

UNIVERSITY OF FLORIDA RESEARCH PROGRAM  
ON SURFACTANT-POLYMER OIL RECOVERY SYSTEMS

By

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ABSTRACT

This program has as its principal objectives improvement in the understanding of the structure and properties of micellar/polymer injection fluids and of their behavior as they interact with brine, oil, and rock after injection. Research is being carried out in the following areas:

1) interfacial phenomena, 2) surfactant-polymer association and flow through porous media, 3) thermodynamics, and 4) rock/fluid interactions. More specifically, studies of the CMC of surfactants under various conditions, distribution of various components of a surfactant formulation between oil and aqueous phases, the structure of surfactant formulations, surfactant-polymer interactions and flow in porous media, the theory of solutions and of micellization, and of various surfactant loss processes including salting-out by indifferent electrolytes and partitioning to oil, precipitation by multivalent cations, and adsorption on rocks, clays, and the like are involved.

INTRODUCTION

The enhanced oil recovery program at the University of Florida has been primarily concerned with elucidation of many of the phenomena associated with surfactant-polymer flooding with a view to improving both understanding and operation of the process. To that end research activities dealing with interfacial phenomena, thermodynamics, and rock/fluid interactions have been undertaken. The sections which follow describe briefly our principal work in these areas during the past year.

INTERFACIAL PHENOMENA

It has been shown by various investigators that ultralow interfacial tension can be achieved in an oil/brine/surfactant system under appropriate conditions of salinity, oil chain length, and surfactant concentrations. The studies carried out in our laboratory have shown that ultra-low interfacial tension can be achieved by petroleum sulfonate as well as by isomerically pure alkyl benzene sulfonate (UT-1). Figure 1 shows that for

a petroleum sulfonate (TRS 10-80), an ultralow IFT minimum exists at a specific salinity, oil chain length, or surfactant concentration. The effect of salt concentration and oil chain length is similar for an isomerically pure alkyl benzene sulfonate (UT-1), i.e., the minimum in interfacial tension occurs at a specific salinity or specific oil chain length. However, the effect of surfactant concentration is different for UT-1 in that increasing the surfactant concentration further decreases the interfacial tension for isomerically pure alkyl benzene sulfonate (UT-1).

Using light scattering, membrane osmometry, surfactant analysis, dye-solubilization, and surface tension measurements we have established that, after equilibration of the oil-brine-surfactant system, the minimum interfacial tension coincides with the critical micelle concentration in the aqueous phase as well as a partition coefficient of near unity. Therefore, from studies of petroleum sulfonates, it appears that the necessary condition to obtain the maximum interfacial surfactant concentration is that the partition coefficient be near unity and that the monomer concentration in the aqueous phase as well as in the oil phase be at the maximum. It is the maximum monomer concentration in the oil phase and the brine phase which leads to the maximum concentration at the interface. This was also confirmed by the electrophoretic mobility of oil droplets in the equilibrated systems.

For isomerically pure di-alkyl benzene sulfonates, the interfacial tension minimum occurred at a specific NaCl concentration and at a specific oil chain length. The same molecular mechanism is applicable for these systems as offered for petroleum sulfonates. However, the surfactant concentration effect showed (Figure 1) that upon increasing the surfactant concentration, the interfacial tension continued to decrease in contrast to the increase in IFT for petroleum sulfonates. It is proposed that for isomerically pure sulfonate solutions, the monomer concentration of the surfactant does not decrease whereas in petroleum sulfonate systems, the formation of mixed micelles between oil-soluble and water-soluble species leads to a decrease in the monomer concentration in the aqueous phase. For isomerically pure surfactant, such mixed micelle formation cannot occur. The further decrease in IFT upon increasing surfactant concentration is attributed to the solubilization of water and oil or brine. The mutual solubilization of oil and brine lead to a further decrease in IFT. Light scattering results also confirmed that a further decrease in IFT beyond the CMC for isomerically pure surfactant coincides with the formation of reverse micelles in the oil phase.

Figure 2 shows our proposed model for the interfacial tension in oil/brine/surfactant systems. The first line shows the 6 variables that are commonly involved in any surfactant/oil/brine system. These variables influence two basic phenomena,

namely, the partition coefficient of surfactant and the effective CMC of the surfactant. The partition coefficient influences the mutual solubility of oil and brine whereas the effect of the CMC represents the monomer concentration in the aqueous phase. These two phenomena determine the three surface parameters, namely the surface concentration of surfactant, surface charge density, and solubilization of oil and brine in each other. It is these three parameters that determine the final magnitude of interfacial tension. From our studies we have found that increasing surface concentration, surface charge density, and/or solubilization of oil and brine in each other can decrease the interfacial tension. Therefore, we view the final magnitude of the interfacial tension as the combined effect of these three parameters.

Figure 3 shows the three dial systems representing the three contributions to the interfacial tension. The first one, surface concentration, the second, surface charge density and the third solubilization of oil and brine. However, further work is in progress to determine quantitatively the magnitude of each of these contributions for the interfacial tension in oil/brine/surfactant systems.

#### THERMODYNAMICS

A theory for all thermodynamic properties of aqueous solution of spherical and chain nonpolar substances has been essentially completed and has very good agreement with experiment. The components of the theory give insight into the fundamental physical processes involved.

The assertion that micellization was entropy-driven by the excluded volume effect of the surfactant tail on the water was advanced some time ago. However, data indicate that at higher temperatures, micelle formation becomes an energy-driven process. A very large heat capacity change associated with cavity formation in water is found and this means that as the temperature increases, the entropy effect of cavities decreases and the enthalpy effect increases dramatically. Since all other steps in the proposed process for micellization are found to be significantly less sensitive to temperature, the excluded volume effect on the water is still the step which drives the process.

Experimental observation of temperature, pressure and dissolved gas effects on the isotropic-anisotropic transitions of lyotropic liquid crystals apparently show that promotion of the anisotropic phase under pressure or with methane is a transient effect. Phase behavior studies using temperature cycling show that surfactants behave differently with regard to stabilizing two or three phases as a function of increased salt and temperature. Apparently, many studies of phase behavior at room temperature have not reached equilibrium although temperature cycling would accelerate the approach to the ultimate state.

