DOE/BC/14884--14

QUARTERLY TECHNICAL PROGRESS REPORT

Title	Surfactant Loss Control in Chemical Flooding: Spectroscopic and Calorimetric Study of Adsorption and Precipitation on Reservoir Minerals
Contract no.	DE-AC22-92BC14884
University	Columbia University in the city of New York Box 20, Low Memorial Library New York, NY 10027.
Date of report	8/31/95
Contract date	9/30/92
Anticipated Completion Date	9/29/95
Government award	$ 602,232 ($ 206,767 for current year)
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Reporting Period	4/1/95 - 6/30/95

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Summary of Technical Progress

Previously, adsorption and desorption behaviors of tetradecyl trimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15) mixtures have been reported. It was observed that there was either synergistic or competitive adsorption between these two surfactants depending on the mixture ratios and the concentrations studied and that their adsorption/desorption behaviors were also rather complex. To better elucidate the mechanisms involved in these adsorption and desorption processes it is important to the understand the exact nature of the physico-chemical interactions between various components in mixtures and, how this in turn, controls the performance of the surfactant systems. Recently we have adapted the ultrafiltration technique to determine monomer concentrations in surfactant mixtures and to study the aggregation phenomenon between TTAC and NP-15. During the current report period, monomer concentrations of TTAC and NP-15 were measured for different mixing ratios at a constant ionic strength of 0.03 M NaCl and after adsorption for 4:1 TTAC:NP-15 mixture system. Possible behaviors of mixed micellization processes in solution are proposed and the relationship between monomer concentration and adsorption density is discussed.

<u>Monomer concentrations of tetradecyl trimethyl ammonium chloride (TTAC) and Pentadecyl ethoxylated nonyl phenol (NP-15) in their mixed solutions</u>

The monomer concentrations of tetradecyl trimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15) at an ionic strength of 0.2 M NaCl have been reported previously. Ionic strength can be expected to have a significant effect on the aggregation of the cationic surfactant which in turn will affect co-aggregation with the nonionic surfactant. To determine such effects, monomer concentrations of TTAC and NP-15 were measured at an ionic strength of 0.03 M NaCl. Two kinds of membranes, (YM-1 and YM-3) from Amicon Company with the molecular weight cut-off of 1000 and 3000 were used to separate TTAC and NP-15 monomers from the same sample: the YM-1 membrane was used to separate TTAC monomers from the mixed micelles and the YM-3 membrane was used to separate NP-15 monomer from the mixed micelles. The purpose of this experimental design was to ensure complete separation of all monomers from the mixed micelles. The monomer concentrations of TTAC and NP-15 thus determined are shown in figures 1 and 2 for different mixing ratios. The monomer concentrations for both TTAC and NP-15 at the lower ionic strength (0.03 M NaCl) are higher than those at higher ionic strength (0.2 M NaCl) reported previously.

