Chapter 16

Interactions Between Pentadecylethoxylated Nonylphenol and Tetradecyltrimethylammonium Chloride Mixtures at the Alumina–Water Interface

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Adsorption behavior of surfactants in mixtures was studied using tetradecyltrimethylammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15). In the single surfactant system, only the cationic TTAC was found to adsorb at the alumina-water interface at pH 10. In the mixed surfactant system, the cationic tetradecyltrimethylammonium chloride (TTAC) was found to induce significant coadsorption of the nonionic NP-15. This was attributed to hydrophobic interactions between the TTAC and NP-15. The adsorption behavior varied with the ratio of the two surfactants in the mixture. In TTAC rich mixtures, adsorption of NP-15 was higher and the adsorption isotherms of NP-15 shifted to lower concentrations. On the other hand, in NP-15 rich mixtures adsorption of TTAC was suppressed due to competitive adsorption and steric hindrance by the larger NP-15 molecules. Zeta potential measurements also showed that with the increase of NP-15 in the mixtures, TTAC molecules could not reach the alumina-water interface easily as their positive charge was partially screened by the co-adsorbed NP-15. Regular solution theory has been used to understand the nature of the interaction between surfactants in the mixtures and the relation between the monomer concentration and adsorption behaviors.

Adsorption of surfactants at solid-liquid interfaces plays a critical role in many important industrial processes. In many of these processes, the use of mixed surfactant systems can significantly improve the performance over that of single component systems. In applications such as enhanced oil recovery processes, surfactant adsorption is not desirable and mixed surfactant systems, if properly designed, may offer some promising advantages over pure components in this regard and reduce the adsorption. In other cases the adsorption of surfactants from mixtures can be higher and past work has clearly shown that the adsorption behavior is much more complex than that of single surfactants (1-3).

Surfactant adsorption from solution is related to the chemical potential of the surfactant molecules in the solution, and the nature of solid. It is widely accepted that surfactant mixtures can form mixed micelles in the solution and that the CMC of a surfactant mixture varies with the mixture composition. This may in turn reduce the chemical potential of the monomers from that for the single surfactant system, thereby reducing its adsorption as well. But on the other hand, the hemimicelle concentration (HMC) may also vary with the mixture composition. It is clear that adsorption from solution containing mixtures of surfactants can be understood only by taking into account the equilibrium among monomers, micelles and hemimicelles. So far the interaction of surfactants in bulk solutions have been studied for many cases (4-8) . Literature on the solution behavior of surfactant mixtures suggests significant deviation from ideal mixing behavior. Generally, mixtures of surfactants with similarly charged head groups behave more ideally in solutions, and very large deviations from ideality are observed for mixtures of oppositely charged surfactants in solutions. However, there is very little information on mixed surfactant interactions at solid/liquid interface, particularly for the case of cationic- nonionic surfactant mixtures . Regular solution approximation has been used to treat nonideal mixing micelles in solution and this approach has been extended to model also adsorption at interface (9-10). Although regular solution theory has been criticized by some researchers (11), it has provided a very useful way to describe the behavior of mixed surfactant aggregates. In this work, the adsorption of binary mixtures of the isometrically pure cationic tetradecyltrimethylammonium chloride(TTAC) and pentadecylethoxylated nonylphenol (NP-15) at alumina-water interface was investigated. The effects of synergism and steric hindrance in this mixed system are discussed, and the possible relationship between adsorption behaviors and monomer concentrations is discussed using regular solution approximation.

Materials and Experimental Procedure

Alumina. Linde A alumina was purchased from Union Carbide Corp. It was specified to be 90% α-Al_2O_3 and 10% γ-Al_2O_3 and to have a mean diameter of 0.3μm. The specific surface area was measured to be 15 m^2/g by N_2 BET adsorption using a Quantasorb system.

Surfactants: The cationic surfactant, n-tetradecyltrimethylammonium chloride, $[CH_3(CH_2)_{13}N(CH_3)_3]Cl$ (TTAC), from American Tokyo Kasei, Inc., and the nonionic pentadecylethoxylated nonylphenol, $C_9H_{19}C_6H_4O(CH_2CH_2O)_{15}H$ (NP-15), from Nikko Chemicals, Japan were used as received.

Reagents: NaCl, used for controlling the ionic strength, was purchased from Fisher Scientific Co. and was of A.C.S. grade certified (purity >99.9%). NaOH, used for adjusting the pH, was purchased from Fisher Scientific Co. and was certified as the volumetric standard solution(0.1M). Water used in all experiments was triple distilled water. Conductivity of triple distilled water was measured to be in the range of (1-2)x10$^-^{6}\Omega^{-1}$.

