxylated alcohols and anionic surfactants range from -5 to -2 [12,13], and -4.6 to -1.0 [14–15] for cationic-nonionic mixtures. Compared with these, the interaction parameter obtained for our systems are not very large. Nevertheless, the adsorption behavior of these surfactants was modified measurably as a result of these interactions. This will be discussed later in this paper.

Adsorption of anionic-nonionic surfactant mixtures

The adsorption isotherms of sodium *p*-octylbenzenesulfonate (C_8PhS) and non-ionic surfactant dodecyloxyheptaethoxyethyl alcohol ($C_{12}EO_8$) on alumina are given in Figure 2. The shape of C_8PhS adsorption isotherm is typical of that obtained for long-chain alkanesulfonates on mineral oxides [16]. Above a concentration of $4.5 \times 10^{-4} \text{ kmol/m}^3$, hemimicellization occurs and this region of accelerated adsorption extends to the concentration of $6.5 \times 10^{-3} \text{ kmol/m}^3$, which corresponds to the critical micelle concentration (CMC) of this surfactant. Compared to the adsorption of sulfonate, the plateau adsorption level of the nonionic $C_{12}EO_8$ is more than three orders of magnitude lower. It is apparent that hemimicellization does not occur in this system, as a region of accelerated adsorption is absent.

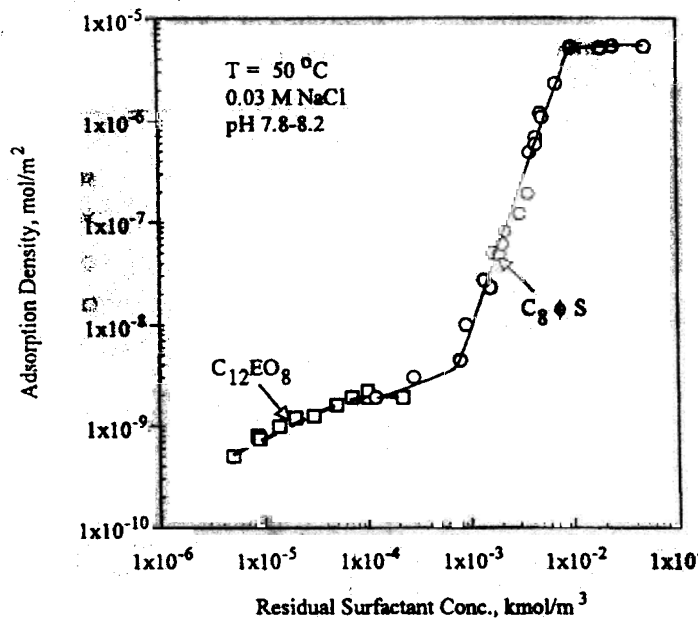


Figure 2. Adsorption of C_8 -benzenesulfonate(O) and $C_{12}EO_8$ alcohol (□) on alumina.

Figure 3 shows the isotherms for adsorption of sodium *p*-octylbenzenesulfonate (C_8PhS) and dodecyloxyheptaethoxyethyl alcohol ($C_{12}EO_8$) on alumina from their 1:1 mixtures. It is seen that the ethoxylated alcohol adsorbs to a much greater extent than the sulfonate, even though it exhibited only trace adsorption in the absence of the sulfonate. The preferential adsorption of $C_{12}EO_8$ from the mixture is also reflected in the surface tension results (Figure 4), where the higher surface tension after adsorption can be considered to result from preferential depletion of the nonionic surfactant from the solution.

between the sulfonate ions in the solloids should enhance sulfonate adsorption by reducing the lateral electrostatic repulsion between the ionic sulfonate head groups. The effect of synergism is also apparent from a comparison of the slopes of the sulfonate adsorption isotherms in the initial hemimicellar region. Co-adsorption of the nonionic surfactant leads to an increase of the slopes to 6.6 from 3.7 for the pure sulfonate adsorption.

