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QUARTERLY TECHNICAL PROGRESS REPORT

Title	Surfactant Loss Control in Chemical Flooding: Spectroscopic and Calorimetric Study of Adsorption and Precipitation on Reservoir Minerals
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Principal Investigator	Prof. P. Somasundaran
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Reporting Period	10/1/94 - 12/31/94

Summary of Technical Progress

The adsorption and desorption behaviors of tetradecyltrimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonylphenol (NP-15) mixtures as reported earlier were rather complex and to better understand the interactions involved fluorescence spectroscopy and ultrafiltration were used during this report period to probe the microstructure of the adsorbed layer and to determine individual surfactant monomer concentration respectively. It was observed that pyrene was solubilized in mixed aggregates (hemimicelles) of a 1:1 TTAC:NP-15 mixture at the alumina-water interface over a wider concentration range than for TTAC alone. It was also observed that the adsorbed aggregate of a 1:1 TTAC:NP-15 mixture is as hydrophobic as the mixed micelle in solution. This is contrary to what was observed for the adsorption of TTAC alone: pyrene was preferentially solubilized in the TTAC micelles rather than the adsorbed aggregate. The preference of pyrene for the mixed adsorbed aggregates over individual aggregates is relevant to the application of surfactant mixtures in enhanced oil recovery and solubilization.

The adsorption/desorption behavior of surfactants is directly related to the monomer concentration of the surfactant, hence it is important to monitor changes in monomer concentration during the adsorption and desorption processes. Ultrafiltration can be used to monitor the monomer concentration in solution and at the interface to determine the partitioning of the surfactants to the solid-liquid interface. During this report period, ultrafiltration techniques was first adopted to determine the monomer concentrations of the individual surfactants which were then compared to those obtained from theory. The results show that ultrafiltration is a reliable method for the TTAC and NP-15 system and the phase separation model is suitable for these two single surfactants.

Fluorescence Probing of Mixed Surfactant Adsorbed Layers

As mentioned in our previous reports, pyrene monomer fluorescence is sensitive to the medium in which pyrene resides. In an hydrophobic environment, the ratio of the intensities of the third to the first peak (I_3/I_1) on a pyrene emission spectrum is higher than that when the pyrene is in a hydrophilic environment. Since this ratio can be used to characterize the polarity of environments, it is termed here as the **polarity parameter**.

The changes in the polarity parameter of pyrene adsorbed at the alumina-water interface in the presence of a 1:1 mixture of tetradecyltrimethylammonium chloride (TTAC) and pentadecylethoxylated nonylphenol (NP-15) are shown in figure 1a. In addition, emission of pyrene in the supernatant after adsorption is also indicated in figure 1 b. It is observed that pyrene goes to the alumina-water interface when the total residual concentration reaches about 1.5×10^{-4} M. The value of the I_3/I_1 ratio (polarity parameter) increases with increase in adsorption density suggesting an increase in the number of hydrophobic aggregates at the interface. In the supernatant too there are hydrophobic aggregates as indicated by the increase in the value of the polarity parameter. It is interesting to note that the CMC of the mixture is 1.7×10^{-4} mol/l (total surfactant conc.) but the adsorption continues to increase even above this concentration. This is proposed to be due to partitioning of the surfactants to the interface which results in different mixture compositions in the bulk and in the adsorbed layer. Rise in the adsorption density which usually is indicative of strong lateral surfactant chain-chain interactions at the solid-liquid interface is less sharp in this case. This is attributed to the poor ability of the surfactant species to pack at the interface.