In the Rock/Fluid Interaction area, it has been reported that surfactant oil-water distribution coefficients change dramatically with surfactant chain length. A brief inquiry into group contribution methods for the effects of alkyl chains on aromatic rings (Tsonopoulos and Prausnitz, 1971, and Pierotti et al., 1959) shows that the effect of surfactant chain length on the infinite dilution distribution coefficient, which goes as the ratio of the activity coefficients of the surfactant in the two phases, should be given by the following expression for two alkyl benzene sulfonates

$$\ln K_n^\infty - \ln K_{n'}^\infty = -0.00113[(n_o - n)^2 - (n_o - n')^2] + 1.073 \left[ \left[ \frac{1}{n-4} \right] - \left[ \frac{1}{n'-4} \right] \right] - 1.34(n-n') \quad (1)$$

where  $n_o$  is the oil chain carbon number, and  $n$  and  $n'$  are the (effective) chain lengths of the two surfactants being compared. For example, in the cases of sodium dodecyl benzene sulfonate ( $n=18$ ) and sodium hexadecyl benzene sulfonate ( $n'=22$ ) with  $n$ -dodecane ( $n_o=12$ ) as the oil,  $K_{12}^\infty/K_{16}^\infty = 230$ , which means that if the hexadecyl benzene sulfonate is found roughly equally partitioned between the aqueous and oil phases, the dodecyl benzene sulfonate should be found essentially completely in the aqueous phase, as it is.

#### ROCK/FLUID INTERACTIONS

The principal activities in this area have been concerned with surfactant salting-out by indifferent electrolytes and partitioning to oil, surfactant precipitation by multivalent cations and precipitate dissolution by excess surfactant, the effect of salt and oil on the CMC of surfactants, and the relation of these phenomena to surfactant adsorption and to surfactant retention in surfactant/polymer flooding. A small effort on polymer adsorption has also been maintained.

Surfactant Salting-Out By Indifferent Electrolytes: The salting-out of several alkyl benzene sulfonates by NaCl has been measured both with respect to surfactant as well as salt concentration. The data for SUL-FON-ATE AA10, a commercial mixture having an average composition near sodium dodecyl benzene sulfonate, are shown in Figure 4. This surfactant is fairly tolerant of salt but NaCl concentrations greater than one wt.% result in very significant salting-out, especially at the higher surfactant concentrations.

The salting-out of two synthetic monoisomeric surfactants [ $2-\phi C_{12}SO_3Na$  (Conoco No. 8209J, and  $8-\phi C_{16}SO_3Na$  (U Texas)] have also been measured. Results are similar to those in Figure 4 but these surfactants are less tolerant of salt than is SUL-FON-ATE AA10.  $2-\phi C_{12}SO_3Na$  was salted-out by one wt.% NaCl

in significant amounts when the initial surfactant concentration was 0.001 wt.% or greater. For  $8-\phi C_{16}SO_3Na$  even 0.01 wt.% NaCl caused appreciable salting-out from both 0.005 and 0.1 wt.% surfactant solutions.

If oil is present, a dramatic chain length difference in surfactant behavior is seen. For example, when the oil/water ratio is either 1/1 or 1/2 and the oil is either n-octane or n-dodecane, salting-out of  $8-\phi C_{16}SO_3Na$  is not observed at any surfactant or salt concentration tested: essentially all of the surfactant partitions to the oil. In contrast, oil appears to have no effect on the salting-out behavior of the dodecyl benzene sulfonates, and essentially no surfactant partitions to the oil. It should be recalled that this behavior is consistent with the predictions of thermodynamics based upon group contribution methods. These calculations predict that essentially no  $C_{12}$  surfactant will partition to the oil if the partition coefficient of the  $C_{16}$  surfactant is near unity.

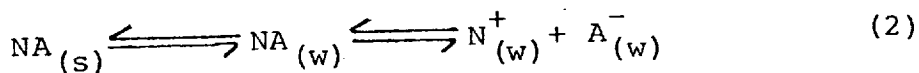
Salting-out appears to be due in part to suppression of surfactant ionization and to a general reduction of surfactant solubility as the ionic strength of the solution increases. These and other aspects of the phenomenon are under continuing investigation.

Surfactant Precipitation By Multivalent Cations: Precipitation of anionic surfactants by multivalent cations is a widely observed phenomenon. Similarly, dissolution of the precipitate or inhibition of its formation by excess surfactant have been described by a number of investigators [O'Brien and Wiers (1974), Corkill and Goodman (1962), Pearson and Lawrence (1967)]. Both precipitation and solubilization of several anionic surfactants have been studied in our laboratories. Calcium lauryl sulfate is a typical example and its behavior is shown in Figure 5, where the fraction of surfactant precipitated is shown as a function of the surfactant to calcium ratio (equiv. surf./equiv. Ca) for a range of constant concentration of calcium. Precipitation of the calcium surfactant,  $CaA_2$ , is observed up to A/Ca ratios of approximately one; at higher A/Ca ratios the precipitate progressively dissolves until it disappears at A/Ca ratios of 3-4. The maximum fraction of surfactant precipitated occurs in the region of A/Ca about unity.

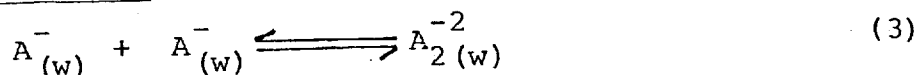
Precipitate dissolution (or inhibition of precipitation) has been attributed by several investigators to fixation of calcium ions in micelles. In the case of lauryl sulfate, however, our calculations and measurements indicate that precipitate dissolution begins at equilibrium surfactant concentrations below the CMC as can be seen in Figure 6. This finding suggests that calcium binding (which may manifest itself either by inhibition of precipitation or precipitate dissolution) can occur by a mechanism other than micellar fixation, possibly calcium binding in complex ions.

