

Desorption Behavior of Surfactant Mixtures at the Alumina–Water Interface

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The desorption behavior of cationic–nonionic surfactant mixtures, tetradecyltrimethylammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15), at the alumina–water interface was studied. It has been found that while nonionic NP-15 itself does not adsorb at alumina–water interface, it will do so with cationic TTAC preadsorbed at the interface. During the desorption process, however, the presence of NP-15 in the system was discovered to cause desorption of TTAC. This is attributed to changes in equilibrium among surfactant monomers, mixed micelles, hemimicelles, and solloids upon the addition of NP-15: The cationic TTAC species at the interface is solubilized in NP-15 rich micelles in the bulk and perturb the equilibrium. This in turn is proposed to cause the desorption of NP-15 significant. The desorption behavior in the mixed surfactant system depends on the mixing ratio of surfactants in the mixtures. In nonionic NP-15 rich mixtures, negative hysteresis is observed for the desorption of both TTAC and NP-15. In cationic TTAC rich mixtures, the effect of NP-15 on the desorption of TTAC is limited and the desorption of TTAC is similar to that in single TTAC system; in this case some positive hysteresis is observed for both TTAC and NP-15.

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Key Words: adsorption/desorption; cationic surfactant; nonionic surfactant; alumina interface; surfactant mixtures.

INTRODUCTION

Adsorption of surfactants at solid–liquid interface plays a crucial role in many important industrial applications. Most of these applications of surfactants involve use of *mixtures* of surfactants (1–3). Since technical-grade surfactants are mixtures of chain length/isomers, which often perform better than the individual components alone: when different surfactants are mixed together, they usually exhibit synergistic or antagonistic effects (4–6). This makes the adsorption from mixed surfactants and their effects a more complex process. On the other hand, this also makes it possible to control the behavior of surfactants at interfaces and utilize them more efficiently. Toward this purpose it becomes help-

ful to understand the adsorption and solution behavior of surfactant mixtures (7–10).

While the adsorption of surfactants has been studied widely, the desorption behavior of surfactant system has received only scant attention (11–15). Although the adsorption of most surfactants on mineral oxides is usually considered as a process of physical adsorption, the results obtained for the desorption of single surfactants indicate that the adsorption/desorption is not completely reversible, and non-equilibrium effects due to changes in system variables such as pH, ionic strength, and dissolved mineral species, can make adsorption/desorption processes more complex. As indicated above, in contrast to the information available on adsorption, the desorption behavior, especially of *mixed* surfactants, is relatively unknown despite its practical significance on many applications. In this work, desorption behavior of cationic and nonionic surfactant mixtures has been studied systematically, and the effect of mixed micelles on the desorption has been discussed.

MATERIALS AND EXPERIMENTAL PROCEDURES

Alumina. Linde A alumina purchased from Union Carbide Corp. was specified to be 90% α -Al₂O₃ and 10% γ -Al₂O₃ and to have a mean diameter of 0.3 μ m. The specific surface measured by N₂ BET adsorption using a Quantasorb system was 15 m²/g.

Surfactants. The cationic surfactant, *n*-tetradecyltrimethylammonium chloride (TTAC), [CH₃(CH₂)₁₃N(CH₃)₃]Cl, from American Tokyo Kasei, Inc., and the nonionic surfactant, pentadecyl ethoxylated nonyl phenol (NP-15), C₉H₁₉C₆H₄O(CH₂CH₂O)₁₅H, from Nikko Chemicals, Japan, were used as received.

Reagents. NaCl, used for controlling the ionic strength, was purchased from Fisher Scientific Co. and was ACS certified-grade (purity >99.9%). NaOH, used for adjusting the pH, was purchased from Fisher Scientific Co. and was certified as the volumetric standard solution (0.1 M). Water used in all experiments was triply distilled water. Conductivity of triply distilled water was measured to be in the range of (1–2) $\times 10^{-6}$ Ω^{-1} cm⁻¹.