Individual component adsorption isotherms for a surfactant mixture initially consisting of 74 mol % sulfonate and 26 mol % alcohol are given in Figure 5. The general shape of the curves and the relative surface activity are similar to the results discussed above for the 1:1 system. However, one striking feature of this system is the increased curvature of the alcohol adsorption isotherm. The slope changes sign between 2×10^{-5} and 3×10^{-5} kmol/m³ and residual concentrations are reduced to 1×10^{-5} kmol/m³ before the onset of adsorption plateau. The surface tension data obtained for the solutions after contact with the alumina clearly support these results. The maximum in surface tension in Figure 6 is caused by higher depletion of the alcohol than of the sulfonate from the solution. A similar trend is also apparent in Figure 4 for the 50 mol % sulfonate system, but to a much less extent. Such a behavior indicates an increase in the adsorption energy of the nonionic species relative to that of the anionic one. As adsorption of the sulfonate increases, the surface becomes more negative and further adsorption of sulfonate becomes unfavorable. The change in the curvature of C₁₂EO₈ isotherm in Figure 5 indicates that incremental sulfonate adsorption requires additional nonionic surfactant coadsorption to reduce electrostatic repulsion, such that the concentration of the nonionic C₁₂EO₈ can actually decrease.

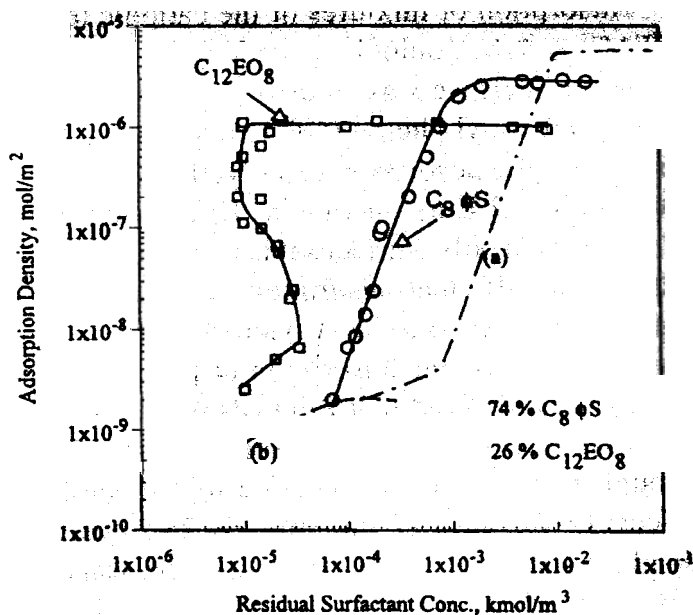


Figure 5. Adsorption of C₈-benzenesulfonate and C₁₂EO₈ alcohol from mixtures at initial mixing ratio of 74 mol% sulfonate and 26 mol% alcohol as a function of individual residual surfactant concentration: (a) adsorption of 100% C₈-benzenesulfonate, (b) adsorption of 100% C₁₂EO₈ alcohol; 50°C; 0.03 M NaCl.

initial mixing
individual surfactant
100% C₁₂EO₈

markedly
more than
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adsorption density at around $5 \times 10^{-4} \text{ kmol/m}^3$ which is due to the formation of surfactant aggregates (solloids)* [20] at the solid-liquid interface. The maximum adsorption density of TTAC on alumina at pH 10 is $\sim 2.5 \times 10^{-6} \text{ mol/m}^2$. This translates to roughly $66 \text{ \AA}^2/\text{molecule}$, which agrees well with values reported for the molecular area at the air/solution interface (61 \AA^2) [19]; this suggests that the adsorption layer is composed of a patch-wise monolayer rather than a bilayer.