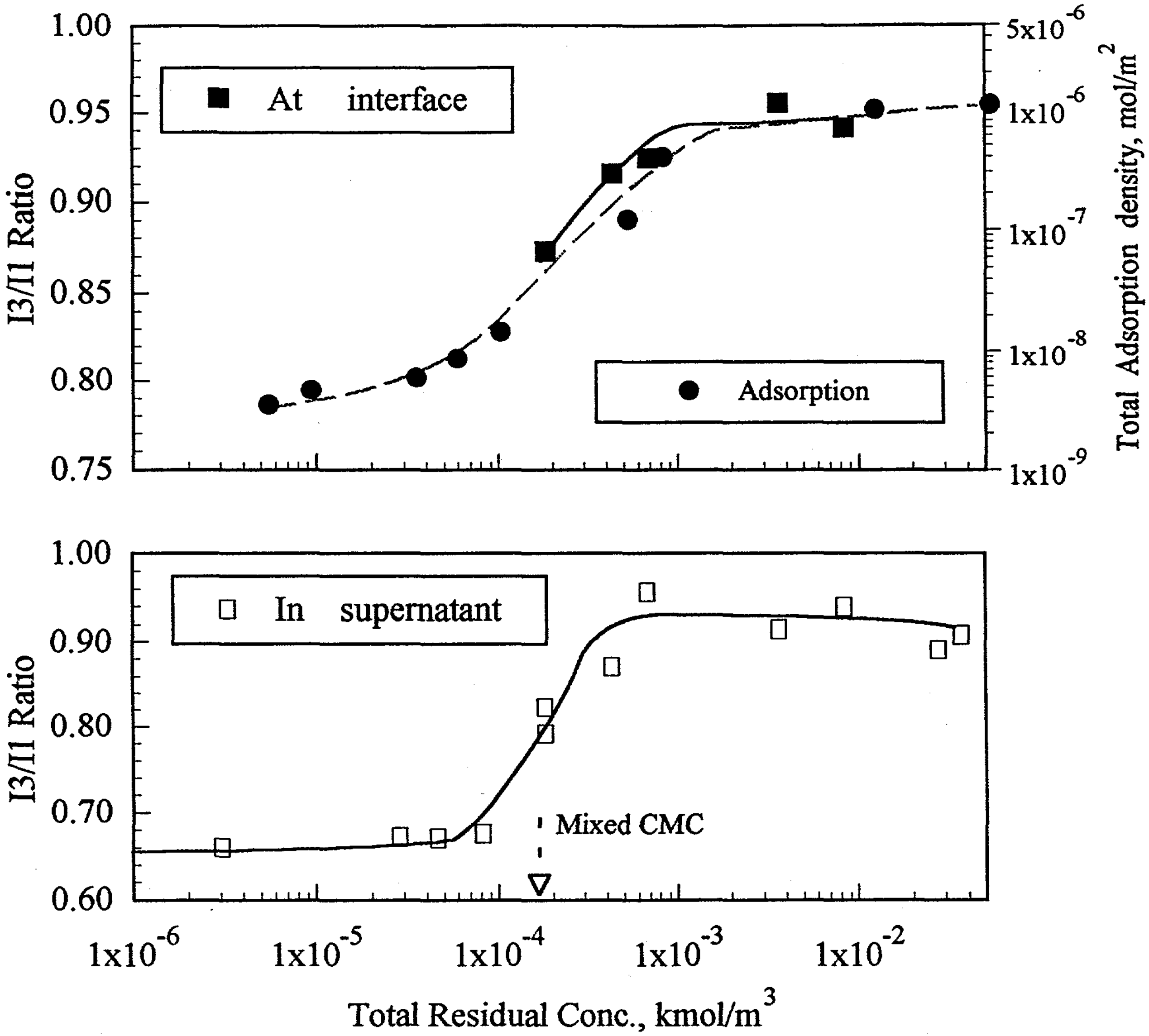

Figure 1 Changes in pyrene polarity parameter at the alumina-water interface in the presence of a 1:1 mixture of tetradecyltrimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15).

It is interesting to compare the behavior of the 1:1 TTAC:NP-15 mixture to that of TTAC alone at the alumina water interface. The adsorption of TTAC alone on alumina along with the emission of pyrene from the adsorbed layer in shown in figure 2.

