

Adsorption Behavior of Cationic and Nonionic Surfactant Mixtures at the Alumina–Water Interface

LEI HUANG, C. MALTESH, AND P. SOMASUNDARAN¹

Langmuir Center for Colloids and Interfaces, Columbia University, New York, New York 10027

Received March 6, 1995; accepted June 7, 1995

The solution and interfacial behavior of surfactant mixtures was investigated using a cationic surfactant, tetradecyl trimethyl ammonium chloride (TTAC), and a nonionic surfactant, pentadecylethoxylated nonyl phenol (NP-15), with alumina as the substrate. The cationic TTAC adsorbed at the alumina–water interface as a result of electrostatic attraction at pH ~10 whereas the nonionic NP-15 did not. Interestingly, in the mixed surfactant system, the tetradecyl trimethyl ammonium chloride forced adsorption of the NP-15 as a result of hydrophobic interactions between the adsorbed surfactant chains at the alumina–water interface. The adsorption behavior was dependent upon the ratio of the two surfactants in the mixture as well as the order of addition. With an increase in TTAC content, the adsorption density of NP-15 increased and the isotherm shifted to lower surfactant concentrations. The adsorption of TTAC decreased under conditions of saturation adsorption due to the bulkiness of the coadsorbed NP-15 as well as competition for common adsorption sites. However, below saturation adsorption conditions, the adsorption of TTAC was increased due to synergistic interactions between the cationic and nonionic heads leading to reduced repulsion among the cationic headgroups. Zeta potential measurements showed that, with an increase of NP-15 in the mixtures, the positive charge of the TTAC was partially screened by the coadsorbed NP-15. Surface tension of the surfactant mixtures was also measured, and regular solution theory was used to model the interactions between the surfactants. Monomer concentrations obtained using the theory were correlated with the adsorption tendencies and it was seen that TTAC adsorption corresponded with its *monomer concentration* but that of NP-15 did not, suggesting the need for adequate theories for interactions between surfactants. © 1996 Academic Press, Inc.

Key Words: ethoxylated alcohols; cationic–nonionic surfactant mixtures; surfactant mixture adsorption; alumina–water interface; tetradecyl trimethyl ammonium chloride (TTAC).

INTRODUCTION

The 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 sig-

nificantly the performance over those of single component systems. In processes such as enhanced oil recovery, however, 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 the 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. 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 can reduce adsorption at the solid–liquid interface. Interaction between surfactants in mixtures has been studied for several systems (4–8). Literature on solution behavior of surfactant mixtures suggests significant deviation 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, especially for the cationic–nonionic surfactant system, which has wide application in several consumer products. The regular solution approximation that has been applied to treat nonideal mixing in solutions has also been extended to model adsorption at the liquid–air interface (9, 10). Although regular solution theory has been criticized in the past (11), it has provided a very useful means to describe the adsorption behavior of mixed surfactant aggregates. In our study, adsorption of binary mixtures of a cationic surfactant, tetradecyl trimethyl ammonium chloride (TTAC), and a nonionic surfactant, pentadecylethoxylated nonylphenol (NP-15), was investigated at alumina–water interface. The synergism and competition between the two surfactants are discussed and rela-

¹ To whom correspondence should be addressed.

tionships between adsorption behavior and monomer concentration are developed using the regular solution approximation.

MATERIALS AND METHODS

Alumina. The substrate for adsorption was 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 and was used as received. The specific surface area was 15 m^2/g , as measured by the BET technique using nitrogen adsorption on a Quantasorb system. In this measurement the sample was degassed at 250°C for 12 h.

Surfactants. The cationic surfactant *n*-tetradecyltrimethylammoniumchloride (TTAC), $[\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3]\text{Cl}$, from American Tokyo Kasei, Inc., and the nonionic pentadecylethoxylated nonyl phenol (NP-15), $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{15}\text{H}$, from Nikko Chemicals, Japan, were used as received. Surface tension measurements confirmed the high purity [$>99\%$] of these samples.

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 h at room temperature. The pH was adjusted as desired and the suspension allowed to equilibrate further for 1 h. 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 h. The pH was measured and, if necessary, adjusted using 0.1 *M* NaOH. The samples were allowed to equilibrate for about three more hours after final pH adjustment and then centrifuged for 25 min at 5000 rpm; about 20 ml of supernatant was then removed with a pipette for analysis.