Adsorption: Adsorption experiments were conducted in capped 20-mL vials. First, 2g

of alumina and 10ml of 0.03 M NaCl solution were mixed and conditioned for 1 hour and then the pH value was adjusted as desired and allowed to equilibrate at the room temperature (22±2 °C) for 1 hour. Then, 10 ml of 0.03M NaCl solution containing the surfactants was added, and the samples were allowed to equilibrate at room temperature (22±2 °C) for 15 hours. pH measurements were then made and, if necessary, adjusted using 0.1 M NaOH. The change in pH during equilibration was usually between 0.2 and 0.4 units. The samples were allowed to equilibrate for about 3 hours after the final pH adjustment, and then centrifuged for 25 min at 5000 rpm. About 20 ml of the supernatant was pipetted out for analysis.

Surfactant analyses: Tetradecyltrimethylammonium chloride (TTAC) concentration was measured by a two-phase titration technique(12). Pentadecylethoxylated nonylphenol (NP-15) concentration was analyzed by UV absorbance using a Shimadzu UV-1201 UV-Vis spectrophotometer. Wavelength scans of NP-15 solution shows two absorbance peaks at 223nm and 275nm. NP-15 concentrations can be measured at either of these wavelengths.

Surface tension: Surface tension was measured using a Fisher Model 20 ring tensiometer. A 15-20 ml portion of the solution was poured into a 25 ml beaker at room temperature (22±2 °C). Three minutes were allowed for equilibration before surface tension measurements.

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

Results and Discussions

Interactions between tetradecyltrimethylammonium chloride (TTAC) and pentadecyl ethoxylated nonylphenol (NP-15) in solution

In an attempt to correlate changes in monomer concentrations of the individual surfactants in the mixtures with their adsorption behavior, mixtures of tetradecyltrimethylammonium chloride (TTAC) and pentadecyl ethoxylated nonylphenol (NP-15) were studied using surface tensiometry and regular solution theory (9). Results obtained for the surface tension of aqueous solutions of pure tetradecyl-trimethylammonium chloride (TTAC) and pure pentadecylethoxylated nonylphenol (NP-15) showed, as expected, the CMC of the nonionic NP-15 to be lower than that for the TTAC, but the results obtained for mixtures showed them to be not as surface active as the nonionic surfactant. The critical micelle concentrations (CMC) of the mixtures are plotted in figure 1 as a function of NP-15 composition. Regular solution model was used to fit these data (figure 1) and an interaction parameter (β) between -1.5 and -1.2 was obtained. A considerable number of binary mixed micellar system 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 cationic-nonionic mixtures, and -0.2 for cationic-cationic mixtures (6). Compared with these, the interaction parameter obtained for the present system is 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.
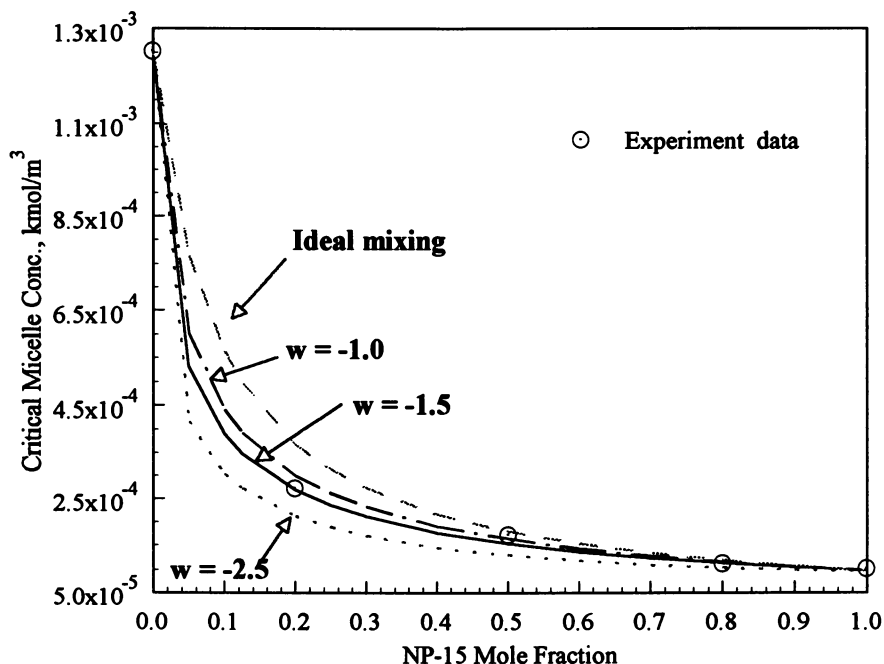
Figure 1   Measured CMC values of mixtures of tetradecyltrimethylammonium chloride (TTAC) and pentadecylethoxylated nonylphenol (NP-15) and their relation to ideal mixing and regular mixing theories.