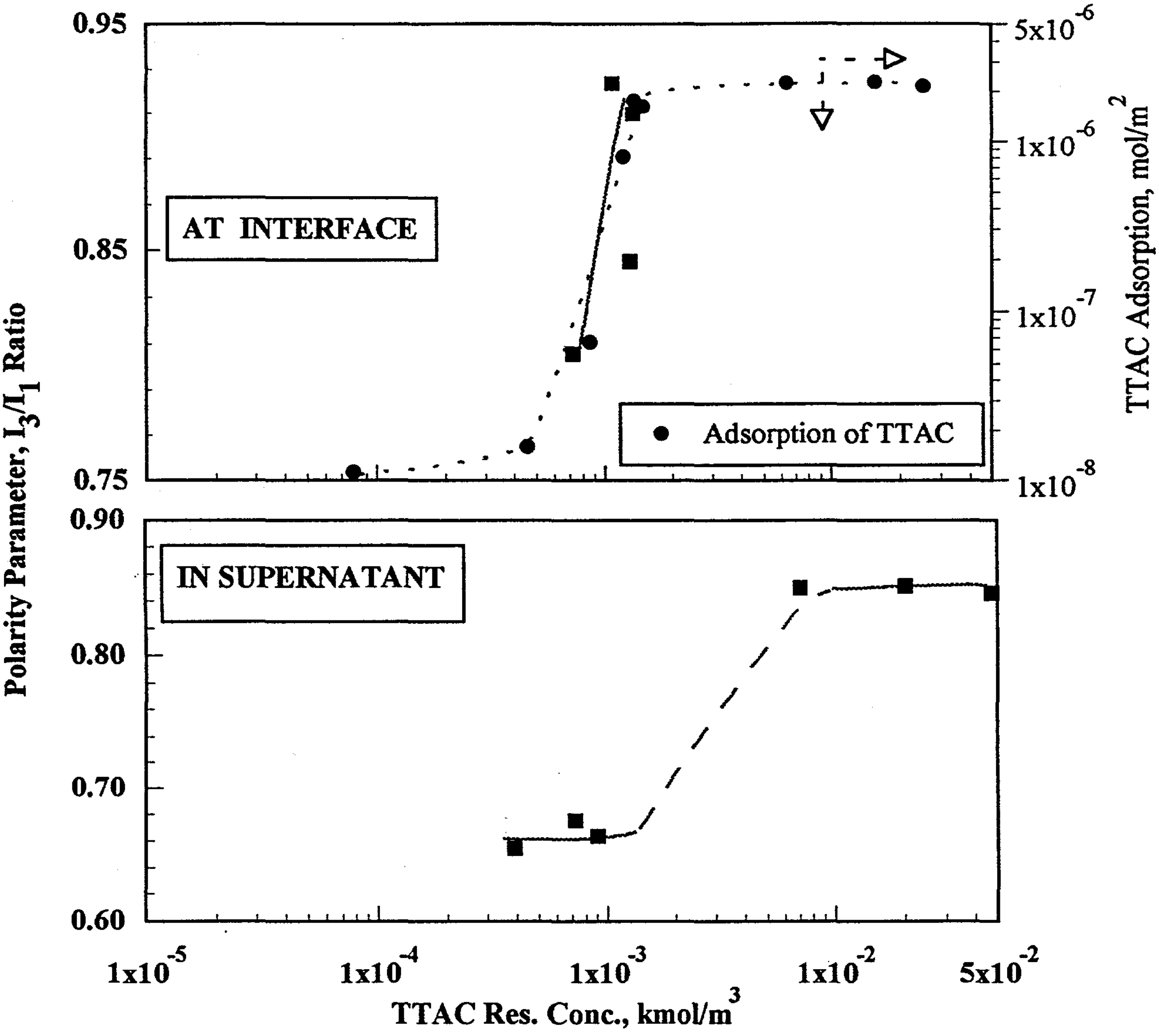

Figure 2 Adsorption isotherm of tetradecyltrimethyl ammonium chloride (TTAC) on alumina and corresponding changes in pyrene monomer fluorescence from the interface and supernatant