One can picture surfactant precipitation and calcium binding both by fixation in complex ions and in micelles in the following manner. Let N represent a monovalent cation, B a divalent cation, A the surfactant anion, and M a surfactant micelle. The subscripts s and w denote solid and aqueous phases, respectively. One can then write the following set of equations to describe the various processes which appear to occur.

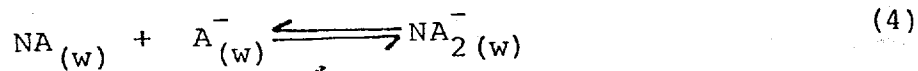
Surfactant Dissolution and Ionization:



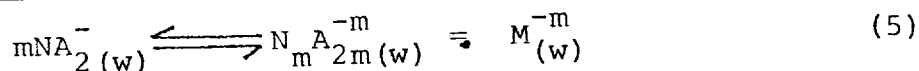
Surfactant Dimerization:



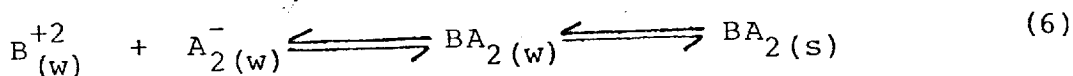
or



Surfactant Micellization:

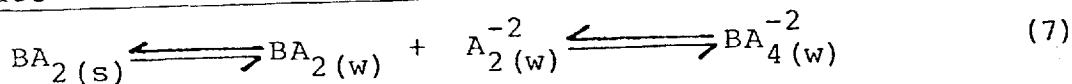


Surfactant Precipitation By Divalent Cations:

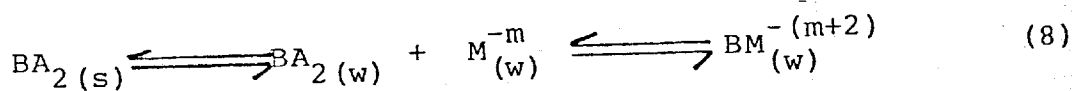


Note: Analysis of calcium surfactant precipitates confirms that the precipitate is  $BA_2$ , as expected.

Precipitate Dissolution and Calcium Binding By Complex Ions:



Precipitate Dissolution and Calcium Binding By Micellar Fixation:



A note of caution seems in order, in that while the processes indicated by Equations 2-8 appear to be reasonably in accord with known theory and observations, much additional work is required to establish them firmly. Nevertheless, they appear

to offer reasonably adequate explanations for the known facts concerning surfactant precipitation and dissolution.

Influence of Oil on Surfactant CMC: Chan (1978) reported that the CMC in distilled water of sodium dodecyl benzene sulfonate was reduced by the presence of excess oil. Since this observation appeared to have important implications for adsorption in that it indicated a significantly decreased maximum monomer concentration, measurements of the effect of excess oil on the CMC of several surfactants of interest for adsorption were undertaken. The CMC was determined from surface tension measurements. Our results tend to both confirm and disagree with those reported by Chan. They agree in that when the surfactant is equilibrated with a small excess of oil, we observe a CMC at a lower concentration than that in distilled water. However, we observe two CMC values (two plateaus in the surface tension vs log surfactant concentration curve) as shown in Figure 7. The lower of two CMC's appears to occur at a surfactant concentration about one-tenth of the CMC in distilled water; the higher CMC appears to be at or near the CMC in distilled water.

Since two CMC's have been found for every anionic surfactant tested when dissolved in distilled water and equilibrated with excess oil, the phenomenon appears to be real. However, it should be noted that the second (low concentration) CMC has been observed only in surface tension measurements; electrical conductivity measurements have shown no clear evidence of it. Experiments using other techniques, e.g. dye solubilization, are underway to confirm the existence of the second CMC in the presence of oil.

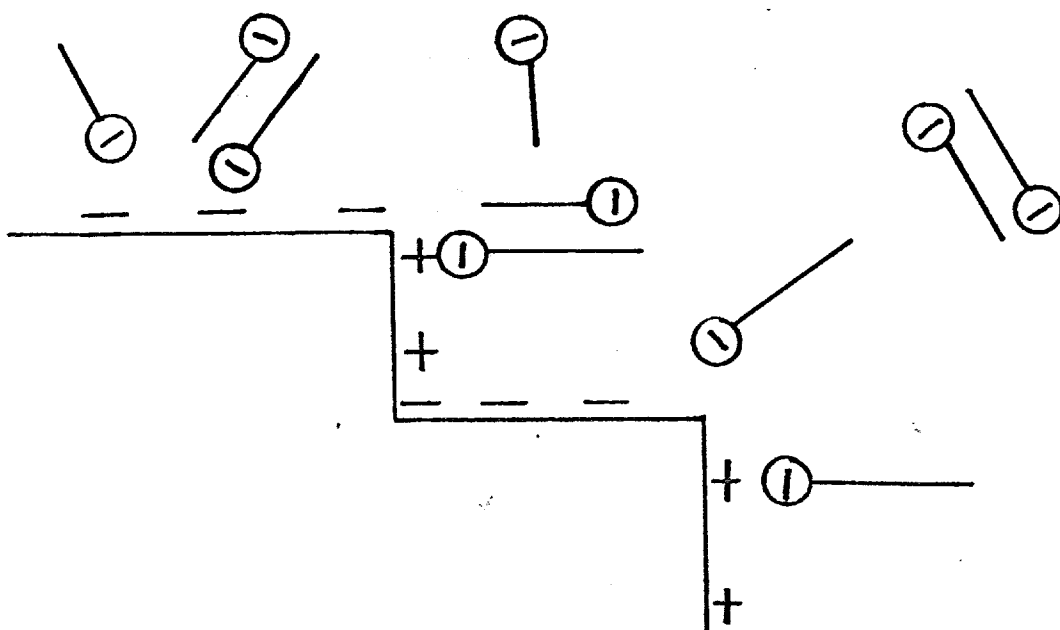
Mechanisms For Anionic Surfactant Adsorption: The adsorption of anionic surfactants on silica gel appears to follow a Langmuir-like mechanism modified by hemimicelle formation at low concentrations. The "toe" of the adsorption isotherm is concave and the adsorption plateau, which is characteristic of the Langmuir mechanism, occurs at or near the CMC of the surfactant indicating that micelles do not normally adsorb. It appears likely that adsorption of anionic surfactants on silica gel occurs by a mechanism involving electrostatic attraction of surfactant anions to positive sites on the silica gel. Such sites exist at crystal edges, at cracks, and at other imperfections in the crystal lattice. For the most part, however, the silica gel is very negatively charged and no surfactant adsorption occurs at the negative sites.