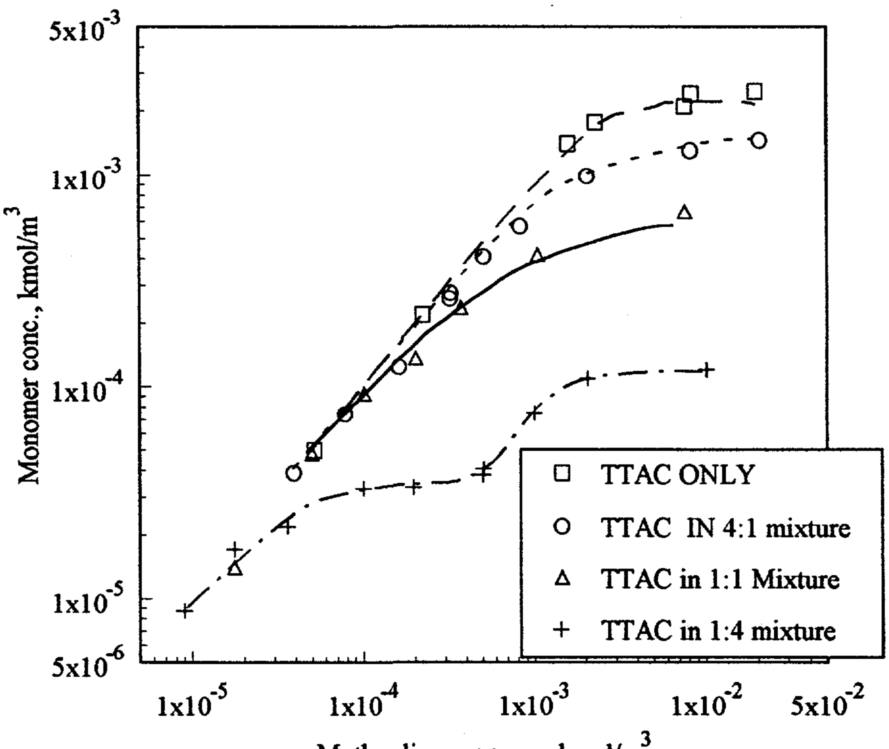

Figure 1 **TTAC monomer concentrations in TTAC:NP-15 mixtures of different compositions. I.S. 0.03 M NaCl.**

This is anticipated for TTAC since the critical micelle concentration (CMC) of ionic surfactants decrease upon the addition of salt, and the monomer concentrations will therefore decrease as well. For NP-15, however, the monomer concentrations are identical at both the ionic strengths.

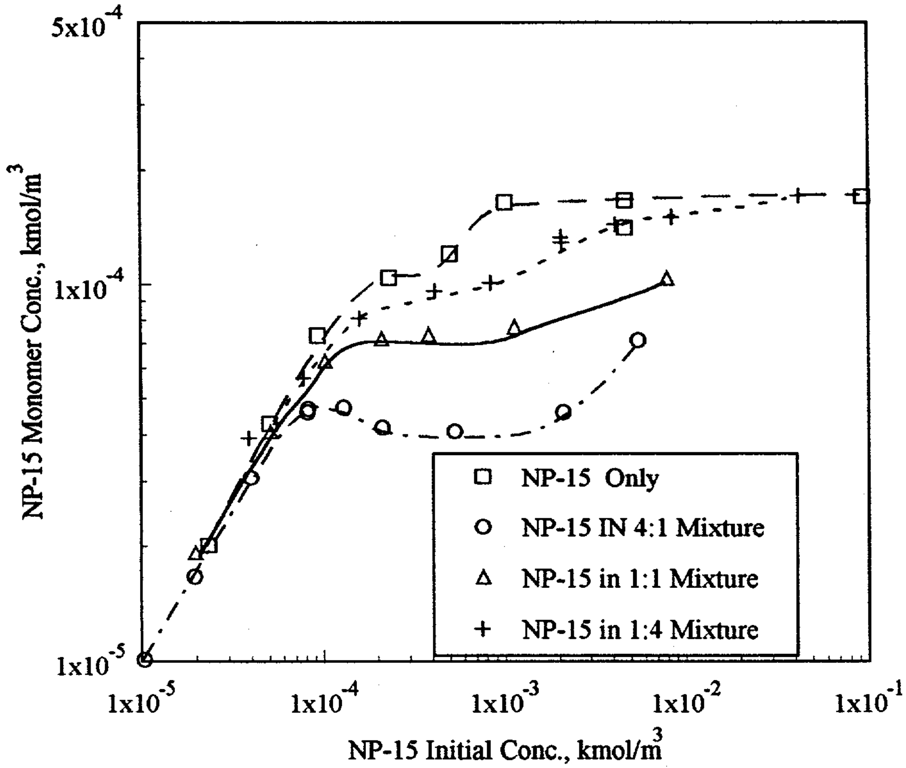

Figure 2 **NP-15 monomer concentrations in TTAC:NP-15 mixtures of different composition. I.S. = 0.03 M NaCl.**

Our earlier work has shown that the CMC of NP-15 is not very sensitive to the addition of salt, particularly in this concentration range. However, in mixtures with TTAC, mixed micelles will be formed and any change in the activity of the ionic surfactant will alter aggregation between NP-15 and TTAC.