Surfactant concentration analyses. Tetradecyltrimethylammoniumchloride concentration was measured using a two-phase titration technique (12). Pentadecylethoxylated nonyl phenol concentration was analyzed by UV absorbance at 223 or 275 nm using a Shimadzu 1201 UV-Vis spectrophotometer.

Surface tension. Surface tension of aqueous surfactant solutions was measured using a Fisher Model 20 ring tensiometer and applying appropriate correction factors.

Electrokinetic studies. Zeta potential measurements were made using a PEN KEM, Inc. Laser zee meter Model 501 system.

Solution conditions. All experiments were conducted at an ionic strength of 0.03 *M* NaCl and at a pH of 10.0 ± 0.5 . Triply distilled water of conductivity $1-2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ was used for preparing all solutions.

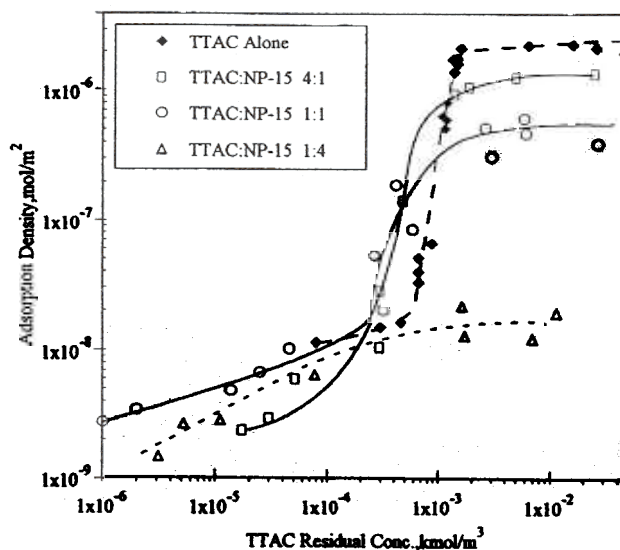


FIG. 1. Adsorption of tetradecyl trimethyl ammonium chloride (TTAC) on alumina in the presence and absence of pentadecylethoxylated nonyl phenol (NP-15). pH 10, I.S. 0.03 *M* NaCl.

RESULTS AND DISCUSSION

The adsorption of mixtures of the cationic tetradecyl trimethyl ammonium chloride and the nonionic pentadecylethoxylated nonyl phenol was studied at the alumina-liquid interface at several ratios. The nonionic pentadecylethoxylated nonyl phenol does not adsorb at the alumina-water interface. In a study on the adsorption of polyethoxylated monolaurate (ML-*n*) and polyethoxyl lauryl ether (LE-*n*) on titania, Fukushima and Kumagai (13) concluded that for adsorption on polar surfaces it is necessary that the nonionic surfactant have a moiety which has sufficient adsorption force to overcome the strong interaction between water molecules and the ethylene oxide groups. This observation is similar to our earlier results on the adsorption of polyethylene oxide (PEO) on different minerals (14). It was reported that PEO adsorbs on silica but not on alumina or hematite, and it was proposed that for PEO to adsorb on oxide surfaces, the polymer has to displace enough water molecules bonded to the solid surface and create a strong entropic effect. In the case of the strongly hydrated alumina surface the polymer cannot displace sufficient water molecules necessary for adsorption. It is therefore reasonable that NP-15 also does not adsorb on alumina.

The cationic surfactant tetradecyl trimethyl ammonium chloride, however, does adsorb on alumina at pH 10 (Fig. 1). At this pH the alumina surface is negatively charged (isoelectric point of alumina is pH 8.9) and hence the electrostatic attraction with the cationic TTAC will be dominant. There is a sharp increase in the adsorption density at around $5 \times 10^{-4} \text{ kmol/m}^3$ which is due to the formation of surfactant aggregates (solloids) at the solid-liquid interface. The maxi-