Adsorption of surfactant mixtures

The adsorption isotherm of TTAC on alumina at pH 10 is shown in figure 2. It is observed that TTAC adsorbs significantly at the alumina-water interface at pH 10. At this pH the alumina surface is negatively charged(isoelectric point of alumina is pH 8.5-9.0) and the electrostatic attraction with the cationic TTAC will be dominant. There is a sharp increase in the adsorption density around 5×10^{-4} kmol/m^3 which is attributed to the formation of surfactant aggregates(solloids) at the solid-liquid interface. The maximum adsorption density of TTAC on alumina at pH 10 is about 2.5×10^{-6} mol/m^2. This translates to roughly 66A^{o2}/molecule which is similar to the molecular area at air/solution interface(61A^{o2}) reported in the literature (15). This suggests that the adsorption layer on alumina is composed mainly of a monolayer than a bilayer or micelles.

Tests with nonionic pentadecylethoxylated nonylphenol (NP-15) showed it not to adsorb at the alumina-water interface. In a study on the adsorption of
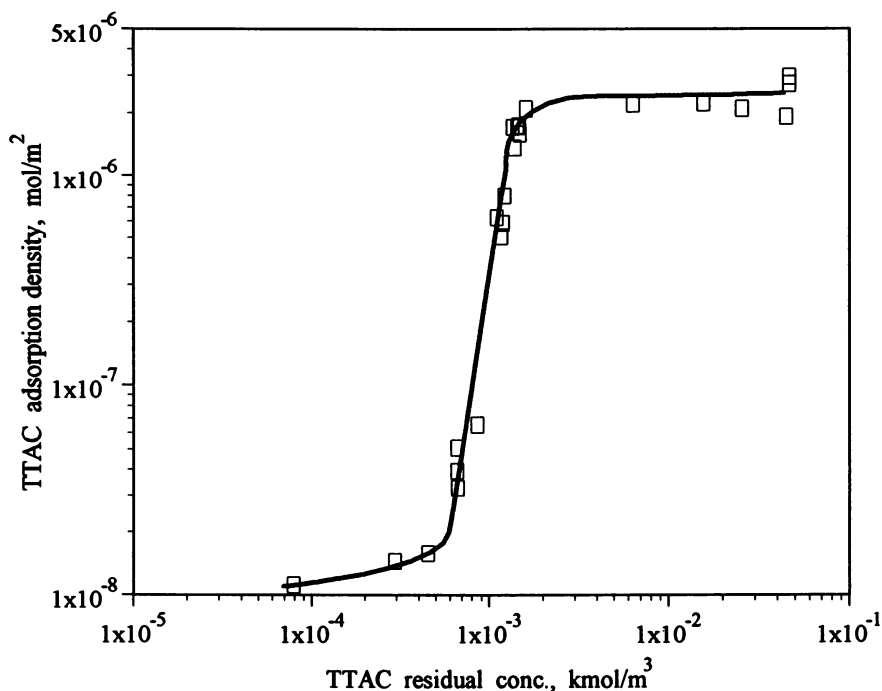
Figure 2   Adsorption of tetradecyltrimethylammonium chloride (TTAC) alone on alumina at pH 10, 0.03M NaCl.

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 radical which has sufficient adsorption force to overcome the strong interaction between water molecules and the ethylene oxide groups. This observation is similar to that in the literature on the adsorption of polyethylene oxide (PEO) on different minerals (14). It has been reported that PEO adsorbs on silica but not on alumina or hematite. 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 molecule is unable to adsorb on it to displace sufficient number of water molecules from the interface. It is reasonable then that NP-15 does not adsorb on the alumina-water interface. Experiments conducted with mixtures show that in the presence of TTAC, NP-15 is forced to adsorb at the alumina-water interface. The adsorption of NP-15 is plotted in figure 3 as a function of TTAC residual concentration. In this series of experiments, the initial NP-15 concentration was the same for all the tests.
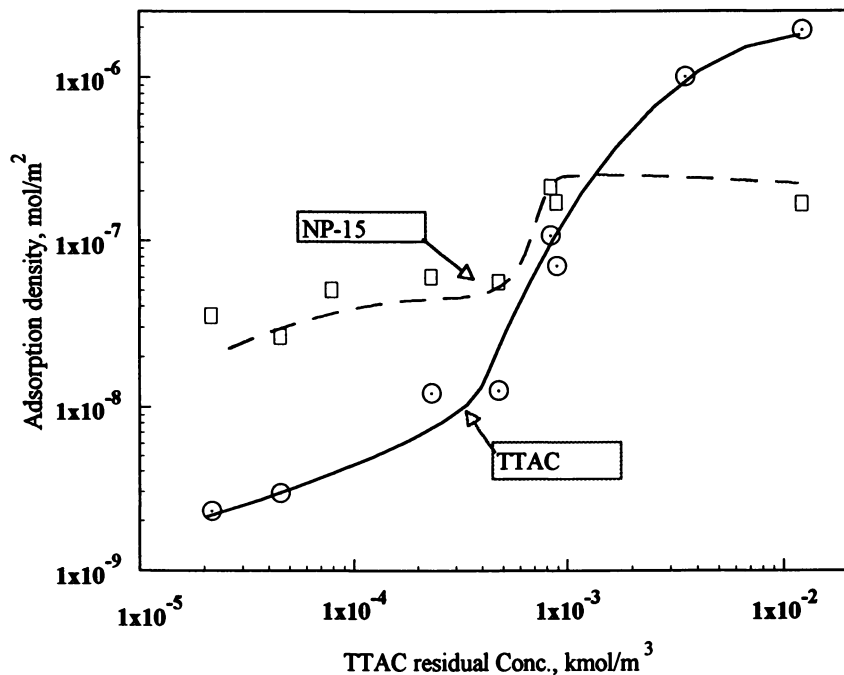
Figure 3   Adsorption of pentadecylethoxylated nonylphenol (NP-15) as a function of tetradecyltrimethylammonium chloride (TTAC) residual concentration, NP-15 initial concentration 2.13×10^{-3} kmol/m$^{3..}$