It is interesting to note that monomer concentrations of both TTAC and NP-15 do not remain constant above the mixed CMC of the system. Considering that the mixed micelles are in equilibrium with these monomers, it can be expected that the composition of the mixed micelles will vary as the total concentration is increased above the CMC of the mixtures. The results obtained for monomer concentrations of pentadecylethoxylated nonyl phenol (NP-15) show that the monomer concentrations are constant over a short concentration range above the mixed CMC (depending on the ratio of mixing) and then increases at higher concentrations. The NP-15 concentrations at the mixed CMC are 8.8×10^{-5} mol/l, 8.5×10^{-5} mol/l and 5.4×10^{-5} mol/l for the 1:4, 1:1 and 4:1 TTAC:NP-15 mixing ratios respectively. The NP-15 concentration at the mixed CMC decreased with increase in TTAC content of the mixture suggesting enhanced synergism with increasing TTAC. Since NP-15 is more surface active than TTAC, it is reasonable to believe that only NP-15 can form micelles immediately above the mixed CMC, and TTAC molecules are then "dissolved" in the micelles of NP-15, similar to solubilization of organic compounds in micelles. At a fixed ionic strength, the TTAC that can be dissolved in NP-15 micelles will depend upon packing constraints of the two surfactants. With an increase in total surfactant concentration to the point at which TTAC itself can form aggregates, a new kind of TTAC-rich micelle may be formed. This may cause some of the TTAC molecules dissolved in the NP-15 rich micelles to rearrange into TTAC rich micelles. This is proposed to be a reason for the increase in NP-15 monomer concentrations at high concentrations. For example, in the 1:4 TTAC:NP-15 mixture system, NP-15 rich micelles will form at an NP-15 concentration of 8.8×10^{-5} mol/l, into which some TTAC molecules can dissolve. This is indicated by a constant monomer concentration of TTAC over a certain concentration range. Above a TTAC concentration of 6×10^{-4} mol/l, TTAC rich micelles may form. The monomer concentrations of both TTAC and NP-15 are seen to increase and reach new plateau values, especially the NP-15 monomer concentration which is similar to that in the pure NP-15 system. In the 4:1 TTAC: NP-15 mixture system NP-15 rich micelles will be formed at an NP-15 concentration of 5.4×10^{-5} mol/l . Due to the strong synergism between NP-15 and TTAC in NP-15 rich micelles, the monomer concentration of NP-15 decreases slightly above the mixed CMC. On the other hand, the monomer concentration for TTAC did not change very much from that in the pure TTAC system. This could be due to the limit on the amount of TTAC that can dissolve in the NP-15 rich micelles. With an increase in total concentration, TTAC itself can form micelles and two kinds of mixed micelles (NP-15 rich and TTAC rich micelle) can co-exist. As a result, NP-15 monomer concentration increases and TTAC monomer concentration approaches a plateau.

Relationship between adsorption at the alumina-water interface and monomer concentration in a 4:1 tetradecyl trimethyl ammonium chloride (TTAC) to pentadecyl ethoxylated nonyl phenol (NP-15) mixture system

Surfactant adsorption at the solid-liquid is related to the chemical potential of the surfactant molecules (monomers) in the solution as well as to the nature of the solid. To better elucidate the mechanisms of adsorption of tetradecyltrimethylammonium chloride (TTAC) :pentadecyl ethoxylated nonyl phenol (NP-15) mixtures, the monomer concentrations of TTAC and NP-15 were measured before and after adsorption and the results obtained are plotted in figures 3 and 4 as a function of equilibrium concentration. The monomer concentrations of both TTAC and NP-15 are similar before and after the adsorption. For tetradecyl trimethyl ammonium chloride (TTAC), the slope of monomer concentration curve after the adsorption is higher than that before the adsorption in the concentration range of 2×10^{-4} to 8×10^{-4} mol/l. This corresponds to the concentration range where TTAC solloids are formed at the interface. For pentadecyl ethoxylated nonyl phenol (NP-15), the monomer concentration curve was shifted to lower concentrations due to the significant adsorption of NP-15