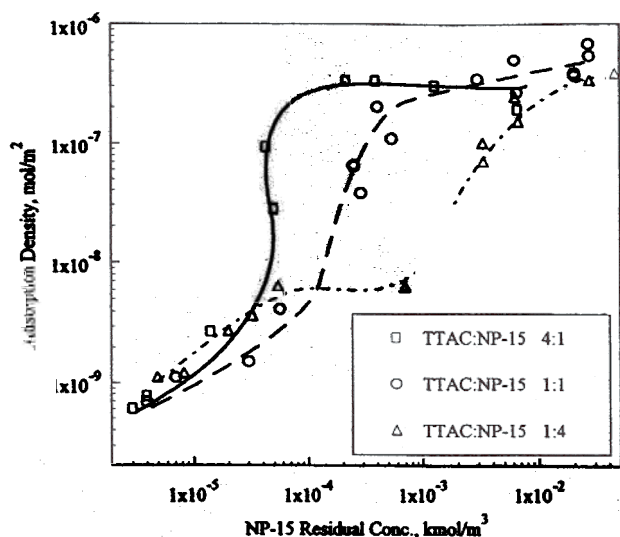


FIG. 2. Adsorption of pentadecylethoxylated nonyl phenol (NP-15) on alumina in the presence of varying amounts of tetradecyl trimethyl ammonium chloride (TTAC). pH 10, I.S. 0.03 *M* NaCl.

imum adsorption density of TTAC on alumina at pH 10 is $\sim 2.5 \times 10^{-6}$ mol/m². This translates to roughly 66 Å²/molecule which agrees well with values reported for the molecular area at the air/solution interface (61 Å²) (15), which suggests that the adsorption layer is composed of a monolayer rather than a bilayer.

The adsorption isotherms of TTAC in the presence of different amounts of NP-15 are also shown in Fig. 1. In all these experiments the tetradecyl trimethyl ammonium chloride and pentadecylethoxylated nonyl phenol were pre-mixed and then equilibrated with the alumina for 15 h at pH 10. It is seen that tetradecyl trimethyl ammonium chloride hemimicelle 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 with TTAC for the adsorption sites under saturated adsorption conditions.

The adsorption isotherms of NP-15 from different mixtures with TTAC are shown in Fig. 2. As mentioned earlier, the pure nonionic surfactant NP-15 does not adsorb on alumina, but it is seen here that the presence of TTAC causes significant adsorption of the NP-15. With an increase in TTAC content in the mixtures, the adsorption of NP-15 is enhanced significantly, and the adsorption isotherms are shifted to lower concentration ranges. The peculiar S-shaped isotherm obtained for NP-15 adsorption as a function of NP-15 residual concentration should be noted and is in agreement with our previous work (2). This is attributed to

the more effective coadsorption of NP-15 as the number of TTAC aggregates at the alumina-water interface increases. It is to be noted that the concentration of tetradecyltrimethylammoniumchloride does vary from point to point along the NP-15 adsorption isotherm.

The NP-15 molecules are much larger than the TTAC molecules and the adsorption of the pentadecylethoxylated nonyl phenol will reduce the area available for TTAC. The microstructure of the hemimicelles and micelles will be different in the single surfactant and the mixed surfactant systems particularly due to the shielding of the ionic heads of the tetradecyl trimethyl ammonium chloride by the coadsorbed NP-15. This in turn will reduce electrostatic attraction between the negatively charged alumina surface and the positively charged TTAC molecules, thereby reducing TTAC adsorption density. This hypothesis was tested by monitoring the zeta potential after adsorption and the results are shown in Fig. 3. The zeta potential of alumina particles will be decided mainly by the adsorption of the oppositely charged TTAC molecules. It is recognized that the nonionic surfactant species at the alumina-water interface can also 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 Fig. 3 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 Figs. 1 and 2, respectively. Comparing the isoelectric point (IEP) for alumina in the presence of mixtures to that in the presence of TTAC alone, it can be seen that the IEP is shifted to higher TTAC concentrations with increase in the NP-15 concentration. Upon examining the adsorption density of TTAC at the isoelectric point, it is evident that the amount of TTAC necessary to cause charge reversal of the alumina particles is higher in mixtures than

