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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Objective

The aim of this contract is to elucidate the mechanisms underlying adsorption and surface precipitation of flooding surfactants on reservoir minerals. Effect of surfactant structure, surfactant combinations and other inorganic and polymeric species will also be determined. Solids of relevant mineralogy and a multi-pronged approach consisting of micro & nano spectroscopy, microcalorimetry, electrokinetics, surface tension and wettability will be used to achieve the goals. The results of this study should help in controlling surfactant loss in chemical flooding and also in developing optimum structures and conditions for efficient chemical flooding processes.

Summary of Technical Progress

Adsorption of single surfactants on silica and alumina as well as the solution behavior of surfactant mixtures was studied during this quarter. The adsorption of surfactants at the solid-liquid interface was correlated with changes in interfacial behavior such as wettability and zeta potential.

Surface tension was used to study interactions between surfactant mixtures in solution. Mixed micellization of sodium dodecyl sulfate and dodecyl phenoxy polyethoxylated alcohol was found to be non-ideal. Regular solution theory adequately describes the interactions.

The adsorption isotherm of a cationic surfactant, tetradecyl trimethyl ammonium chloride (TTAC), on alumina was determined at two values of pH. Changes in the settling rate of alumina suspensions after TTAC adsorption were also followed to describe the

evolution of the adsorbed layer. At high surface coverage it was observed that the alumina surface became hydrophilic suggesting the formation of a TTAC bilayer at the surface.

Wettability of silica after adsorption of nonyl phenyl polyethoxylated alcohols (with number of polyethylene oxide groups varying from 10-40) was measured using flotation to determine the orientation of the adsorbed layer. Effect of number of ethylene oxide groups was also determined. The amount of silica floated after the nonionic surfactant adsorption was same irrespective of the ethylene oxide chain length.

Cationic surfactant adsorption on alumina

To determine the effect of surfactant charge on their adsorption/desorption behavior, adsorption of a cationic surfactant, tetradecyl trimethyl ammonium chloride (TTAC) was studied at the alumina/water interface. The adsorption isotherms of TTAC on alumina at two different pH values are shown in figure 1a. Alumina is positively charged at pH 8 but negatively charged at pH 10 and thus the adsorption of the cationic TTAC is higher when the alumina is negatively charged. There is a sharp increase in the adsorption at ~5 x 10^{-4} kmol/m^3 TTAC only at pH 10 which can be attributed to surfactant aggregate formation at the alumina-water interface. At pH 8, negatively charged sites on the alumina surface are proposed to be few and far apart to induce any surfactant aggregation. The settling rate of the alumina suspensions after TTAC adsorption at pH 10 was measured and the results are shown in figure 1b. In the absence of and at low surfactant adsorption, the alumina suspension in water is dispersed and the settling rate is low. Once the surfactant forms

aggregates at the interface, the alumina surface becomes hydrophobic and the settling rate is markedly increased.

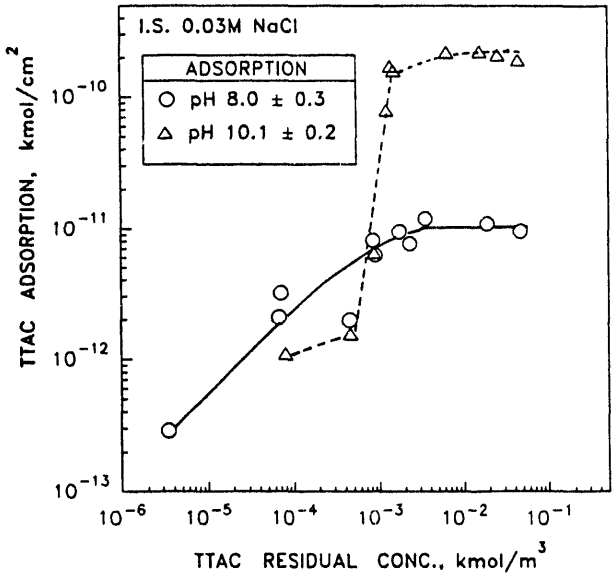

Figure 1a: **Adsorption of tetradecyl trimethyl ammonium chloride (TTAC) on alumina at two values of pH**