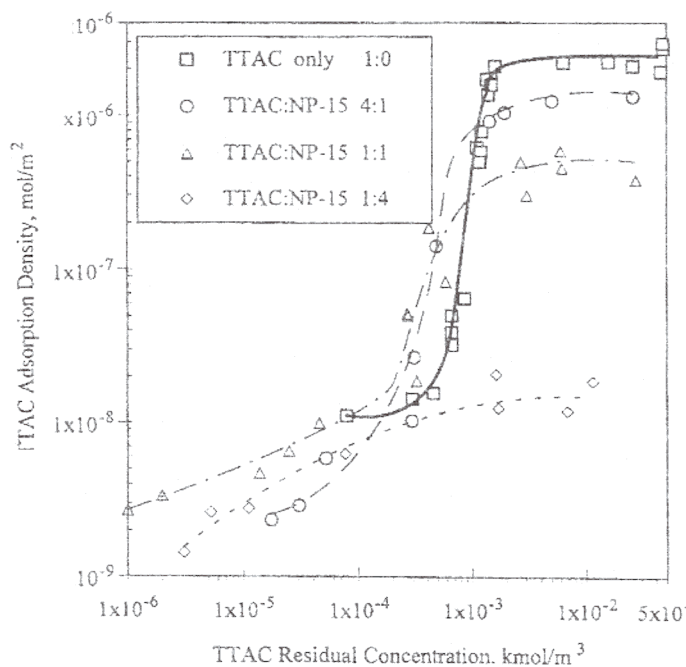


Figure 7. Adsorption of tetradecyl trimethyl ammonium chloride (TTAC) on alumina in the presence and absence of pentadecylethoxylated nonyl phenol (NP-15). pH 10, I.S. 0.03 M NaCl.

The adsorption isotherms of TTAC in the presence of different amounts of NP-15 are also shown in Figure 7. In all these experiments the tetradecyl trimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15) were premixed and then equilibrated with the alumina for 15 hours at pH 10. It is seen that tetradecyl trimethyl ammonium chloride (TTAC) solloid* formation occurs at lower TTAC concentrations in the presence of the nonionic NP-15 but only at the 4:1 and 1:1 TTAC:NP-15 ratios. At the 1:4 ratio, however, the sharp increase in adsorption density, corresponding to such aggregation is not observed over the entire concentration range studied. In all cases, the plateau adsorption density decreases markedly upon the addition of the nonionic surfactant. This is attributed to the competition of the bulky nonionic pentadecylethoxylated nonyl phenol (NP-15) with TTAC for the adsorption sites under saturated adsorption conditions.

* Solloid is the generic term used for adsorbed aggregates, hemimicelles, admicelles and bilayers etc.

TTAC are shown not adsorb on adsorption of NP-15 lower concentration as a agreement with is attributed colloids at the of tetradecyl along the NP-15

species at the alumina-water interface can mask the surface charge and also cause a reduction in the magnitude of the zeta potential, but will not alter the isoelectric point of the alumina. From Figure 9 it is seen that with an increase of NP-15 in the mixture, the zeta potential of alumina decreases drastically, especially in the high concentration range. This observation is in agreement with the adsorption isotherms of TTAC and NP-15 in Figures 7 and 8 respectively. Comparing the isoelectric point (IEP) of alumina in the presence of mixtures to that in the presence of cationic TTAC alone, it can be seen that the IEP is shifted to higher TTAC concentrations with increase in the nonionic NP-15 concentration. Upon examining the adsorption density of TTAC at the isoelectric point (IEP), it is evident that the amount of TTAC necessary to cause charge reversal of the alumina particles is higher in mixtures than that required with TTAC alone. This means that the effect of TTAC in mixtures on zeta potential reduction is less than that of TTAC when present alone. It can be concluded from this that the positive charge of the TTAC ionic head is partially screened by the co-adsorbed nonionic NP-15 molecule. For the case of the 1:4 TTAC:NP-15 system, there is no charge reversal obtained which lends support to our hypothesis. At this mixture ratio, the concentration of the cationic TTAC in the adsorbed layer is low and it is possible that the adsorbed aggregate consists predominantly of NP-15 preventing any possibility of charge reversal. It is interesting to note for TTAC alone that adsorption continues to take place, leading to monolayer coverage even after the particles have become similarly charged (Figures 7 and 9). This highlights the predominating role of the hydrophobic interactions between the hydrocarbon tails in causing adsorption. On the other hand, lack of adsorption of the nonionic pentadecylethoxylated nonyl phenol (NP-15) without the synergism of the cationic TTAC shows the essential role of the electrostatic interaction as well.