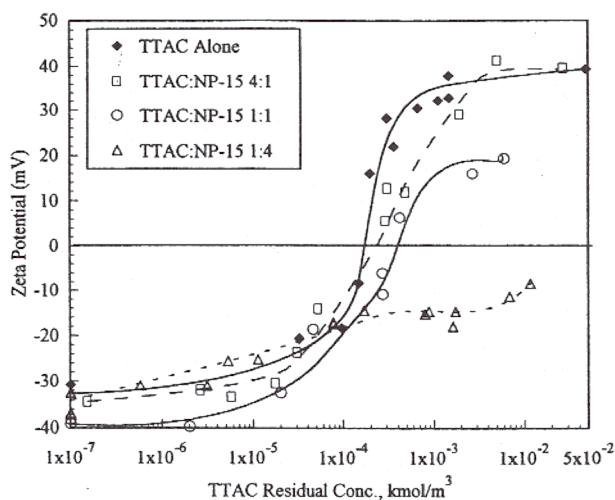


FIG. 3. Zeta potential of alumina particles after adsorption of TTAC:NP-15 mixtures of different composition. pH 10, I.S. 0.03 *M* NaCl.

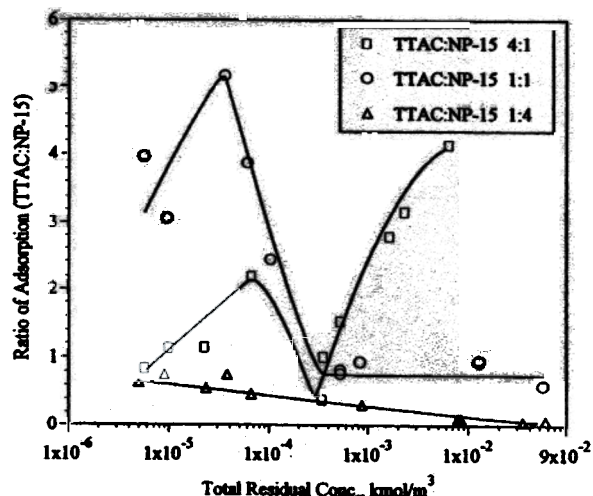


FIG. 4. Ratio of adsorption densities of TTAC:NP-15 on alumina for different surfactant mixtures. pH 10, I.S. 0.03 M NaCl.

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 coadsorbed 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 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 (Figs. 1 and 3). This suggests the predominant role of hydrophobic interactions between the hydrocarbon tails in causing adsorption. On the other hand, lack of adsorption of the *nonionic* pentadecylethoxylated nonyl phenol without the synergism of the *cationic* TTAC shows the essential role of the electrostatic interaction as well.

The ratio of adsorption densities of TTAC and NP-15 at the alumina-water interface is examined in Fig. 4 as a function of the total residual concentration. It can be seen that the ability of the two surfactants to cooperate/compete at the alumina-water interface changes over the entire concentration range. This suggests that the monomer composition and adsorption mechanism are changing over the concentration range studied.

Order of Addition

In the results discussed so far, the cationic and nonionic surfactants were mixed *together* in solution prior to addition to the alumina suspension for adsorption. The effect of the order of addition on the adsorption behavior was determined

and the results obtained are shown in Fig. 5. Since the NP-15 does not adsorb on alumina by itself, only the TTAC could be preadsorbed and its subsequent effect on NP-15 adsorption determined.

Preadsorbed TTAC functions as anchor molecules for NP-15 and causes adsorption of the nonionic surfactant. With an increase in preadsorbed TTAC density the adsorption of NP-15 also increases and the adsorption isotherms are shifted to lower NP-15 concentrations. It is also observed that once the TTAC forms hemimicelles at the alumina-water interface there is no further effect of increasing the preadsorbed TTAC density on the adsorption of NP-15. Desorption and reorientation of surfactants adsorbed as aggregates will depend to a large extent on the activation barrier involved in dehemimicellization. The results also show that the order of addition of the surfactants has a marked effect on the adsorption of NP-15. If NP-15 and TTAC were premixed and added to the alumina suspension together, the adsorption density of NP-15 is higher, particularly in the low concentration range. This indicates that NP-15 adsorption from mixtures with TTAC is controlled by the packing of the molecules at the alumina-water interface.