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Adsorption. Adsorption experiments were conducted in capped 20 ml vials. 2-g samples of alumina were first mixed in 10 ml of 0.03 M NaCl solution for 1 h, and then the pH was adjusted to 10 and allowed to further equilibrate at the room temperature ($22 \pm 2^\circ\text{C}$) for 1 h. 10 ml of 0.03 M NaCl solution containing the surfactants was then added, and the samples were allowed to equilibrate for 15 h. pH was then measured and, if necessary, adjusted using 0.1 M NaOH. The samples were allowed to equilibrate for about 3 h after the final pH adjustment, and then centrifuged for 25 min at 5000 rpm. About 20 ml of the supernatant was pipeted out for analysis.

Desorption. After adsorption, desorption tests were conducted by adding the same volume of diluent adjusted to the system ionic strength and pH (0.03 M NaCl and pH 10) as the volume of the supernatant removed. The total volume and thus the solid to liquid ratio remained constant as the dilution step was repeated many times with the surfactant concentration monitored at each step. The equilibrium time for desorption process is the same as that for adsorption process. Adsorption density at each step was calculated from the changes in concentrations of the surfactants.

Surfactant concentration analyses. The TTAC concentration was determined using a two-phase titration technique (16). Pentadecyl ethoxylated nonyl phenol (NP-15) was analyzed by determining UV absorbance at 223 or 275 nm using a Shimadzu 1201 UV-vis spectrophotometer.

RESULTS AND DISCUSSION

Adsorption behavior of a cationic surfactant (TTAC) and a nonionic surfactant (NP-15) at the solid-liquid interface

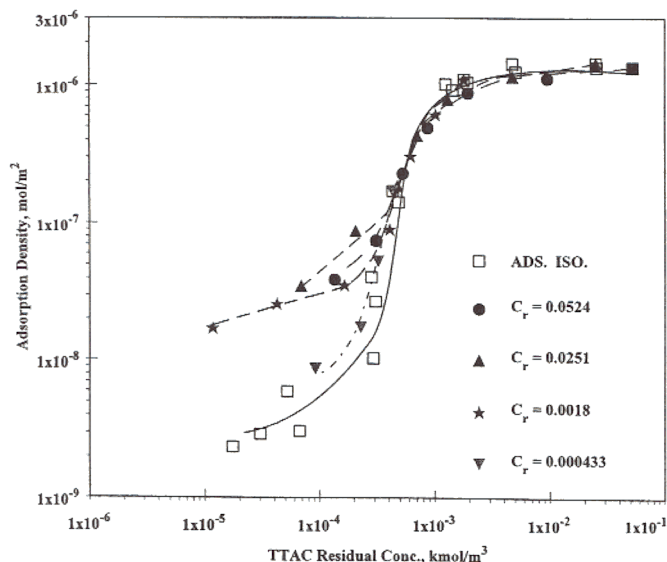


FIG. 1. Desorption of tetradecyl trimethyl ammonium chloride (TTAC) at alumina-water interface upon dilution from different residual concentrations (C_r), TTAC:NP-15 ratio 4:1, pH 10, ionic strength 0.03 M NaCl.

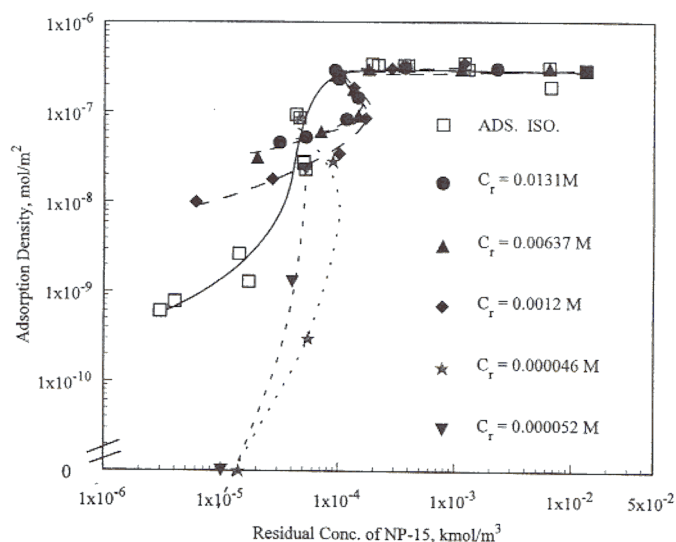


FIG. 2. Desorption of pentadecylethoxylated nonyl phenol (NP-15) at alumina-water interface upon dilution from different residual concentrations (C_r), TTAC:NP-15 ratio 4:1, pH 10, ionic strength 0.03 M NaCl.