It can be seen that adsorption of NP-15 increases with increase in TTAC concentration. It is also to be noted that when TTAC molecules form hemimicelles at the interface, NP-15 adsorption increased markedly. Above the hemimicelle concentration however, there is no further effect of any increase in the TTAC adsorption density on the adsorption of NP-15.

Figure 4 shows the adsorption isotherms of pentadecylethoxylated nonylphenol with pre-adsorbed TTAC on it along with one isotherm for adsorption of it when added along with TTAC. It is noted that tetradecyl trimethylammonium chloride(TTAC) does force the adsorption of NP-15 on alumina. Pre-adsorbed TTAC molecules function as anchors for the adsorption of NP-15. With an increase in TTAC initial concentration, the adsorption of NP-15 increases and the isotherm is shifted to lower NP-15 concentrations. 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 are pre-mixed and added to the alumina suspension, the adsorption density of NP-15 is markedly higher below the saturation coverage. This indicates that NP-15 adsorption from mixtures with TTAC is not completely reversible, but is controlled by the nature of molecular packing at the interface. Although NP-15 itself does not adsorb on alumina, coadsorbed NP-15 does affect the adsorption of TTAC as shown in figure 5.
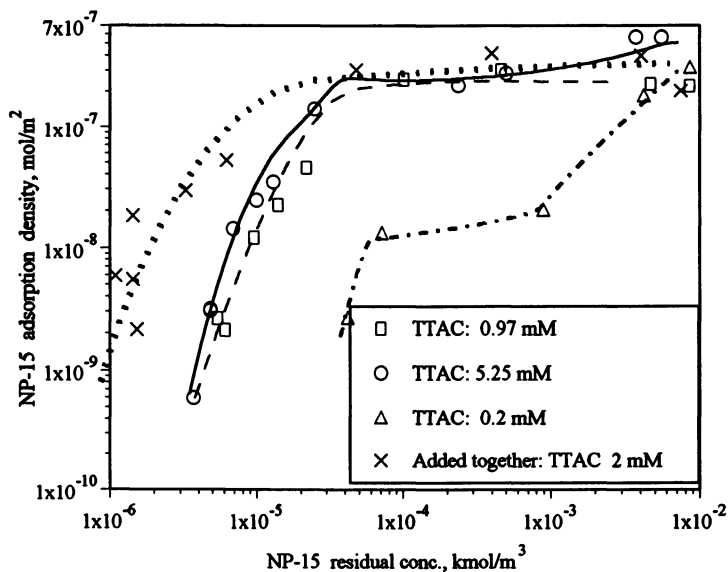
Figure 4   Adsorption of NP-15 on alumina in the presence of preadsorbed TTAC or when added together with TTAC. pH 10, 0.03M NaCl.
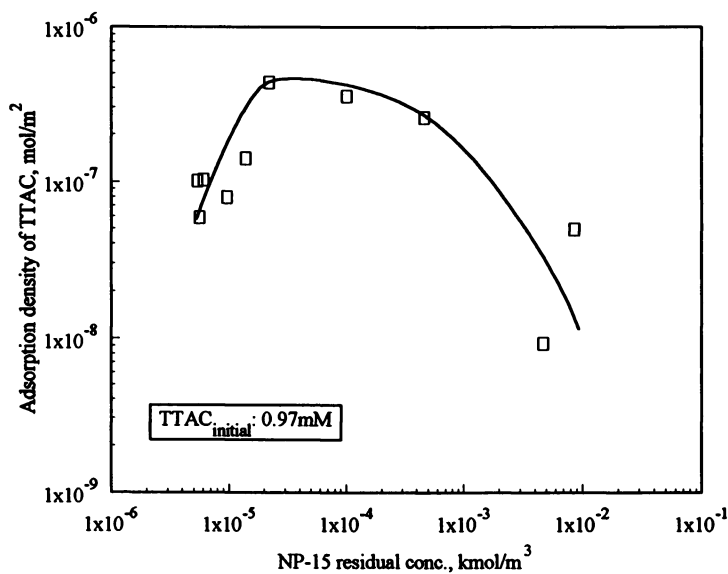

Figure 5   Effect of coadsorbed NP-15 on the adsorption of TTAC. pH 10, 0.03M NaCl

In this experiment pre-adsorbed TTAC amounts are the same for all the samples, but with the increase of NP-15 concentration the adsorption of TTAC first increased, reached a maximum, and then decreased. This suggests both cooperation and competitive interactions between TTAC and NP-15 can take place depending on the concentration region.