Interactions between Tetradecyl Trimethyl Ammonium Chloride and Pentadecyl Ethoxylated Nonyl Phenol in Solution

In an attempt to correlate changes in monomer concentration of the individual surfactants in the mixtures with their adsorption behavior, interactions between tetradecyl trimethyl ammonium chloride and pentadecyl ethoxylated nonyl phenol in bulk solution were studied using surface

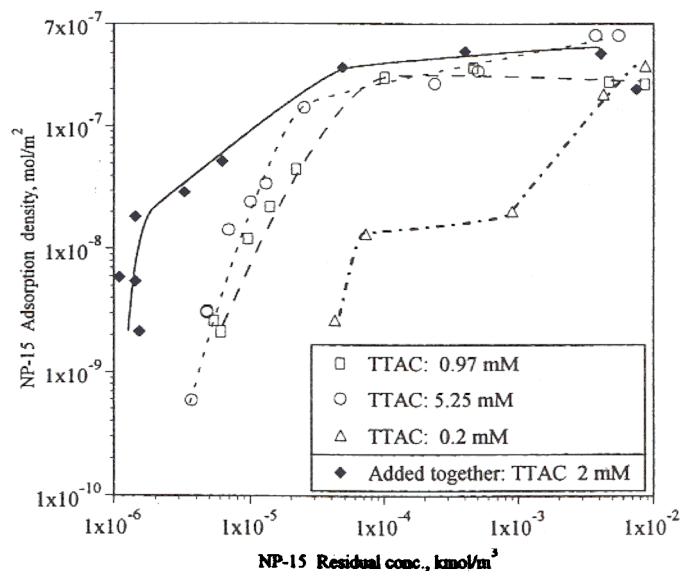


FIG. 5. Effect of TTAC order of addition on NP-15 adsorption on alumina, varying amounts of preadsorbed TTAC and NP-15 added together with TTAC. pH 10, I.S. 0.03 M NaCl.

TABLE 1

Critical Micelle Concentrations (CMCs) of Tetradecyl Trimethyl Ammonium Chloride (TTAC) and Pentadecylethoxylated Nonyl Phenol (NP-15) Mixtures of Varying Composition

Surfactant mixture ratio	CMC (kmol/m ³)
TTAC alone (0% NP-15)	1.2×10^{-3}
4:1 TTAC:NP-15 (20% NP-15)	2.7×10^{-4}
1:1 TTAC:NP-15 (50% NP-15)	1.7×10^{-4}
1:4 TTAC:NP-15 (80% NP-15)	1.1×10^{-4}
NP-15 alone (100% NP-15)	9.8×10^{-5}

tensiometry and regular solution theory. The surface tension of aqueous solutions of tetradecyl trimethyl ammonium chloride alone and pentadecylethoxylated nonyl phenol alone along with that of mixtures of varying composition were determined and the critical micelle concentrations obtained from these measurements are listed in Table 1. As can be expected, the CMC of the nonionic NP-15 is lower than that for the TTAC, but the mixtures are not as surface active as the nonionic surfactant alone (higher CMC).

Regular solution approximation (5). The regular solution approximation is introduced by assuming that the excess entropy of mixing is zero. In the case of mixed surfactant systems, an interaction parameter, β , is defined which can be interpreted as a parameter representing the excess heat of mixing. The net interaction parameter, β , in a binary mixed surfactant system can be determined from a single measured value of the mixed CMC and the CMCs of the pure surfactant components. This is directly obtained following iterative solution of the following equation:

$$\beta = \ln \left[\frac{\alpha_1 \cdot C_{\text{mix}}^*}{x_1 \cdot C_1^*} \right] / (1 - x_1)^2$$

$$= \ln \left[\frac{\alpha_2 \cdot C_{\text{mix}}^*}{(1 - x_1) \cdot C_2^*} \right] / x_1^2,$$

where α_1 and α_2 are mole fractions of the component surfactants in the mixture, C_1^* and C_2^* are CMCs of the pure surfactant components, C_{mix}^* is the CMC of the mixed surfactant system, and x_1 is the mole fraction of surfactant 1 in the mixed micelle.

The critical micelle concentrations of the mixtures are plotted in Fig. 6 as a function of NP-15 composition. The regular solution model was used to fit these, and an interaction parameter (β) between -1.5 and -1.2 was obtained. A considerable number of binary mixed micellar systems have been studied using this procedure (4–8) and the interaction parameters obtained are about -25.5 for cationic–anionic systems (4), -4.6 to -1.0 (16, 17) for anionic–