was studied in our previous work (17). While the cationic TTAC adsorbed on the negatively charged alumina as expected, the nonionic NP-15 adsorbed only in the presence of the cationic surfactant. The interaction parameter determined using the regular solution theory (18,19) showed molecular level association between TTAC and NP-15 to be 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 induced adsorption of NP-15 on alumina surface where the latter normally does not adsorb. The adsorption densities of both TTAC and NP-15 were 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. While the increase under submonolayer coverage was attributed to cooperation due to reduced repulsion between the cationic heads owing to shielding by the nonionic surfactant, the decrease under saturation conditions was attributed to competition between NP-15 and the TTAC for adsorption sites.

The desorption behavior of single cationic TTAC has also been discussed in our early work (20). It has been shown that the desorption of TTAC from the alumina-water interface was reversible at high concentrations but was irreversible at lower concentrations. This was attributed to changes in the structure of the adsorbed layer upon dilution and the activation energy needed for the formation of surfactant solid-like aggregates (22).

The results obtained for the adsorption/desorption behavior of mixed surfactants (4:1 TTAC:NP-15) are shown in Figs. 1 and 2. The solid line represents the initial adsorption isotherm. It is noted that the desorption of TTAC from a

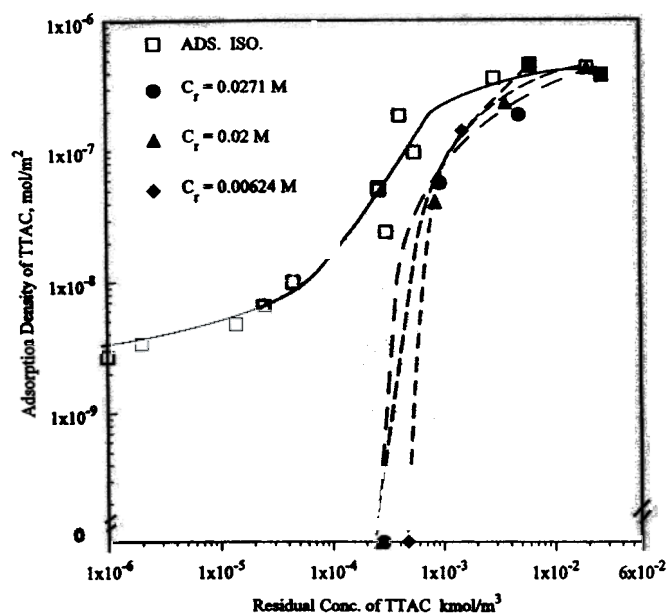


FIG. 3. Desorption of TTAC at alumina-water interface upon dilution from different residual concentrations (C_r), TTAC:NP-15 ratio 1:1, pH 10, ionic strength 0.03 M NaCl.

4:1 mixture is similar to that for TTAC alone (20). At high concentrations the adsorption of TTAC is reversible, but at low concentrations the desorption shows some positive hysteresis, i.e. at the same residual concentrations, the adsorption density is higher after desorption than that before. This is possibly due to the hysteresis involved in the deaggregation of the solloids from the interface. The desorption isotherms of NP-15 suggest that the fully grown NP-15 solloidal aggregates do not come off the surface easily upon dilution whereas the incipient ones do. At high concentrations, the adsorption density of TTAC does not change measurably upon dilution, and neither does NP-15 desorb from the interface under these conditions. However in cases where TTAC desorbs from the interface, desorption of NP-15 is significant and S-shape desorption isotherms are obtained. It can be concluded that the desorption of NP-15 is facilitated in this case by the desorption of TTAC. For dilutions starting from high concentrations, the desorption of NP-15 shows some positive hysteresis (similar to the positive hysteresis of TTAC) but only when the residual concentration becomes low due to dilution. Since the adsorption of NP-15 on alumina requires the TTAC to coadsorb and act as an anchor, it is then reasonable to expect the desorption behavior of the NP-15 to be controlled by the desorption of TTAC, and this is discussed in detail later.