The adsorption isotherms of TTAC in the presence of different amounts of NP-15 are shown in figure 6 along with that in the absence of it. In all these experiments, the tetradecyl trimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15) were pre-mixed and then equilibrated with alumina for 15 hours at pH 10. It is seen that tetradecyltrimethylammonium chloride (TTAC) solloid aggregation 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. For the 1:4 ratio, however, the sharp increase in adsorption density corresponding to such aggregation is not observed. It is to be noted that the plateau adsorption density decreases continuously upon the addition of the nonionic surfactant. This is attributed to the steric hinderance and competition provided by the bulky nonionic pentadecylethoxylated nonylphenol (NP-15) for the adsorption sites.
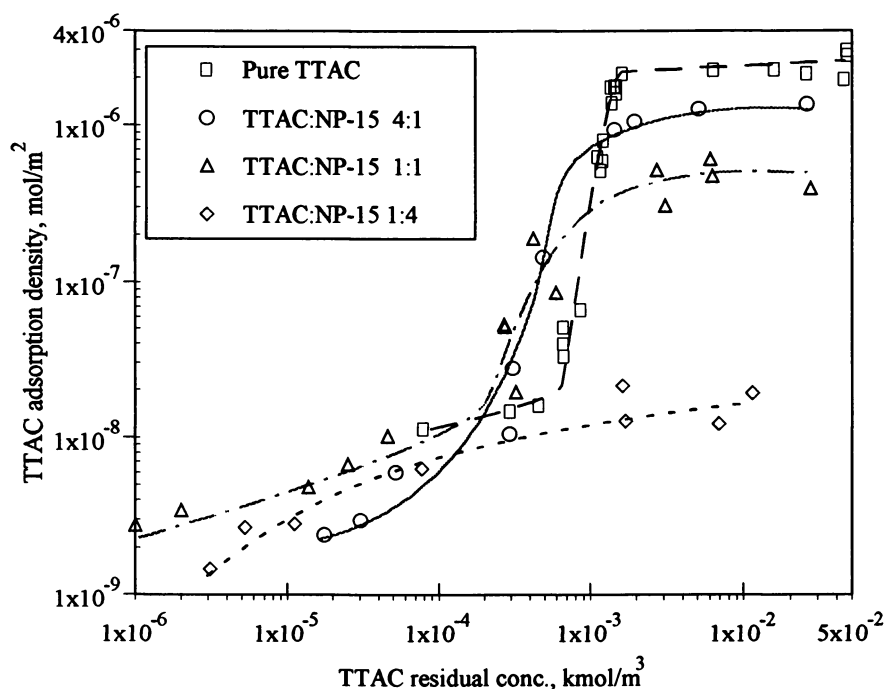

Figure 6   Adsorption of tetradecyltrimethylammonium chloride (TTAC) in the presence and absence of pentadecylethoxylated nonylphenol (NP-15), pH 10, 0.03M NaCl

The adsorption isotherms of NP-15 from different mixtures with TTAC are shown in figure 7. As mentioned earlier whereas the pure nonionic surfactant NP-15 did not adsorb on alumina, 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.
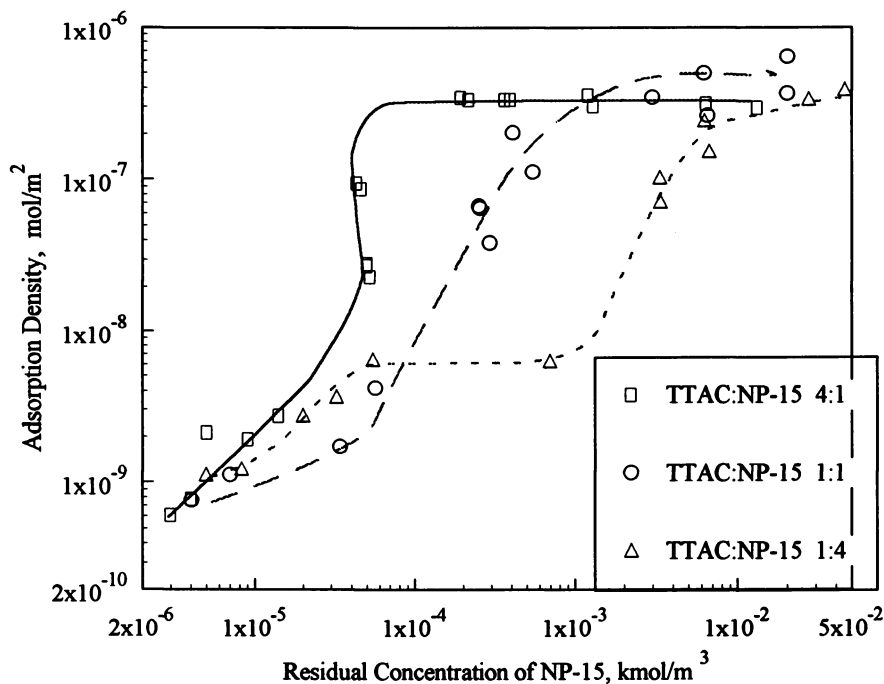