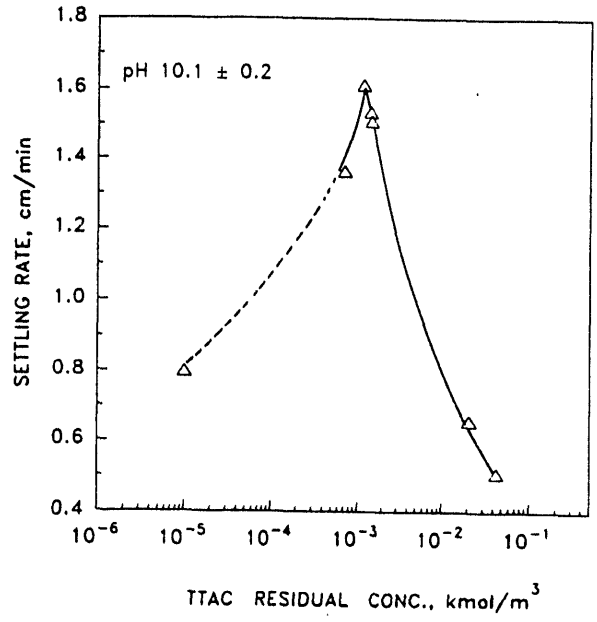

Figure 1b: **Settling rate of alumina suspension after TTAC adsorption at pH 10**

The settling rate decreases above 10^{-3} kmol/m^3 which is proposed to be the concentration at which the TTAC forms a bilayer at the alumina-water interface exposing a polar surface towards the solution. This model will be tested by measuring the zeta potential of the alumina particles after TTAC adsorption.

Interfacial Behavior of Nonionic Surfactants

The study of the effect of the number of ethylene oxide (EO) groups on the adsorption behavior of polyethoxylated alkyl phenols on silica was continued this quarter. The number of EO groups on the surfactants, 10, 15, 20 and 40, offered a wide range. It

was observed that with an increase in the number of EO groups, adsorption both at the solid-liquid and liquid-air interfaces decreased. The effect of the adsorption on interfacial characteristics such as zeta potential and wettability was determined during this quarter.

Changes in the electrokinetic properties of silica after adsorption of nonylphenol polyethoxylated alcohol with 10 and 15 ethylene oxide groups (NP-10 and NP-15 resp.) are shown in figures 2 and 3 along with the adsorption isotherms. In both cases, adsorption of the nonionic surfactant decreases the surface charge of silica.

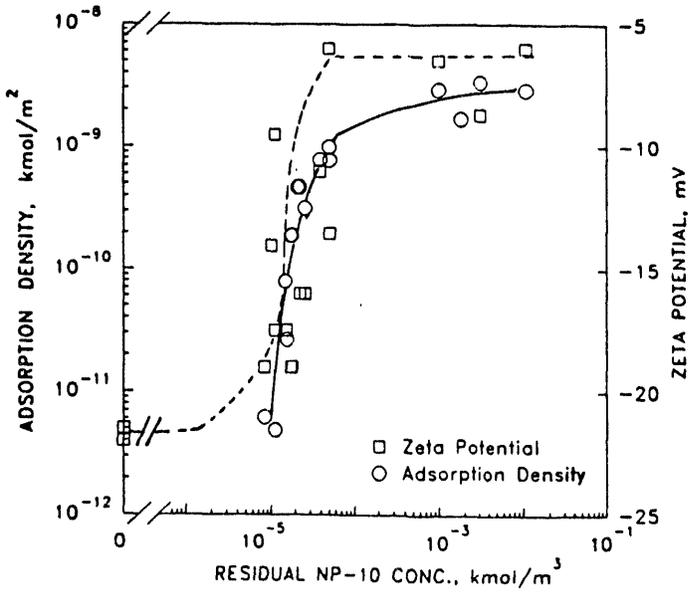

Figure 2: **Effect of NP-10 adsorption on the zeta potential of silica (pH ≈ 6)**