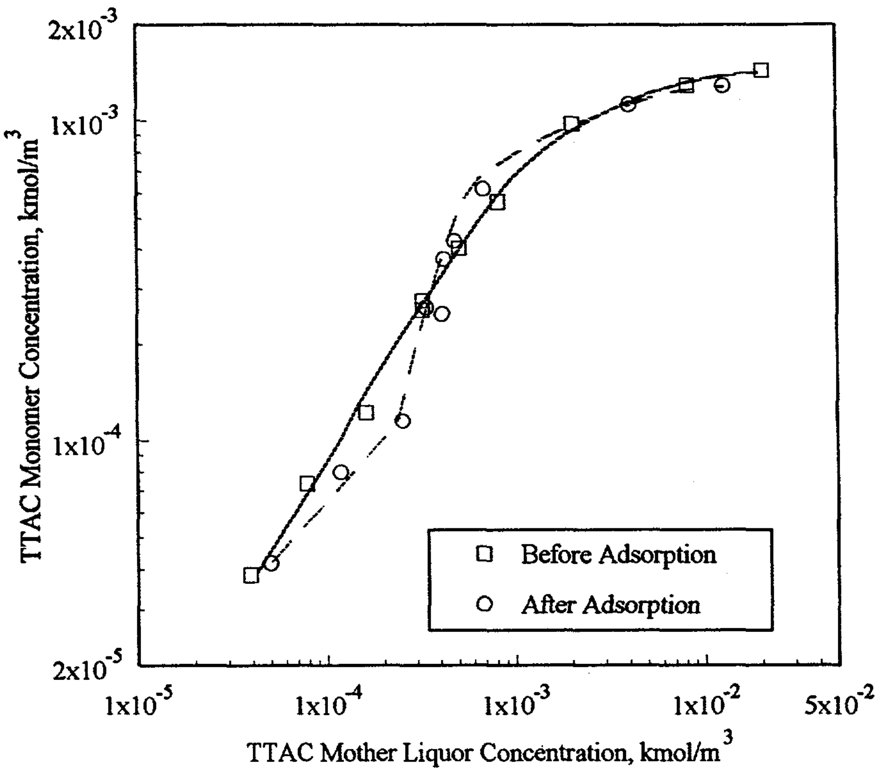

Figure 3 **Change in TTAC monomer concentrations before and after adsorption on alumina from a 4:1 TTAC:NP-15 mixture.**

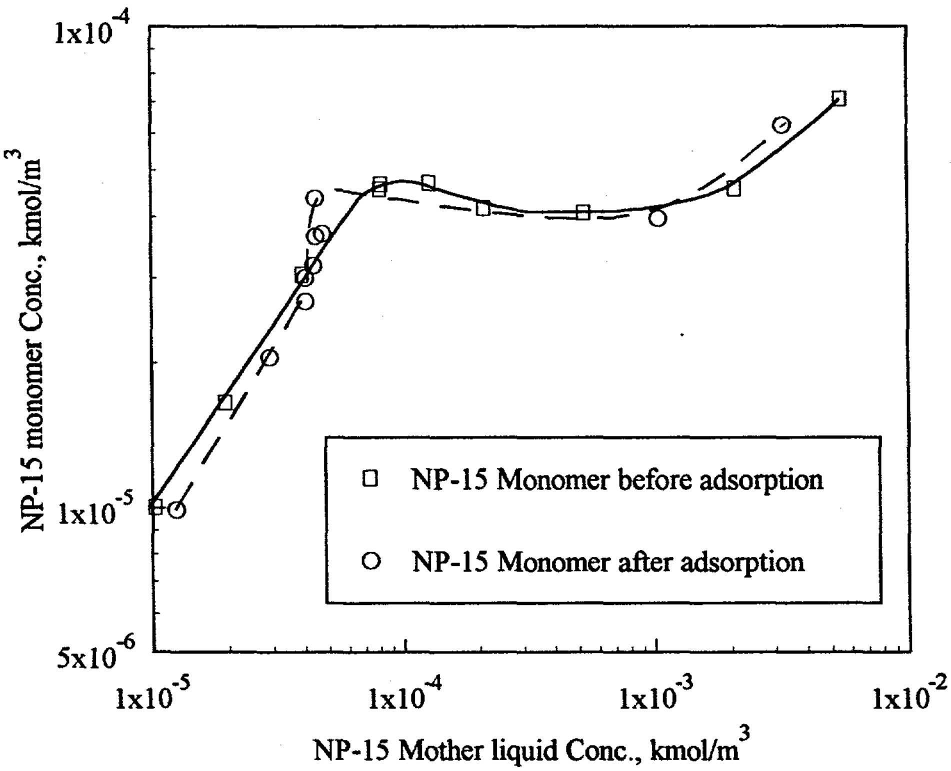

Figure 4 **Change in NP-15 monomer concentrations before and adsorption on alumina from a 4:1 TTAC:NP-15 mixture.**

at the alumina interface. Clearly, the adsorption mechanisms for cationic TTAC are different from those for the non-ionic NP-15.