It is seen that pyrene dissolves in 1:1 TTAC:NP-15 mixture aggregates once they form at the interface and remains in the mixed aggregates even after the formation of mixed micelles in the supernatant. In contrast, in the case of tetradecyltrimethyl ammonium chloride (TTAC) alone, pyrene goes to the alumina-water interface over a narrow concentration range. Once TTAC micelles appear in the supernatant pyrene is preferentially solubilized into these micelles and does not go to the alumina-water interface despite the presence of TTAC aggregates. This indicates that for TTAC alone the hydrophobicity of micelles of TTAC is higher than that of adsorbed TTAC. This is most interesting and different from earlier observations with linear alkyl surfactants such as sodium dodecyl sulfate (SDS). Also, in the 1:1 TTAC:NP-15 mixture system the hydrophobicity of adsorbed aggregates and micelles is almost the same over the concentration range studied. Presence of the nonionic surfactant in the mixed aggregate will reduce the repulsion between the cationic heads of the adsorbed surfactant and assist the packing (and hydrophobicity). It may also be geometrically easier to pack the two together than TTAC alone which has a bulky head group. It will be useful to determine the composition of the adsorbed aggregates to ascertain the partitioning of the component surfactants to the interface. It is to be noted that partitioning of organic compounds in enhanced oil recovery process will be dictated by the relative hydrophobicity of the adsorbed aggregates and micelles in the system, and hence it is important to understand the nature of hydrophobicity changes in mixed surfactant systems. Experiments will be done in the future to elucidate these important effects.

Measurement of Monomer Concentration by Ultrafiltration

As suggested earlier, information on changes in the monomer concentration of individual surfactants in mixtures during the adsorption is vital since the adsorption behaviors are directly related to the monomer concentration of each component in the mixtures. Ultrafiltration is a method which can be used to separate the monomer and micelles directly. During this report period ultrafiltration was used for determining tetradecyltrimethylammonium chloride (TTAC) and pentadecylethoxylated nonylphenol (NP-15) monomer concentrations.

The cell and membrane used in this study were obtained from Amicon Company (model 8050 and YM-3 membrane). The membrane chosen was specified to exclude molecules with molecular weight greater than 3000. Since the micelles of both TTAC and NP-15 will be considerably larger than this molecular weight cutoff this membrane was considered satisfactory for separating monomers from micelles. A constant pressure of 910 mm mercury was exerted on the mother liquor using compressed nitrogen and the effluent was collected at atmospheric pressure. All experiments were performed at an ionic strength of 0.2 M NaCl so that the effects of diffusion potential on the transport of dispersed surfactant through membrane was negligible.

The results obtained from ultrafiltration experiments are shown in figures 3 and 4. It is observed that when the mother liquor concentrations are lower than the CMC of the surfactants,

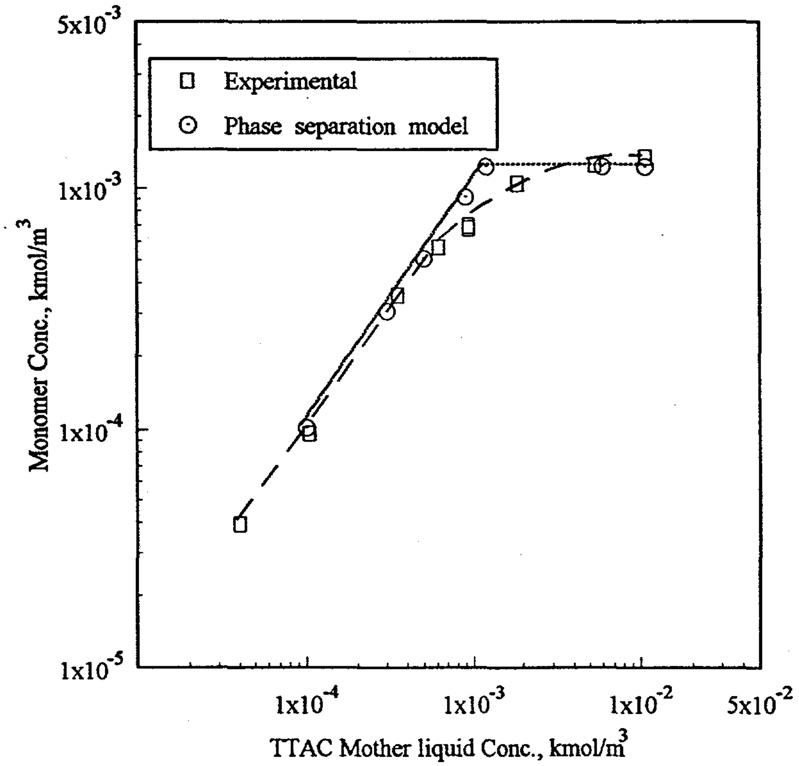

Figure 3 **Monomer concentration of Tetradecyltrimethylammonium chloride (TTAC) as the function of total concentration**