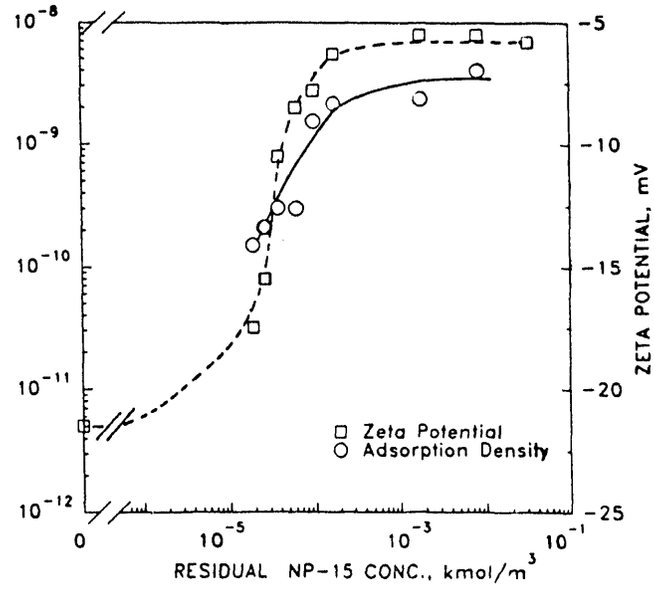

Figure 3: **Effect of NP-15 adsorption on the zeta potential of silica**

The adsorbed layers of NP-10 and NP-15 are proposed to cause a shift in the shear plane and the magnitude of the zeta potential decreases. It can be expected that there will be no significant difference in the adsorbed layer thickness for NP-10 and NP-15 and as a result their effect on the surface charge of silica will be identical. Studies with NP-40 are in

progress.

The wettability of silica after adsorption of nonionic surfactant was measured by determining flotation using a modified Hallimond tube and the results are shown in figures 4 and 5. The surfactants chosen were nonyl phenols with 10 and 40 ethylene oxide groups. Based on adsorption results it was proposed that the NP-10 formed aggregates at the silica-water interface whereas the bulky NP-40 did not. Presence and absence of aggregates at the interface can be expected to affect the wettability to different extents. From figures 4 and 5 it is seen