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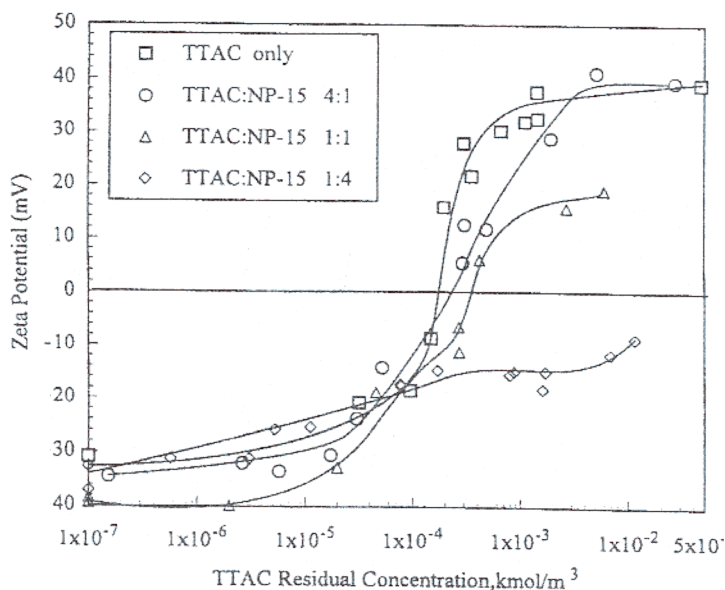


Figure 9. Zeta potential of alumina particles after adsorption of TTAC:NP-15 mixtures of different composition.

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Comparing the adsorption isotherms with these monomer concentrations, it can be seen that the adsorption of NP-15 does not depend upon its monomer concentrations in the mixtures. For example, the adsorption of NP-15 is more significant in 4:1 TTAC:NP-15 mixtures than in other mixtures, but its monomer concentrations are the lowest. This further confirms the postulate that the adsorption of NP-15 requires the anchoring effect of the **pre-adsorbed** TTAC. It is accepted that the residual surfactant concentration at which maximum (or plateau) adsorption density is attained, usually corresponds to the critical micelle concentration (CMC) of the surfactant under the operating conditions. The isotherm shifts to lower concentrations if the CMC of the surfactant is lowered. In the present system, the onset of the plateau for adsorption of NP-15 from its mixtures with TTAC does not correspond to the CMC of the mixtures. For example, the CMC of the 4:1 mixture is the highest of the mixtures (2.7×10^{-4} M) but the isotherm of NP-15 from this mixture is located in the lowest concentration region (Figure 8). This implies that the adsorption of NP-15 is controlled not only by the CMC of its mixture but also by the adsorption of TTAC, the change in monomer composition and the structure of the adsorbed layer.

In contrast to nonionic NP-15, the adsorption density of TTAC corresponds to its monomer concentrations in the mixtures. Higher the TTAC monomer concentrations, higher is its adsorption density. Considering the synergism and steric hindrance in this system, it may be concluded that all these phenomena will be decided by the relative **as well as** absolute quantities of NP-15. If the relative and absolute quantities of NP-15 are lower, synergism between these two surfactants is seen. In the high concentration range or at high NP-15 mixing ratio, the absolute quantity of NP-15 is high, and steric hindrance will be dominant thus suppressing the adsorption of TTAC.