The desorption isotherms for 1:1 TTAC:NP-15 mixtures are shown in Figs. 3 and 4. Similar to the desorption in 4:1 TTAC:NP-15 mixtures, the desorption of NP-15 is facilitated by the desorption of TTAC significantly. At this mixing ratio, the desorption of TTAC also becomes significant and

the desorption isotherms of both TTAC and NP-15 show negative hysteresis, i.e. the surfactant adsorption at the interface is lower after desorption than that before at the same residual concentration. This suggests that although the desorption behavior of NP-15 is controlled by the co-adsorbed TTAC molecules acting as anchors, the presence of NP-15 in the mixtures does also affect the affinity of TTAC to the alumina-water interface.

The desorption behavior of 1:4 TTAC:NP-15 mixed system is illustrated in Figs. 5 and 6. At this ratio adsorption of TTAC is very low. Nevertheless, desorption of TTAC in this system shows some negative hysteresis and the desorption of NP-15 is mostly reversible. Clearly the results obtained at different mixing ratios indicate that mechanism of desorption in this mixed system is more complex than that for single surfactant system.

It is evident that the desorption behavior of this mixed system depends upon the ratio of surfactants in the mixtures. With an increase of NP-15 in the mixture the desorption of TTAC becomes easy. A reason for this kind of behavior is that as the NP-15 content in the mixture increases, the positively charged head group of the TTAC will be partially shielded from each other by the coadsorbed nonionic NP-15 molecules. This will decrease the electrostatic attraction between the cationic TTAC molecules and the negatively charged alumina surface and facilitate desorption.

On the other hand, it is well known that adsorption of surfactants at interfaces is directly related to the monomer concentrations in the system. For single surfactant systems, solloid will usually form at a concentration much lower than

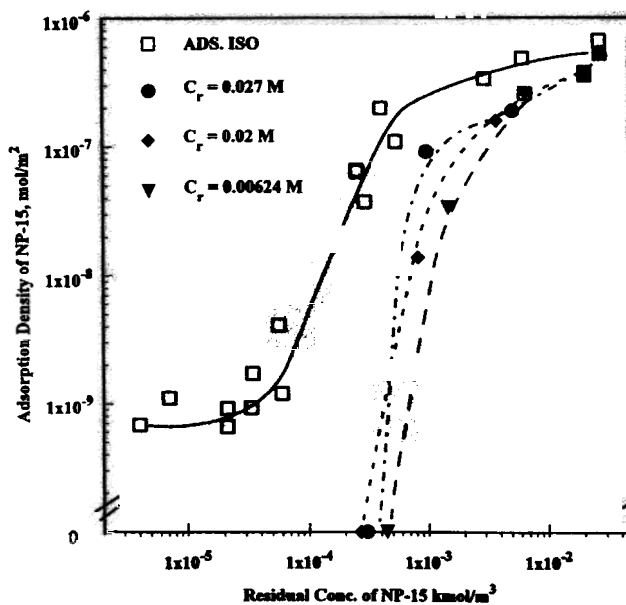


FIG. 4. Desorption of NP-15 at alumina-water interface upon dilution from different residual concentrations (C_r), TTAC:NP-15 ratio 1:1, pH 10, ionic strength 0.03 M NaCl.