Figure 7   Adsorption of pentadecylethoxylated nonylphenol (NP-15) on alumina in the presence of different amounts of tetradecyltrimethylammonium chloride (TTAC), pH 10, 0.03M NaCl.

The peculiar S-shape isotherm obtained for NP-15 adsorption as a function of its 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 solloids at the alumina-water interface increase, since the concentration of tetradecyl trimethyl ammonium chloride (TTAC) 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 adsorbed NP-15 molecules will occupy more area than the TTAC spaces thus reducing the area available for TTAC. The structure of the solloids and micelles will be different in the single surfactant and the mixed surfactant systems and the charge of the ionic head

of the tetradecyl trimethyl ammonium chloride (TTAC) will be shielded by the NP-15 as its content in the mixtures increases. This in turn will reduce electrostatic attraction between the negatively charged alumina surface and the positively charged TTAC molecules thereby reducing the TTAC adsorption density.   This hypothesis was tested by measuring the zeta potential after adsorption and the results are shown in figure 8. The zeta potential of alumina particles will be decided mainly by the adsorption of the oppositely charged TTAC molecules, even though the adsorbed nonionic species can also contribute to reduction in zeta potential by masking the surface and by shifting the shear plane
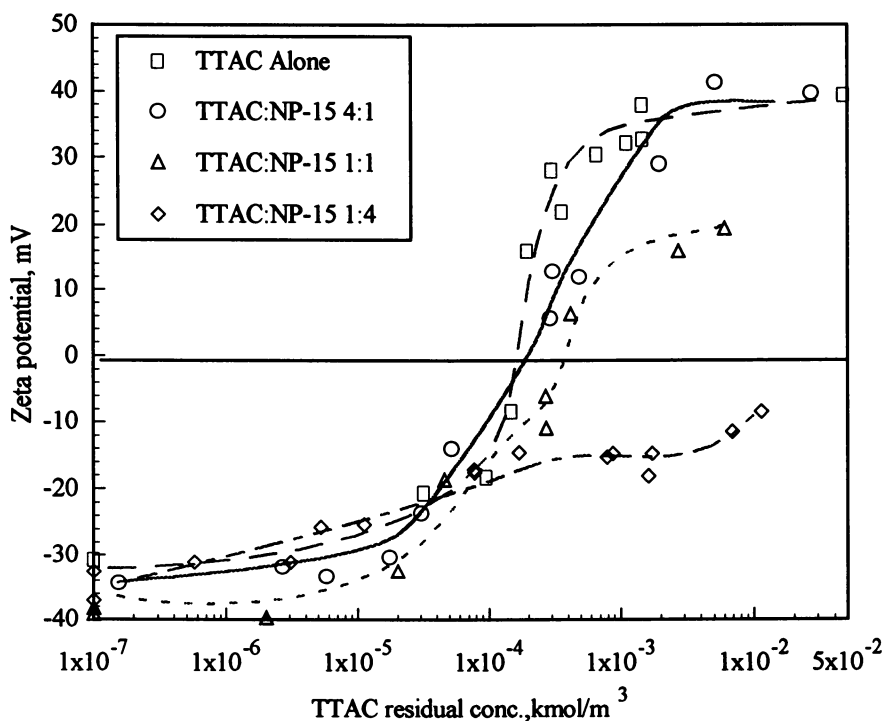

Figure 8   Zeta potential of alumina particles after adsorption of TTAC:NP-15 mixtures of different composition.

From figure 8 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 is in agreement with the adsorption isotherms of TTAC and NP-15 in figures 6 & 7 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 an increase in the NP-15. Upon examining the adsorption density of TTAC at the isoelectric point, it is evident that the adsorption density of TTAC from mixtures is higher than that for 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 that the positive charge of the TTAC ionic head is partially screened by the co-adsorbed nonionic NP-15 molecule. The fact that adsorption of the cationic tetra decyl trimethyl ammonium chloride (TTAC) continues to take place leading to monolayer coverage even after the particles have become similarly charged (figure 2) suggests the predominating role of 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.