ixtures calculated

Effect of surfactant structure on the adsorption of mixture

To understand the effect of surfactant structure on the adsorption of mixed surfactant system, the adsorption of 1:1 SDS/ C_nEO_8 ($n = 10, 12, 14, 16$) mixtures on kaolinite was studied. The results are shown in Figure 12 and 13. It is interesting to note from Figure 12 that the isotherms for the adsorption of sodium dodecyl sulfate (SDS) are identical when the hydrocarbon chain length of the nonionic surfactants is equal to or longer than that of the anionic SDS (C_{12}). When the hydrocarbon chain length of the nonionic surfactant is shorter ($C_{10}EO_8$) than that of the anionic SDS, however, a different isotherm is obtained. The presence of the anionic SDS is seen in Figure 13 to enhance the plateau adsorption of the nonionic C_nEO_8 and the isotherms are shifted to lower concentration regions. This structure effect on surfactant mixture adsorption is schematically illustrated in Figure 14. When the hydrocarbon chain length of the nonionic surfactant is equal to or longer than that of the anionic SDS, the hydrocarbon chains of SDS are equally shielded from hydrophilic environment by the hydrocarbon chains of the co-adsorbing nonionic surfactant. The identical residing environment leads to a common isotherm for SDS adsorption on kaolinite. When the hydrocarbon chain of nonionic surfactant is shorter than that of the anionic SDS, however, part of the SDS hydrocarbon chain is exposed to the hydrophilic environment (aqueous solution or the hydrophilic ethoxyl chains of the

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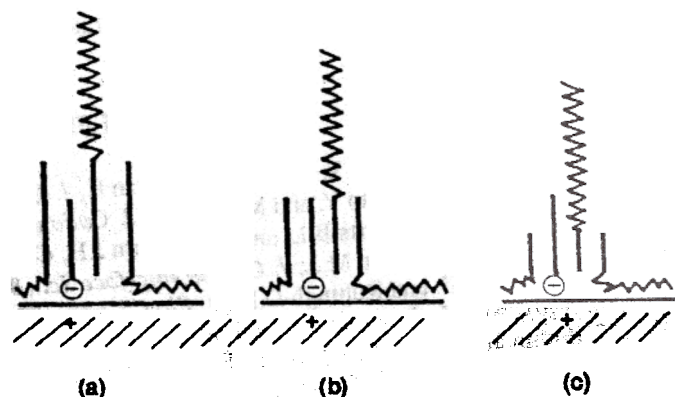


Figure 14. Schematic presentation of the effect of nonionic surfactant hydrocarbon chain length on the adsorption of the anionic sodium dodecyl sulfate (SDS). (a) Nonionic surfactant hydrocarbon chains longer than that of SDS; (b) Nonionic surfactant hydrocarbon chain length equal to that of SDS; (c) Nonionic surfactant hydrocarbon chain length shorter than that of SDS, partially exposing SDS hydrocarbon chains to the aqueous solution or the hydrophilic ethoxyl chains of the nonionic surfactant.

SUMMARY AND CONCLUSIONS

Mixed surfactant systems exhibit more complex behavior than single surfactant systems. Nonionic surfactants studied here show no adsorption or only trace adsorption on alumina, but the adsorption of these surfactants were significant in the presence of an ionic surfactant in the system. It is proposed that the electrostatic adsorption of ionic surfactants provides a sufficient number of hydrophobic sites for solloid type adsorption of nonionic surfactant. The interaction parameter shows molecular level association between tetradecyl trimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15) to be weaker than that between anionic and nonionic surfactants. Nevertheless, significant adsorption of the nonionic NP-15 occurred as a result of the above interactions. Presence of the cationic TTAC essentially forced the adsorption of NP-15 on a surface (alumina) where the latter normally does not adsorb. The adsorption densities of both TTAC and NP-15 depend on the composition of the surfactant mixture. Presence of coadsorbed NP-15 increased the adsorption of TTAC below saturation adsorption and decreased it above. While the increase under sub-monolayer coverage is attributed to reduced repulsion between the cationic heads owing to shielding by the nonionic surfactant, the decrease in saturation conditions is attributed to competition between the nonionic NP-15 and the cationic TTAC for adsorption sites. The results also show the important role of surfactant structure on the adsorption of surfactant mixtures. Importantly, the opportunity to manipulate the adsorption behavior of surfactant mixtures by adjusting the relative structural parameters of surfactants, when the interactions between various components are well understood should be noted.

f C_nEO_8 from