In sandstones the specific surface area associated with the silica sand is quite small, and anionic surfactant adsorption is small or negligible. This has been confirmed by measurements of several investigators. On the other hand, clays and related minerals generally have large to very large specific surface areas, and by reason of their structure they have many more potential positive sites at crystal edges, cracks, etc. In addition, multivalent cations in the cation exchange sites make

possible alternate mechanisms by which surfactant can be retained by the clay.

### 1. Surfactant Adsorption at Positive Sites

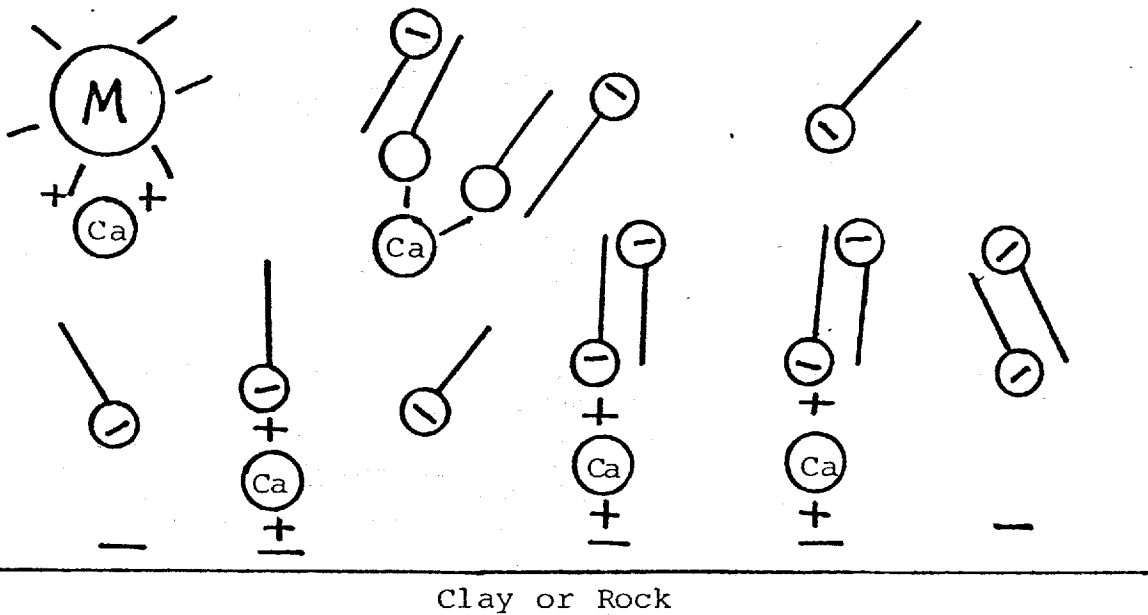
Surfactant anions are attracted to positive sites on clay crystals, and either monomers or dimers can adsorb by reason of electrostatic attraction. Equilibrium adsorption isotherms suggest the onset of hemimicelle (two-dimensional surfactant association) at relatively low equilibrium surfactant concentrations, followed by a "shoulder" and an adsorption plateau near the CMC of the surfactant. Thus, the adsorption isotherm is Langmuir-like. The process can be represented schematically as shown in the diagram below; both monomers and dimers are shown in solution and adsorbing.



### 2. Surfactant Adsorption By Calcium Bridging

When calcium ions (or other multivalent cations) are in cation exchange sites on clays or rocks, they can serve as "bridges" between negatively charged surface sites and surfactant anions (either monomer or dimer). Thus, a second kind of Langmuir-like adsorption mechanism can become operative; however, owing to the binding of calcium ions by complex ions or micelles, this isotherm would have a maximum. The process is depicted in the schematic diagram below.



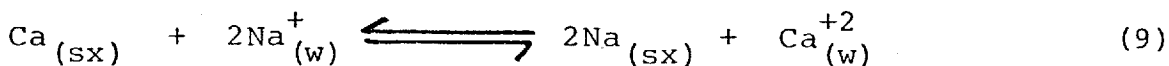


In this diagram we have shown both monomer and dimer adsorption by calcium bridging, and we have indicated schematically calcium fixation in both complex ions and micelles.

### 3. Apparent Surfactant Adsorption By Calcium Exchange and Precipitation

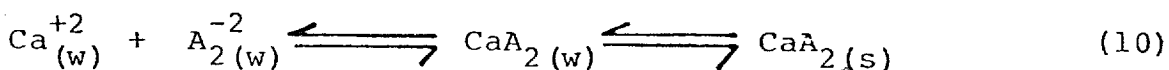
Most reservoir brines contain substantial amounts of NaCl, as do surfactant slugs for enhanced oil recovery. Sodium ions in the brine or surfactant solution readily displace the multivalent cations in the exchange sites of clays and make possible surfactant precipitation; higher surfactant concentrations can inhibit precipitation or dissolve precipitates already formed. Since it is nearly impossible to separate adsorbent and precipitated surfactants in adsorption measurements, it seems clear that if significant cation exchange involving multivalent cations has occurred, an apparent adsorption isotherm with a maximum will be found. However, the surfactant loss will be due to both adsorption and multivalent cation precipitation. The several processes involved in cation exchange, precipitation, and dissolution are shown in the following equations:

#### Cation Exchange:

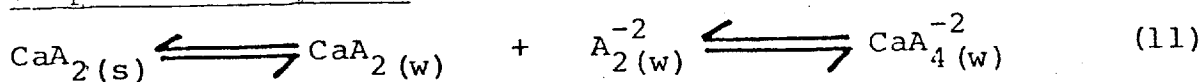


(sx) indicates a cation exchange site on the surface of the adsorbent.