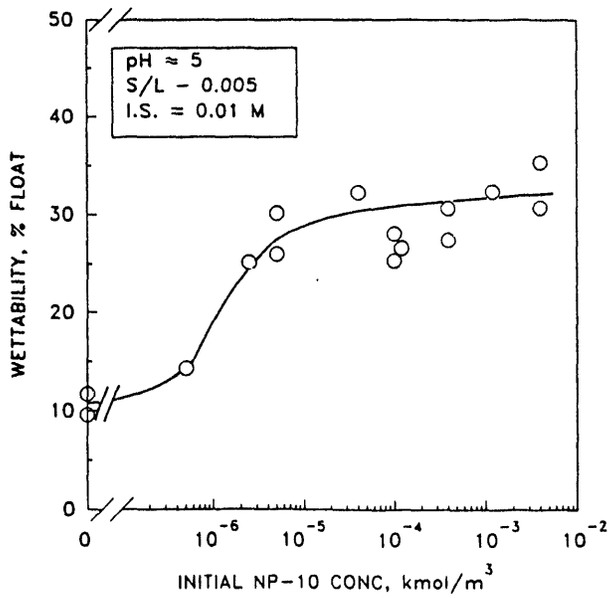

Figure 4: **Wettability of silica after NP-10 adsorption**

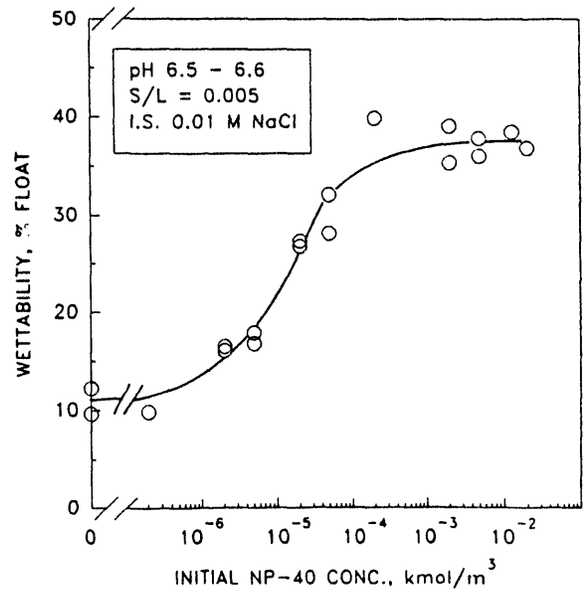

Figure 5: **Wettability of silica after NP-40 adsorption**

that in the absence of surfactant, silica is hydrophilic and floats very little. Surfactant adsorption, which is known to be via hydrogen bonding between the ether oxygens of the EO group and surface silanol groups, will expose a hydrocarbon chain into solution; render the silica surface hydrophobic thereby increasing the floatability. Interestingly, the maximum

hydrophobicity achieved in the presence of both the adsorbed surfactants is identical. This suggests that the microstructure of the adsorbed layers of both NP-10 and NP-40 are similar. It is to be noted that the flotation results in figure 4 and 5 are plotted as a function of initial surfactant concentration. Since the adsorption of NP-10 is significantly higher than NP-40 it is likely that the adsorbed layers for similar initial concentrations will be vastly different. The residual concentrations could not be measured at the time of flotation: a complete set of results will be presented in the next report. Nevertheless, it is interesting that the flotation recovery reaches a maximum and does not decrease above a certain surfactant concentration. This suggests that these surfactants do not form a bilayer at the interface: formation of a bilayer at the interface would create a hydrophilic surface and reduce flotation. Spectroscopic studies are in progress to probe this aspect further.

Interfacial and Solution Behavior of Anionic - Nonionic Surfactant Mixtures

Mixtures of anionic and nonionic surfactants offer improved solution and interfacial properties as compared to that of the individual components. In this study the interactions between two commonly used surfactants: anionic sodium dodecyl sulfate (SDS) and the nonionic dodecyl phenoxy polyethoxylated alcohol (TRITON) were studied using surface tension and the interactions were modelled using regular mixing theory. Understanding the activity of the surfactants at the air-water interface will help to explain the differences in the behavior of the surfactants at the solid-liquid interface.

The surface tension of mixtures of SDS and TRITON of varying compositions are shown in figure 6. The measurements were made with a Wilhelmy Plate tensiometer using

a sand blasted platinum as the sensor. With an increase in the concentration of the nonionic surfactant, the surface tension of the mixture is drastically reduced.