The ratio of adsorption densities of TTAC and NP-15 at the alumina-water interface is examined in figure 9 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 keeps changing over the entire concentration range. This suggests that the monomer composition and adsorption mechanism are changing over the concentration range studied.
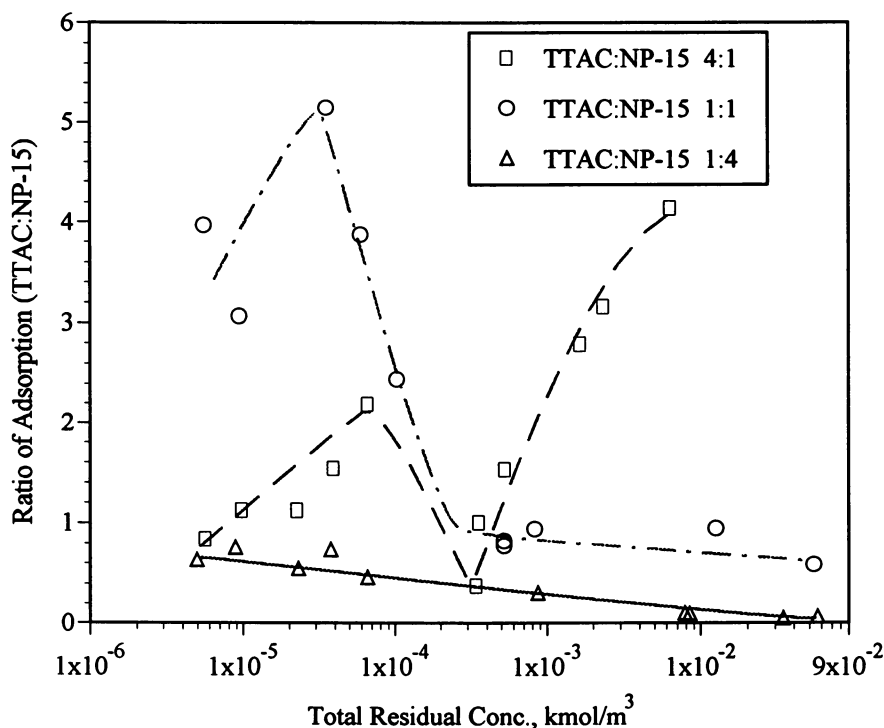

Figure 9   Ratio of adsorption densities of TTAC:NP-15 for different surfactant mixtures.

To better understand the relation between the adsorption mechanism and the monomer concentrations, the monomer concentrations of solutions of different mixtures in this system were calculated using the regular solution theory with an interaction parameter of -1.5. The results are shown in Figures 10 and 11.
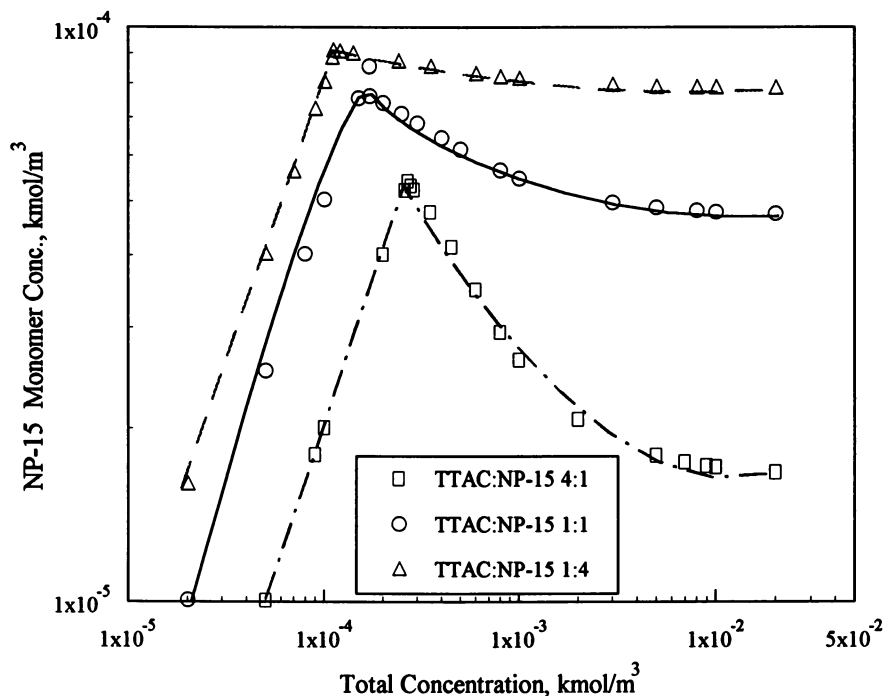
Figure 10 Monomer concentrations of NP-15 in different TTAC:NP-15 mixtures calculated from regular mixing theory with interaction parameter $\beta=-1.5$