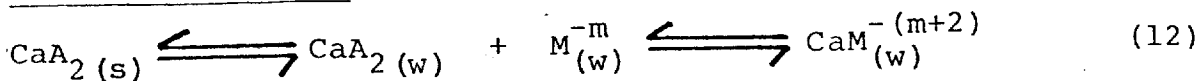
#### Precipitation:



Complex Ion Binding:



Micellar Binding:



In summary, it appears that in practice at least three mechanisms can be operative in the adsorption (or apparent adsorption) of anionic surfactants on clays and rocks. These include (1) electrostatic attraction of surfactant anions to positively charged sites on the crystal, (2) bridging by multivalent cations in exchange sites, and (3) surfactant precipitation by multivalent cations derived from rock or clay by cation exchange.

ACKNOWLEDGEMENTS

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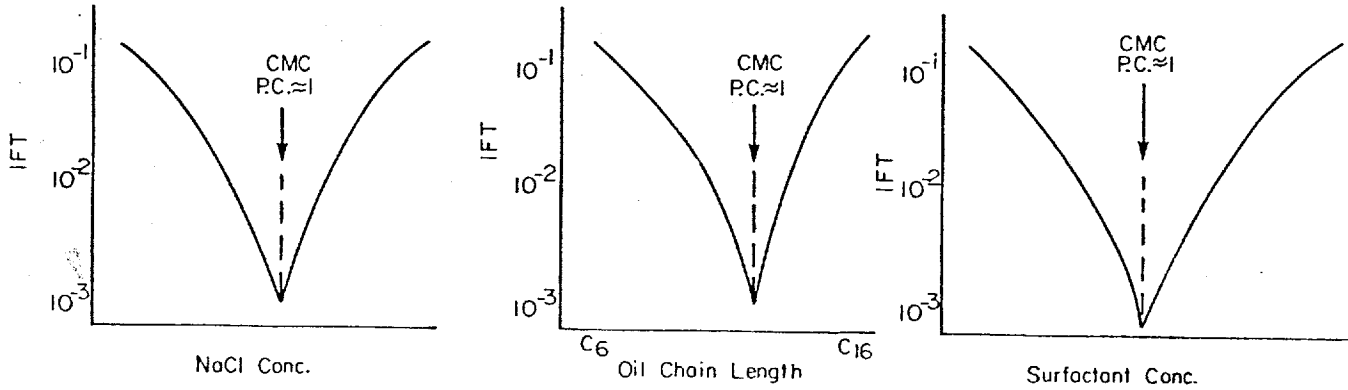
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Figure 1

THE EFFECT OF SALT CONCENTRATION, OIL CHAIN LENGTH AND SURFACTANT CONCENTRATION ON INTERFACIAL TENSION

PETROLEUM SULFONATES:



ISOMERICALLY PURE ALKYL BENZENE SULFONATES:

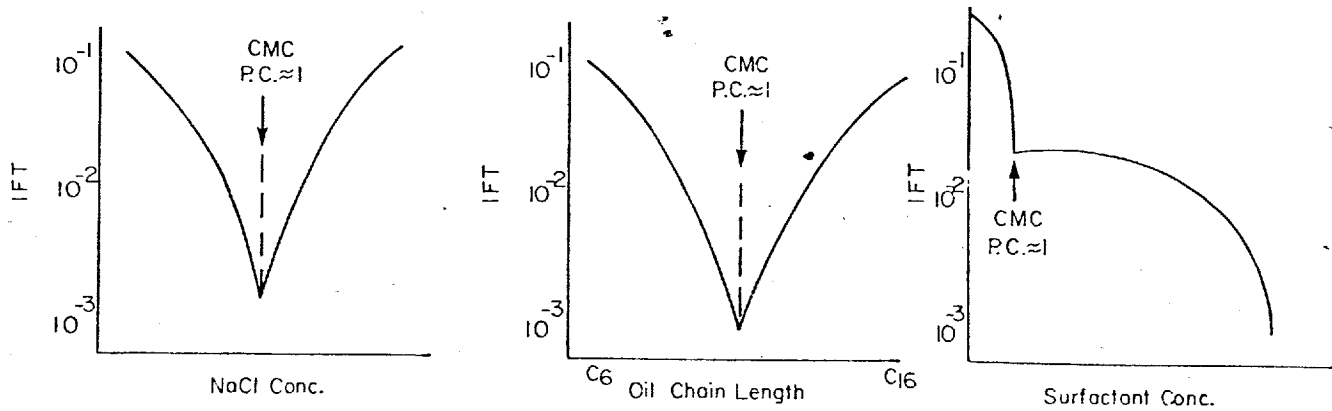


Figure 2

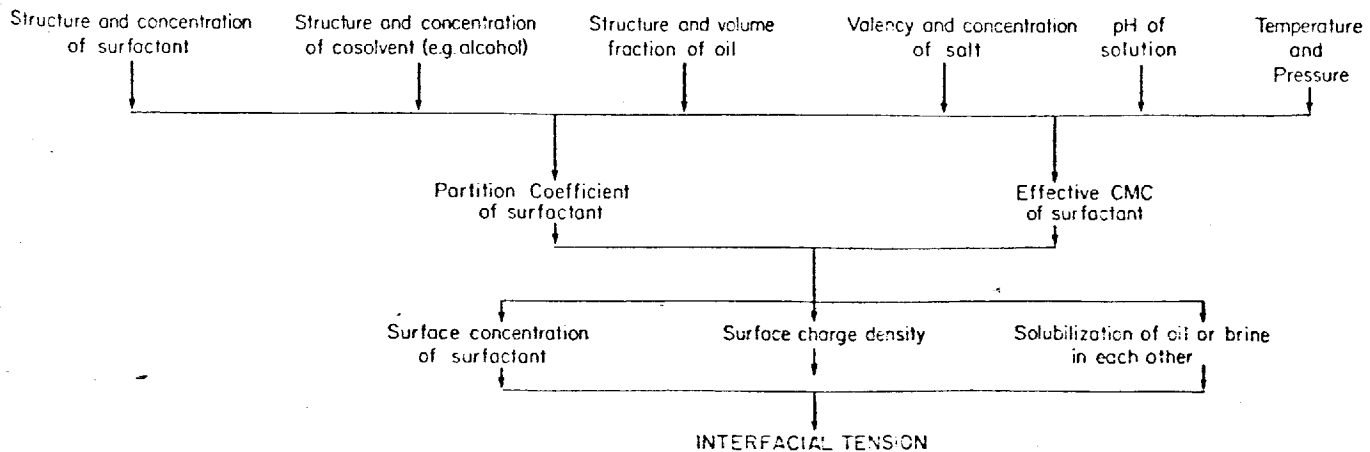


Figure 3

### THREE COMPONENTS OF INTERFACIAL TENSION

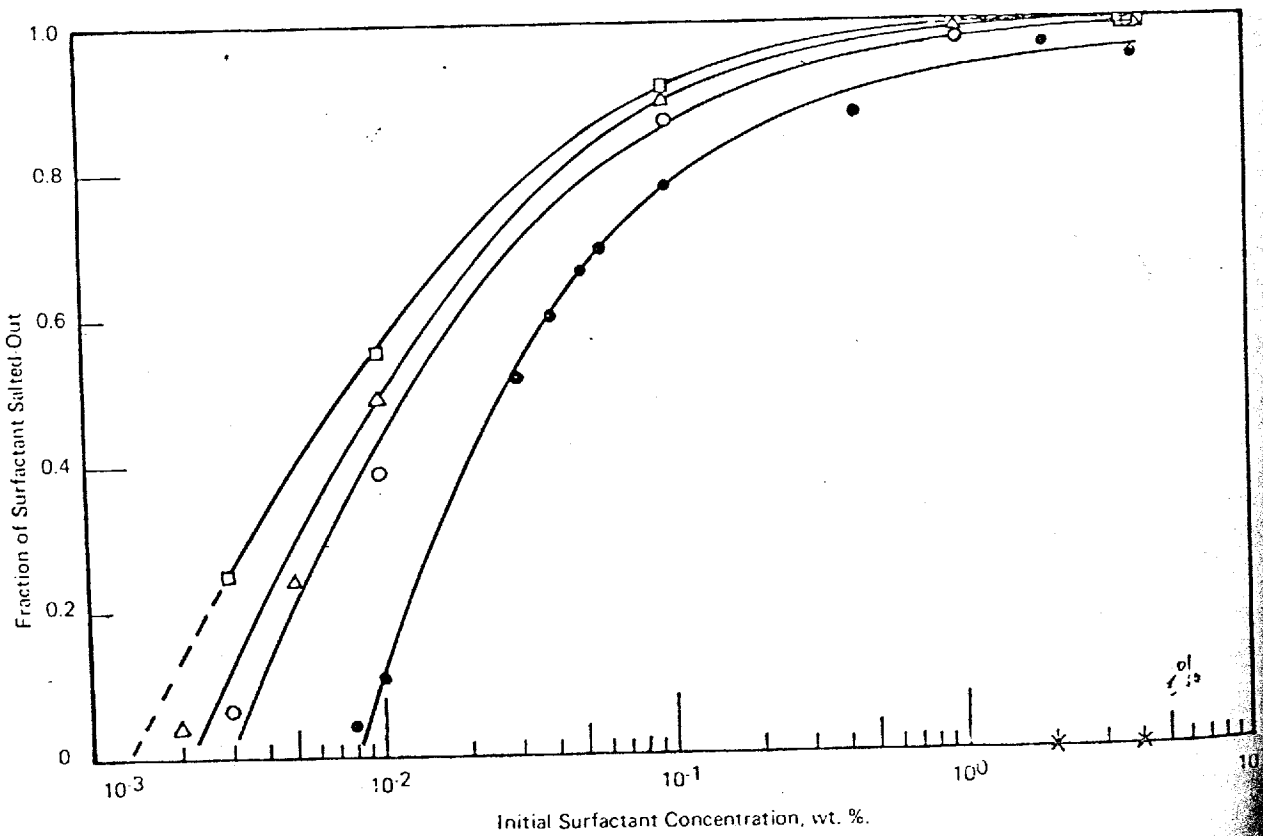
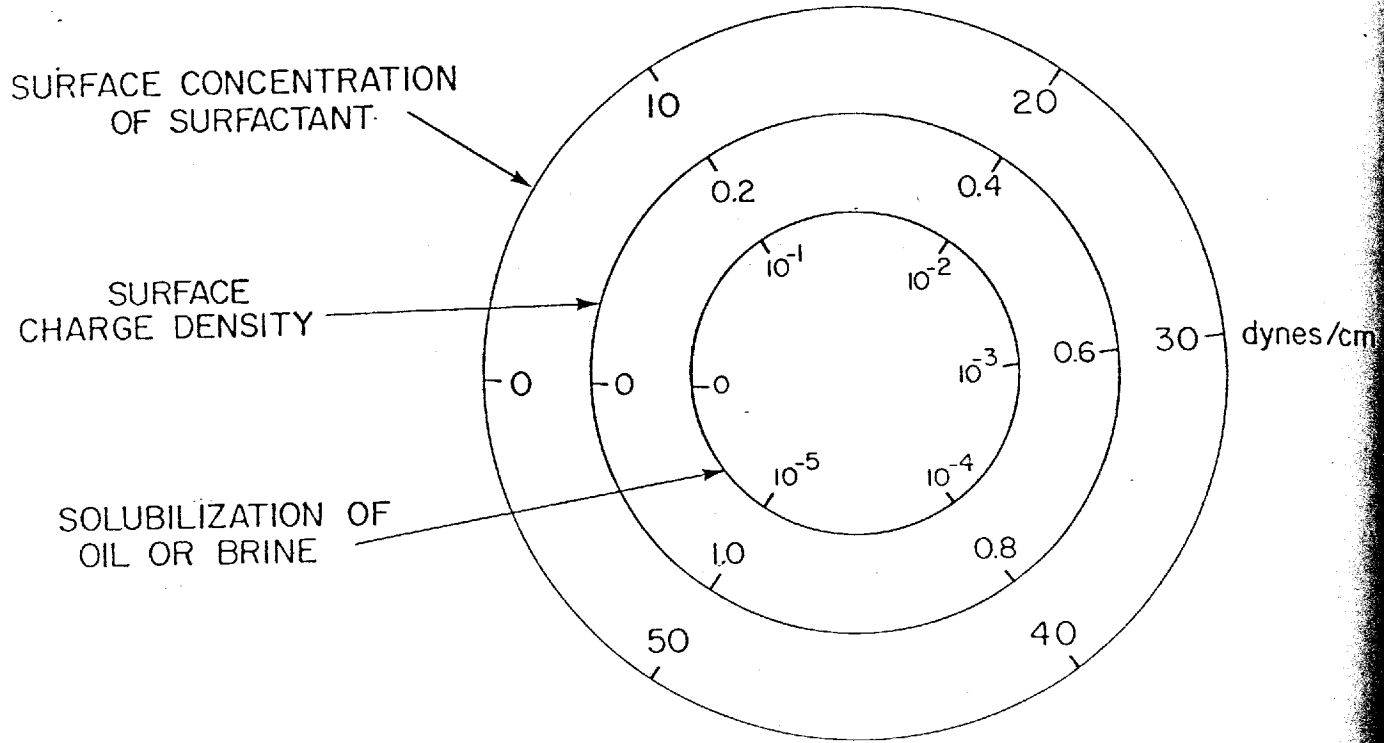