The adsorption density is compared with the monomer concentrations for both TTAC and NP-15 in figures 5 and 6. The relationship between TTAC adsorption density and its monomer concentrations can be described by two straight lines with different slopes. The point of intersection of these two lines is around the TTAC monomer concentration of 3.5 - 4.0 x10^{-4} mol/l and the adsorption density corresponds to the surface coverage at which the alumina surface charge is neutralized. This indicates that there are two kinds of mechanisms involved in the adsorption of TTAC at this mixture ratio.

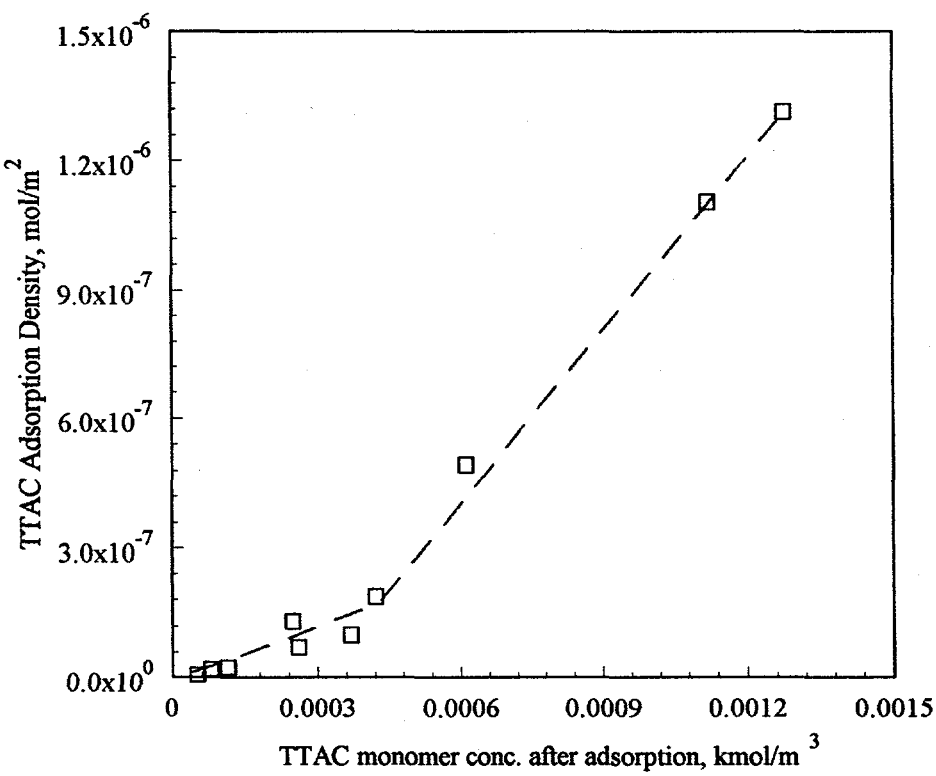

Figure 5 **Relationship between TTAC monomer concentration and adsorption density for a 4:1 TTAC:NP-15 mixture system.**

At low concentrations, the monomer concentration is equal to the total bulk concentration of the surfactant. The adsorption mechanism in this region is clearly electrostatic and can be described by the Stern-Graham equation. At high concentrations, mixed micelles are formed and the monomer concentration is different from the total bulk concentration. The adsorption mechanism in this region is rather complex and merits further investigation.