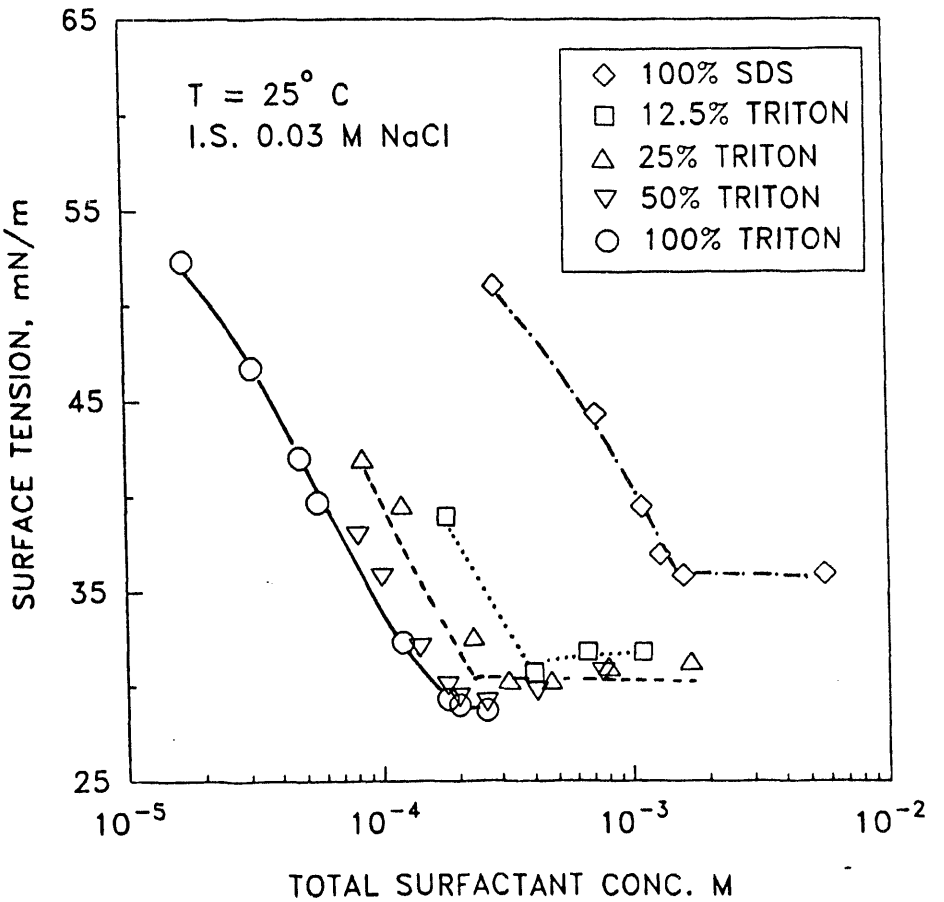

Figure 6: **Surface tension of mixtures of sodium dodecyl sulfate (SDS) and dodecyl phenol polyethoxylated alcohol (TRITON)**

Table I lists the results obtained for critical micellization concentration (CMC) at different mole fractions (α) of the nonionic surfactant, TRITON.

Table I: Mixed CMC (C^*) at different mole fractions of TRITON

α	0	0.125	0.25	0.50	1.00
C^* (kmol/m^3)	1.6×10^{-3}	4×10^{-4}	3.4×10^{-4}	2.0×10^{-4}	1.8×10^{-4}

Regular mixing theory is based on the assumption that the excess Gibbs free energy of mixing is given by:

$$\Delta G_{mix} = X_1 X_2 W R T \tag{1}$$

where X_1 and X_2 are the mole fractions of the two surfactants in the mixed micelle and W the interaction parameter. Regular solution also assumes that the excess entropy and volume of mixing are zero and hence the excess enthalpy of mixing is given by:

$$\Delta H_{mix} = X_1 X_2 W R T \tag{2}$$

It is of interest to find the interaction parameter W as an experimental parameter from CMC measurements and apply this W to interpret subsequent experiments. This is appropriate for the calculation of monomer concentrations for the interpretation of adsorption results with mixed systems. If C_1 and C_2 are the CMC values of the pure surfactants and C^* that of the mixed system, the following relationships[1] permit solution for W in terms of C_1, C_2 and C^*:

$$\frac{X_1^2 \ln\left(\frac{C^* \alpha}{C_1 x}\right)}{(1-X_1)^2 \ln\left[\frac{C^*(1-\alpha)}{C_2 (1-X_1)}\right]} = 1 \tag{3}$$

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[1] D.N. Rubingh, "Mixed Micelle Solutions", in Solution Chemistry of Surfactants, Vol. 1, Plenum Press, 1978, pp 337-354.

$$W = \frac{\ln\left(\frac{C^{*}\alpha}{C_1 X_1}\right)}{(1-X_1)^2} \tag{4}$$

where X_1 is the mole fraction of surfactant 1 in the mixed micelle and α is the mole fraction of surfactant 1 in the total mixed solute. Equation (3) must be solved iteratively for X_1, whereupon substitution of this X_1 into equation (4) results in immediate solution for W. C_1 and C_2 in this case are 1.8×10^{-4} and 1.6×10^{-3} respectively and using values of -3.5 and -4.0 for W, results obtained are shown in Table II.

Experimental data and calculated results are plotted in figure 7. It can be seen that the experimental data show negative deviation from ideal mixing predictions. The effectiveness of regular solution theory can be seen from the fit using W = -4.0. The negative values of W results in CMC and monomer concentration values which are less than that predicted by the ideal solution theory. When the two surfactants with dissimilar polar heads form micelles, electrostatic repulsion between the SDS molecules is reduced by the presence of TRITON molecules.