Figure 4 SALTING-OUT OF SUL-FON-ATE AA10 BY NaCl.  
\* = 1 wt. % NaCl; ● = 2 wt. % NaCl; ○ = 3 wt. % NaCl; △ = 4 wt. % NaCl; □ = 5 wt. % NaCl.

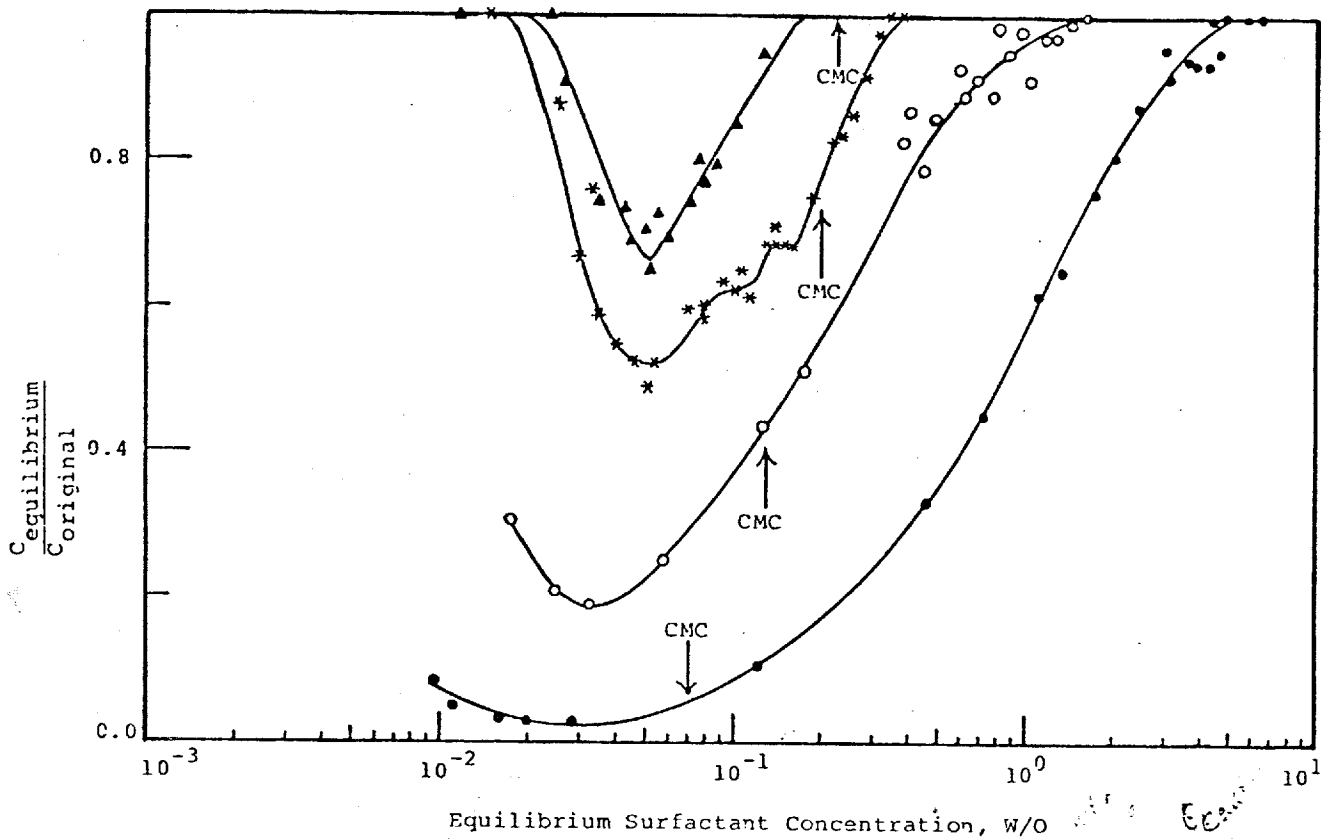


Figure 5 Precipitation of Lauryl Sulfate By Calcium Ions.  
 $T = 25 \pm 1^\circ\text{C}$   $\blacktriangle = 7 \times 10^{-4}$  moles  $\text{Ca}^{2+}/\ell$ ;  $* = 1.25 \times 10^{-3}$  moles  $\text{Ca}^{2+}/\ell$ ;  $\circ = 200$  ppm =  $5 \times 10^{-3}$  moles  $\text{Ca}^{2+}/\ell$ ;  $\bullet = 800$  ppm  $\text{Ca}^{2+} = 2 \times 10^{-2}$  moles  $\text{Ca}^{2+}/\ell$ .