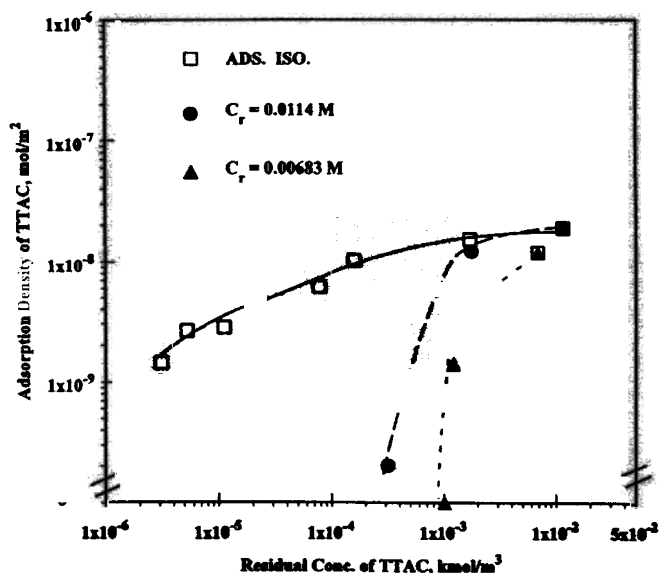


FIG. 5. Desorption of TTAC at alumina-water interface upon dilution from different residual concentrations (C_r), TTAC:NP-15 ratio 1:4, pH 10, ionic strength 0.03 M NaCl.

the CMC of the surfactant (21). Once the CMC is reached, the monomer concentration will be constant, and the adsorption will reach a plateau. In contrast, for mixed surfactant systems, the monomer concentrations of surfactants continue to change even above the CMC of the mixed systems, and hence the adsorption quantities of surfactants at interfaces also continue to change above mixed CMC. In other words, the equilibrium among micelles, solloids, and monomers will change over a much wider concentration range than that in a single-surfactant system. For example, in the 1:1 TTAC:NP-15 mixture system, the mixed CMC is 1.7×10^{-4} M total concentration. At CMC, the concentrations of cationic TTAC and nonionic NP-15 in the bulk are about 8.5×10^{-4} M. From Figs. 3 and 4, it can be seen that solloids of TTAC and NP-15 are formed just at this concentration. It is obvious that the adsorption/desorption in this mixture will be controlled by the micellization processes in the bulk. As mentioned earlier, NP-15 molecules do not adsorb at the alumina-water interface themselves, but once NP-15 is adsorbed at the interface with the help of preadsorbed TTAC, the synergism between NP-15 and TTAC in turn enhances the adsorption of TTAC. It is expected that desorption of NP-15 from the interface can also facilitate the desorption of TTAC.

Since NP-15 is more surface active, NP-15 micelles form at lower concentration in the bulk than that of TTAC. During the dilution process, new equilibria among solloid, micelle, and monomers will be established with the only source of surfactants for desorption being from that at the interface. Some of the TTAC molecules at the interface may be solubilized in NP-15 micelles. The desorption of TTAC molecules

will always be enhanced, therefore, whenever NP-15 micelles exist in the bulk. In other words, synergism between TTAC and NP-15 will occur for the desorption process also. This is supported by the fact that negative hysteresis occurs in the 1:1 TTAC:NP-15 mixture system. Similar desorption behavior has also been observed in the 1:4 TTAC:NP-15 mixture system. But at this mixing ratio, the solution is NP-15 rich and the adsorption density of TTAC is very low, so the effect of TTAC on the desorption of NP-15 is minimal and the desorption of NP-15 is not enhanced significantly.