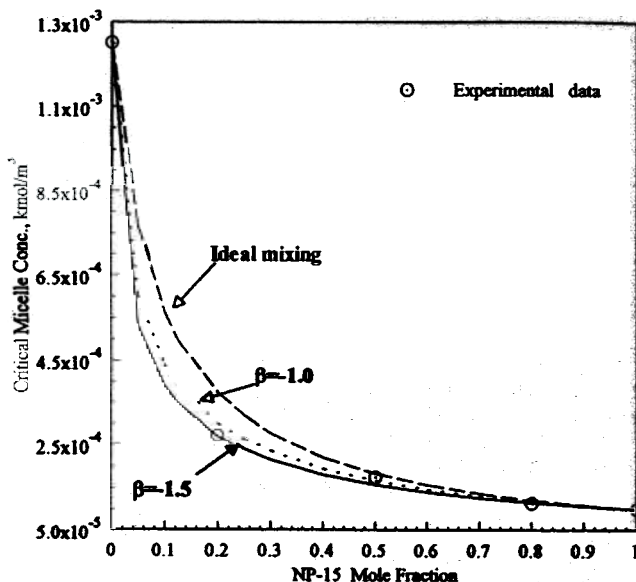


FIG. 6. Measured CMC and theoretical CMC calculated from ideal mixing and regular mixing theories for mixtures of TTAC and NP-15. I.S. 0.03 M NaCl.

nonionic mixtures, and -0.2 for cationic–cationic mixtures (6). Compared with these, the interaction parameter (β) obtained for this system is not very large. In addition to the type of the mixture, the interaction parameter will also be affected by the structure of the surfactant molecules as well as the ionic strength. The monomer concentrations of different mixtures in this system were determined using regular solution theory and an interaction parameter of -1.5 . The results obtained are shown in Figs. 7–9. Comparing the

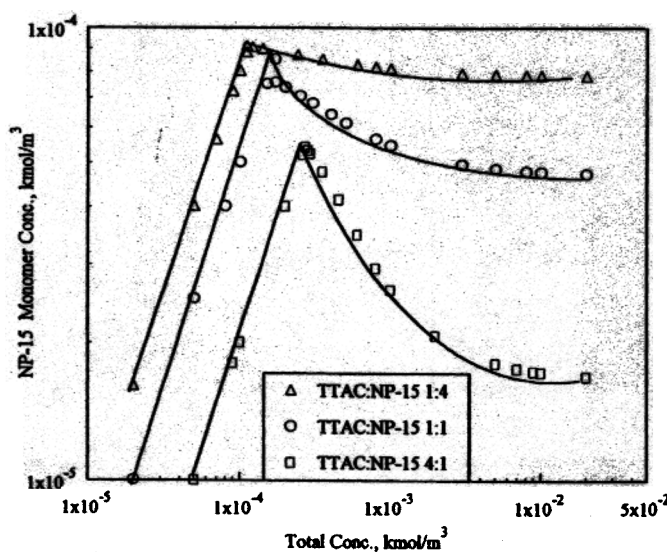


FIG. 7. NP-15 monomer concentrations in different TTAC:NP-15 mixtures calculated using regular solution theory with an interaction parameter (β) = -1.5 .

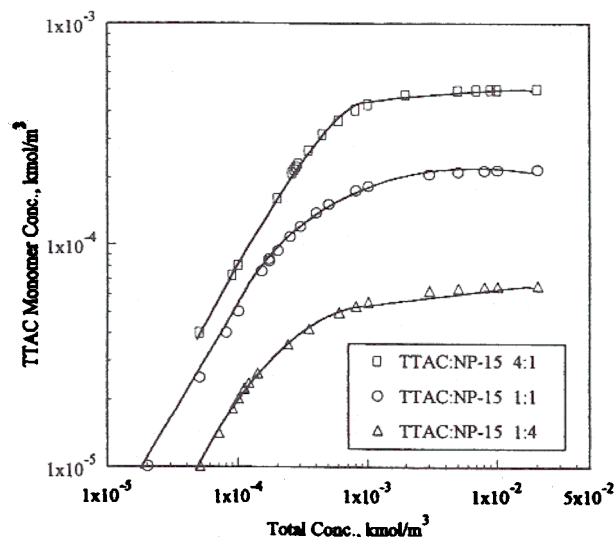


FIG. 8. TTAC monomer concentrations in different TTAC:NP-15 mixtures calculated using regular solution theory with an interaction parameter (β) = -1.5.

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 *preadsorbed* 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 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 (Table 1) but the isotherm of NP-15 from this mixture is located in the lowest concentration region (Fig. 2). 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.