monomer concentrations (or filtrate concentrations) are the same as the mother liquor concentrations and increase linearly with concentration. Above the CMC, the monomer concentrations obtained by ultrafiltration are relatively constant.

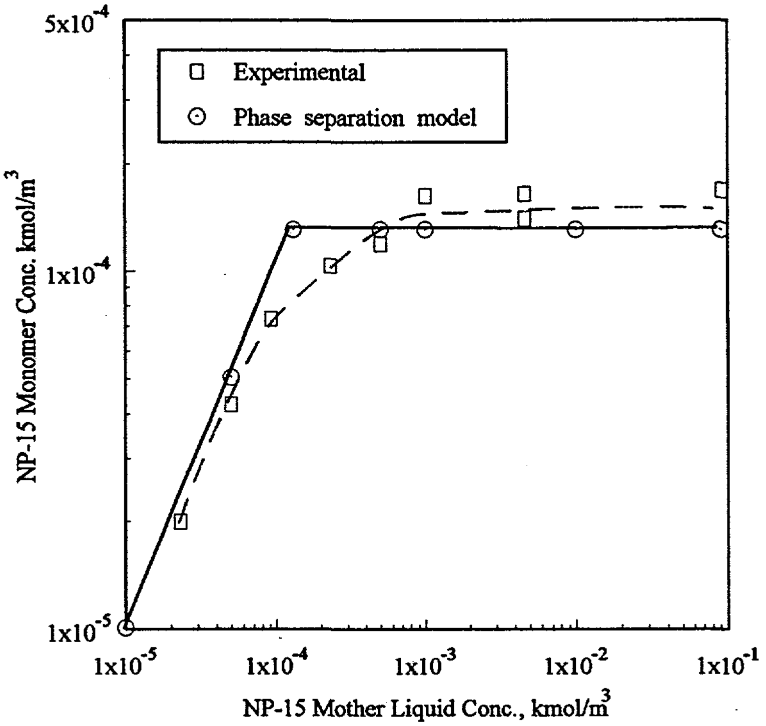

Figure 4 **Monomer concentration of pentadecylethoxylated nonylphenol (NP-15) as the function of total concentration**

These results show that ultrafiltration method is suitable for separating monomers from micelles in this system. To compare the results from ultrafiltration results with phase separation model, the monomer concentration predicted by phase separation model are also plotted in figures 3 and 4. It can be found that experimental results and phase separation model are almost the same except around CMC. In this concentration range, the monomer concentrations obtained from ultrafiltration are lower than the concentrations predicted by phase separation model. This may indicate formation of some pre-micellar aggregates in solution, and this aspect merits further investigation. The monomer concentrations for the mixed surfactant systems will be measured in our subsequent work.

Future work:

Monomer concentration measurement for mixed surfactant system.

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U.S. DEPARTMENT OF ENERGY

MILESTONE SCHEDULE ☐ PLAN ☒ STATUS REPORT

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1.1	adsorption desorption																
1.2	surface tension																
1.3	electro-kinetics																
1.4	spectro-scopy																
1.5	thermo-dynamics	▨	▨	▨													
2.0	SURFACTANT MIXTURES																
2.1	adsorption																
2.2	surface tension																
2.3	hysteresis																
2.4	chromato-graphy	▨	▨	▨													
2.5	spectro-scopy	▨	▨	▨													
2.6	thermo-dynamics	▨	▨	▨													
3.0	REPORTS			☒			☐			☐			☐				

11. SIGNATURE OF PARTICIPANT'S PROJECT MANAGER AND DATE