Table II: Calculated results of X_1 and C^* by regular solution theory

α	$\alpha/(1-\alpha)$	W = -3.5		W = -4.0	
		X_1	C^* (10^{-4})	X_1	C^* (10^{-4})
0.05	0.053	0.538	9.16	0.538	8.09
0.10	0.111	0.605	6.31	0.597	5.60
0.125	0.143	0.628	5.56	0.617	4.94
0.20	0.25	0.677	4.22	0.662	3.78
0.25	0.333	0.701	3.69	0.685	3.32
0.30	0.428	0.722	3.31	0.705	2.99
0.40	0.67	0.759	2.78	0.739	2.53
0.50	1	0.791	2.44	0.769	2.24
0.60	1.5	0.821	2.2	0.799	2.04
0.80	4	0.886	1.9	0.863	1.8
0.90	9	0.928	1.82	0.908	1.76
0.95	19	0.957	1.8	0.941	1.76

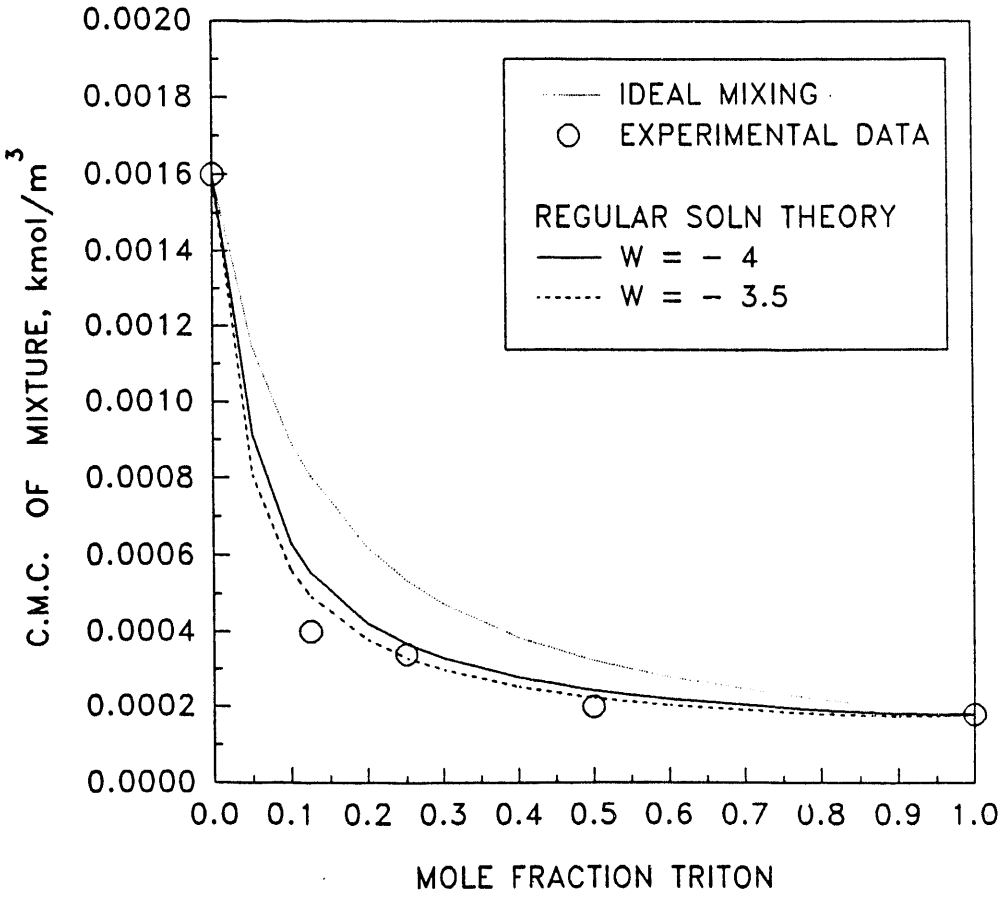

Figure 7: **Correlation of CMC of a mixture of SDS and TRITON with mole fraction of TRITON**

Future Work:

1. Spectroscopic studies of adsorbed layer of nonionic surfactant on silica.
2. Desorption of cationic surfactant from alumina.
3. Calorimetry of surfactant mixtures.

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