The adsorption density of TTAC corresponds to its monomer concentrations in the mixtures. The higher the TTAC monomer concentrations, the higher is its adsorption density. It is interesting to compare the curves of monomer concentration ratios (Fig. 9) with the curves of adsorption density ratios in this mixture system (Fig. 4). The adsorption behavior in this system depends on the relative ratio of the monomer concentrations. Considering the synergism and steric hindrance in this system, it may be concluded that all these phenomena will be decided by the relative *and* absolute

quantity of NP-15. If the relative and absolute quantity of NP-15 is lower, synergism between these two surfactants is seen. At high concentrations the absolute quantity of NP-15 is high, and steric hindrance will be dominant thus suppressing the adsorption of TTAC. This is proposed to be the reason for the maximum in the ratio in Fig. 4 at low concentration range. For the 1:4 TTAC:NP-15 mixture there is no maximum because the relative quantity of NP-15 is very high.

SUMMARY AND CONCLUSIONS

Interactions between a cationic surfactant and a nonionic surfactant at the solid-liquid interface were studied by determining the adsorption isotherms of individual and mixed surfactants at the alumina-water interface and modeling the same using the regular solution theory. While the cationic tetradecyl trimethyl ammonium chloride adsorbed on the negatively charged alumina as expected, the pentadecylethoxylated nonyl phenol adsorbed only in the presence of the cationic surfactant. The interaction parameter determined indicated that molecular-level association between tetradecyl trimethyl ammonium chloride and pentadecylethoxylated nonyl phenol is weaker than that between an anionic and a nonionic surfactant. Nevertheless, significant adsorption of the nonionic NP-15 occurred as a result of these interactions. Presence of TTAC forced the adsorption of NP-15 on a surface (alumina) where the latter normally does not adsorb. The adsorption density of both TTAC and NP-15 was dependent upon the composition of the surfactant mixture. Presence of coadsorbed NP-15 increased the adsorption of TTAC below saturation adsorption and decreased it above. The increase under submonolayer coverage is attributed to re-

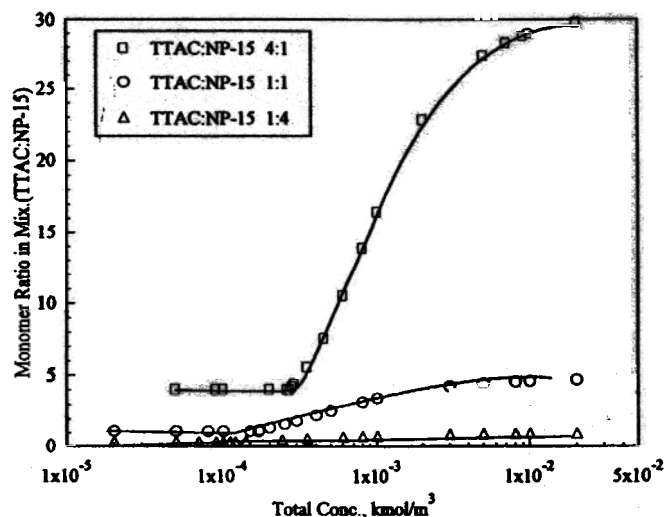


FIG. 9. Ratio of NP-15 to TTAC monomer concentrations in different mixtures calculated using regular solution theory with an interaction parameter (β) = -1.5.

duced repulsion between the cationic heads owing to shielding by the nonionic surfactant, and the decrease under saturation conditions is attributed to competition between NP-15 and TTAC for adsorption sites. Interestingly the adsorption of NP-15 on alumina was not dependent on its monomer concentration but on the [TTAC]:[NP-15] ratio. The mode of addition of the TTAC:NP-15 mixture also had a significant effect on the adsorption densities of both surfactants. Adsorption was higher when the two surfactants were premixed than that when the TTAC was preadsorbed. Evidently coadsorption of NP-15 is not as easily achieved once the cationic surfactant forms colloidal aggregates on the solid particles. Thus the amount of each surfactant adsorbed and possibly the nature of the adsorbed layer are dependent both on the surfactant mix and the mode of addition.

ACKNOWLEDGMENTS

The Department of Energy (DE-AC22-92BC14884) and the National Science Foundation (CTS-9212759) provided support for this work.

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