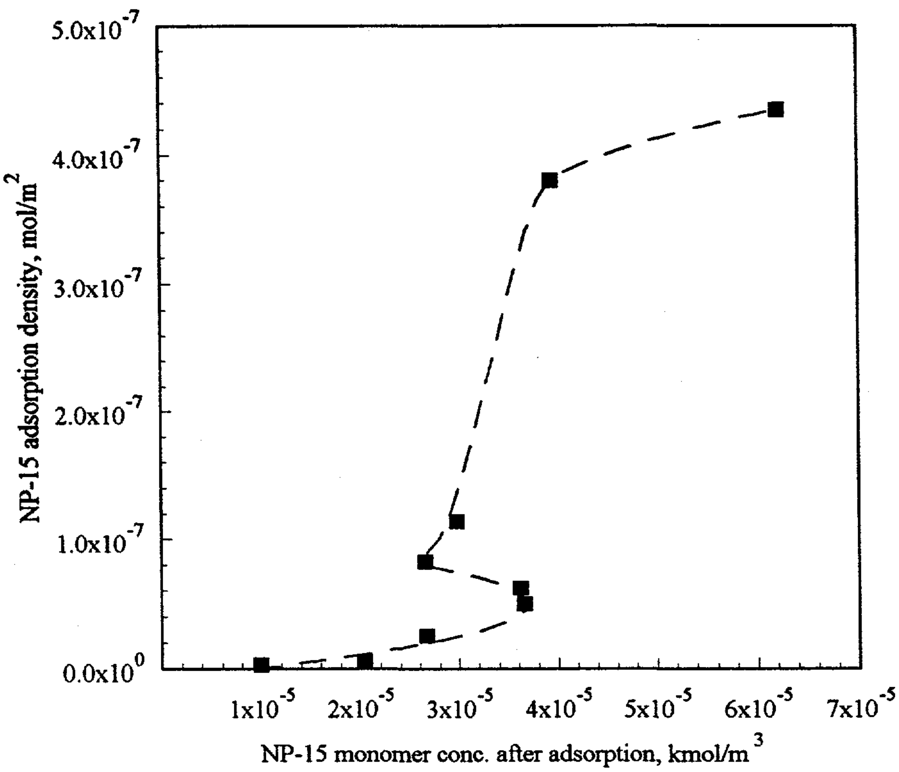

Figure 6 **Relationship between NP-15 monomer concentration and adsorption density on alumina from a 4:1 TTAC:NP-15 mixture.**

The adsorption mechanism for NP-15 is different from that of TTAC (see figure 6). There is a steady increase in adsorption density with increase in monomer concentration upto ~3x10^{-5} mol/l. Above this concentration, an increase in adsorption is accompanied by a decrease in monomer concentration. This is due to the more efficient solubilization of NP-15 into TTAC aggregates which are formed on the alumina surface at this stage. Strong synergy between adsorbed TTAC and NP-15 is indicated by this behavior. Subsequent to the initial extraction of residual NP-15 into the adsorbed aggregates, further increase in monomer concentration leads to increased adsorption followed by surface saturation at high NP-15 concentrations.

It is interesting to examine the monomer ratio in the supernatant from the adsorption behavior point of view in the system (Figures 7 and 8). The ratio of surfactant mother liquor concentration to the monomer concentration can be used as an indication of mixed micelle formation. If no mixed micelles are formed, this ratio will be equal to 1 and ratios higher than 1 indicate the formation of micelles.