In the case of the 4:1 TTAC:NP-15 mixture, the CMC is 2.7×10^{-4} M. At this CMC, the NP-15 concentration is 5.4×10^{-5} M. Above this concentration, the NP-15 micelles will facilitate desorption of NP-15, and S-shape desorption isotherms have been observed for NP-15 due to significant desorption around this concentration range. For TTAC, since bulk and the interface are rich in TTAC, the effect of NP-15 micelles on the desorption of TTAC is relatively small. When the desorption process starts from a concentration corresponding to plateau of TTAC adsorption, there will be many TTAC hemimicelles still at the interface as NP-15 micelles are depleted from the bulk solution upon dilution. Hence the desorption of TTAC becomes similar to that from single TTAC system, and as discussed before (20) positive hysteresis observed. Under these desorption conditions, some NP-15 molecules can be trapped in TTAC hemimicelles and this will indeed result in positive hysteresis for NP-15. When desorption process starts from a concentration at which adsorption density of TTAC is lower than the plateau value, the effect of NP-15 micelles on the desorption becomes significant. Desorption of NP-15 then shows negative

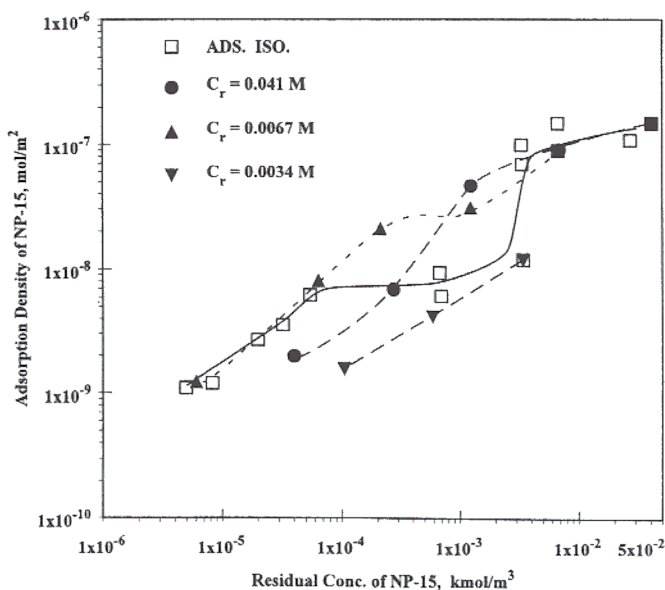


FIG. 6. Desorption of NP-15 at alumina-water interface upon dilution from different residual concentrations (C_r), TTAC:NP-15 ratio 1:4, pH 10, ionic strength 0.03 M NaCl.

hysteresis, and desorption of TTAC is reversible. Considering the positive hysteresis characteristics in the single TTAC system, this suggests that the desorption of TTAC is enhanced by the NP-15 in the mixed system. From above discussion, it is clear that the desorption and the hysteresis are dependent upon the relative ratio of surfactants in the mixtures. It is also clear that adsorption/desorption in the system are not completely reversible.

CONCLUSIONS

The desorption behavior of cationic–nonionic surfactant mixtures of TTAC and NP-15 at the alumina–water interface shows unique features which throw light on interactions between the species at the interface and in the bulk. While the nonionic NP-15 itself does not adsorb at the alumina–water interface, it is induced to do so by preadsorption of the cationic TTAC at the interface. During the desorption process, however, NP-15 in the system facilitates the desorption of TTAC due to the changes in equilibrium among surfactant monomers, mixed micelles, and solloids. Since NP-15 is more surface active than TTAC, NP-15 micelles form in a lower concentration range in the bulk solution, and the cationic TTAC species at the interface is solubilized by NP-15 rich micelles. This in turn enhances the desorption of NP-15 also. Thus the synergism between the cationic TTAC and nonionic NP-15 is observed not only in the adsorption process, but also in the desorption process. The desorption behavior of the mixed surfactant system is dependent on the relative amounts of surfactants in the mixtures. In nonionic NP-15 rich mixtures, negative hysteresis is seen for the desorption of both TTAC and NP-15. In cationic TTAC rich mixtures, the effect of NP-15 on the desorption of TTAC is limited and the desorption of TTAC is similar to that in single TTAC system, positive hysteresis is observed for both TTAC and NP-15. It is clear that desorption behavior of surfactant mixtures is much more complex than that of single surfactant systems, and it can be controlled by adjusting the relative ratio of surfactants in the mixtures. This is very important in many industrial applications such as enhanced oil recovery processes in which surfactant loss due to adsorption should be minimized.

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