Although the initial mixed ratio of studied surfactant system will have some changes after adsorption, it is still interesting to compare the adsorption isotherms in Figures 6 and 7 with the results for the monomer concentrations, which were calculated from regular solution with initial mixed ratio. It can be found that the adsorption of NP-15 does not depend upon its monomer concentrations in the feed mixtures. For example, the adsorption of NP-15 in 4:1 TTAC:NP-15 mixture is the highest in all these mixtures, but its monomer concentrations are the lowest. This further confirms that the adsorption of NP-15 is very much controlled by the <u>pre-adsorbed</u> TTAC as anchors. For the adsorption of TTAC, the adsorption quantities corresponds to its monomer concentrations in the mixtures. The higher the monomer concentration, the higher is the adsorption density. On examining the synergistic and competitive effects in this system, it becomes evident that these phenomena are decided mostly by the relative as well as the absolute quantities of NP-15. Only when the relative and absolute quantities of NP-15 are low, synergism between these two surfactants can be seen, and the maximum exhibited in Figure 8 is attributed to this behavior. There is no this kind of maximum exhibited in the case of 1:4 TTAC:NP-15 mixture because the relative quantity of NP-15 is too high. In the high concentration range the absolute quantity of NP-15 is higher, and steric hindrance will be dominant thus suppressing the adsorption of TTAC. It will be

interesting to determine the monomer concentrations experimentally using suitable techniques to confirm the results of regular solution theory.
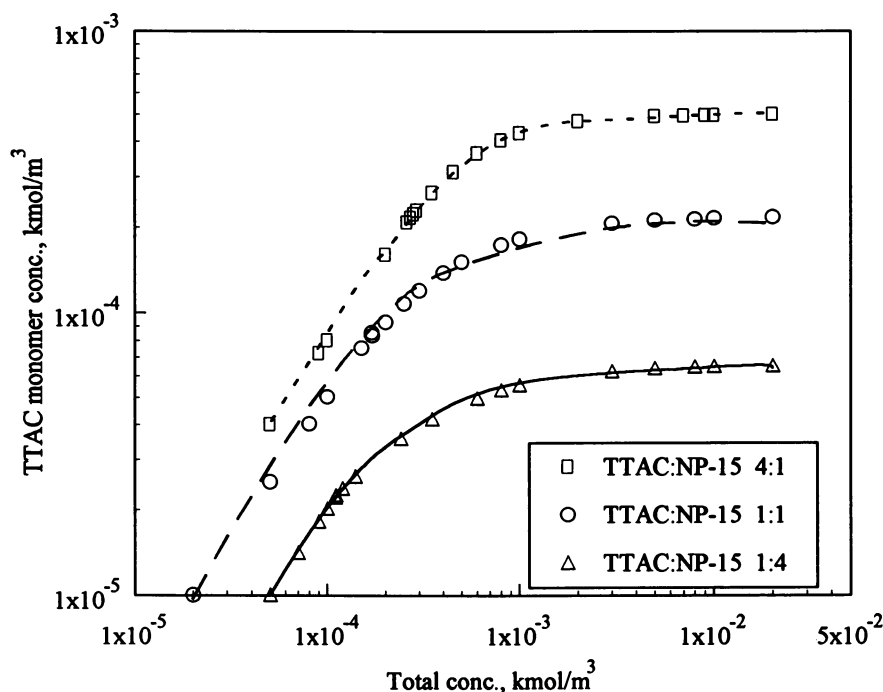

Figure 11   Monomer concentrations of TTAC in different TTAC:NP-15 mixtures calculated from regular mixing theory with interaction parameter $\beta = -1.5$

SUMMARY & CONCLUSIONS

Interactions between a cationic surfactant and a nonionic surfactant were studied using tetradecyl trimethylammonium chloride and pentadecylethoxlated nonylphenol. The interaction parameter determined using the regular solution theory indicated the molecular level associations between tetradecyl trimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15) to be much weaker than those between an anionic surfactant and a nonionic surfactant. Nevertheless, the adsorption behavior of the nonionic NP-15 was modified significantly as a result of these interactions. Presence of TTAC in this system forced adsorption of NP-15 on alumina where the latter does not normally adsorb. The adsorption density of both TTAC and NP-15 could be varied by altering the composition of the surfactant mixture. Presence of coadsorbed NP-15 lowered the adsorption of TTAC due to competition and steric

hindrance. As a result of mixed aggregation between the nonionic and the cationic surfactant, electrostatic attraction between TTAC and the negatively charged alumina surface was reduced which also contributed to the lower adsorption of TTAC from its mixtures with NP-15. Importantly 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 when the TTAC was preadsorbed. This is attributed to more favorable interactions and more possible ways to arrange surfactants coaggregates at the alumina-water interface.

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