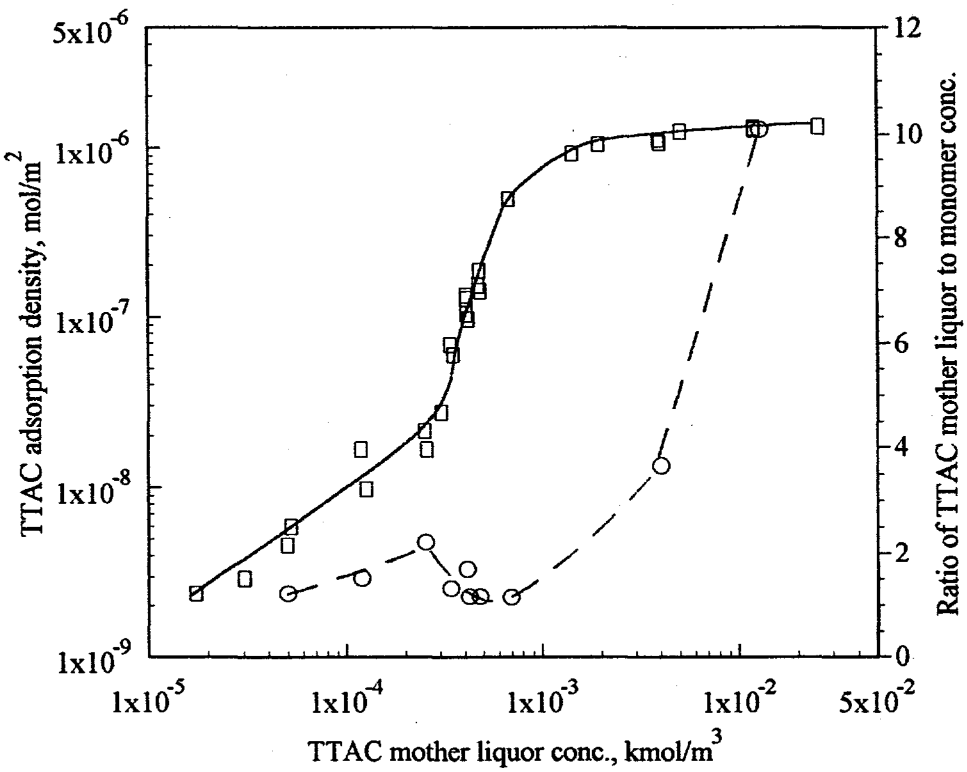

Figure 7 **Correlation between adsorption density and monomer ratio after adsorption for TTAC from a 4:1 TTAC:NP-15 mixture.**

The CMC for the 4:1 TTAC:NP-15 mixture is ~2.7x10^{-4} mol/l (total concentration). This corresponds to 5.4x10^{-5} mol/l NP-15 and 2.16x10^{-4} mol/l TTAC. From figures 7 and 8 it is seen that the adsorption densities for both TTAC and NP-15 continue to increase **above** these concentrations.

In single surfactant systems, formation of micelles in bulk solution is accompanied by a **plateau** in adsorption. Adsorption of both TTAC and NP-15 from the 4:1 thus involve complex equilibria between micelles of different compositions and monomers.

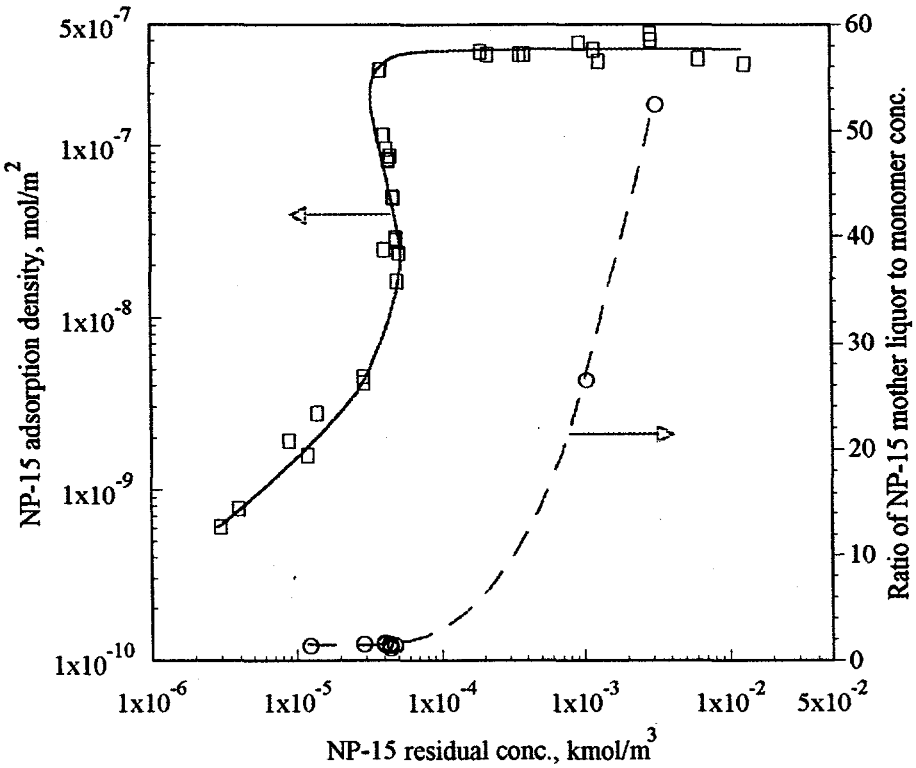

Figure 8 **Correlation between NP-15 adsorption density and monomer ratio after adsorption from a 4:1 TTAC:NP-15 mixture.**

Further investigation is warranted to fully understand the interesting equilibria among solloids, mixed micelles and monomer concentration.

Future work: Monomer concentrations for 1:1 and 1:4 TTAC:NP-15 mixtures will be measured after adsorption to complete the range of rations investigated during the adsorption study.