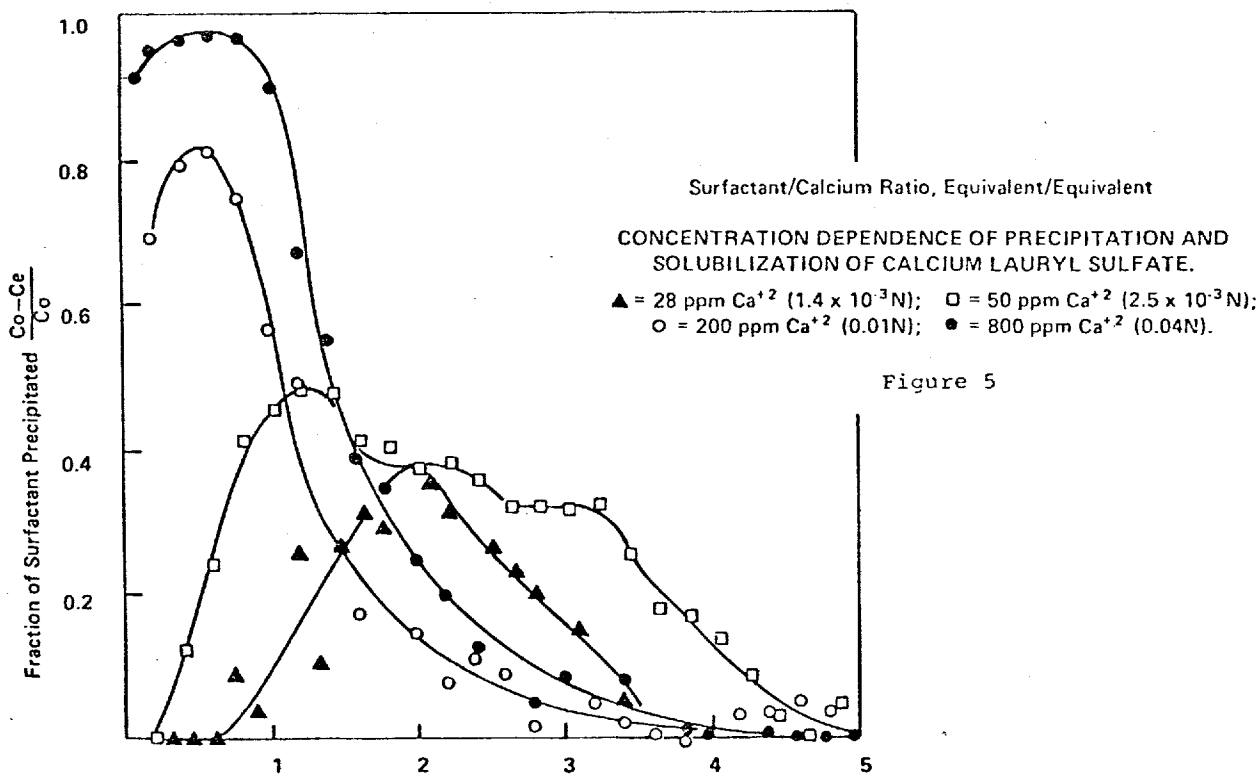
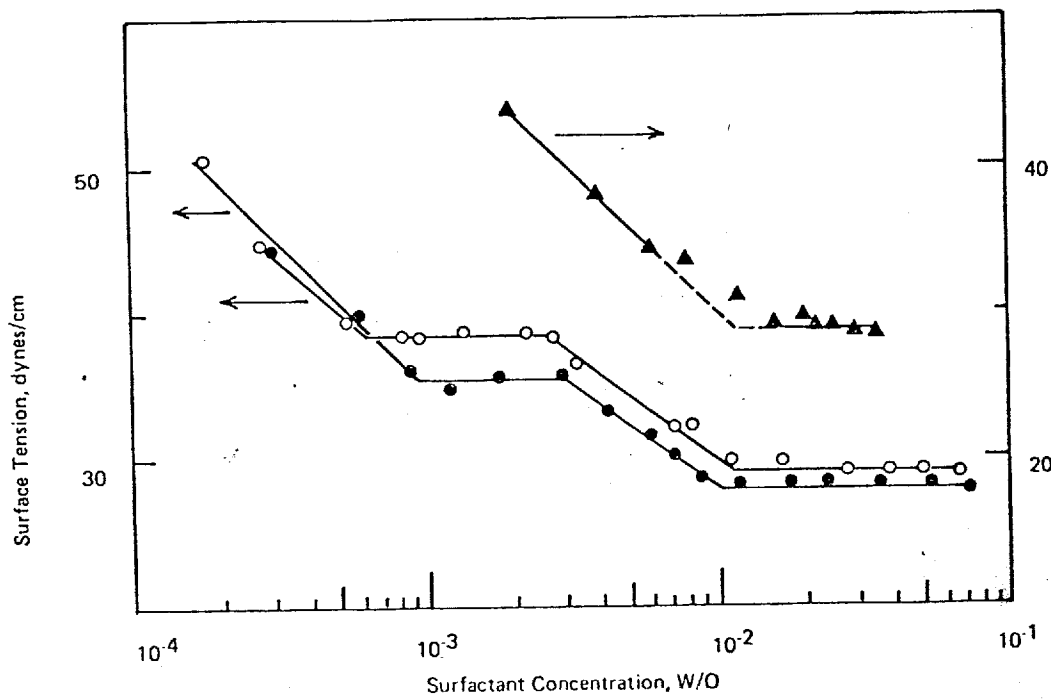


Figure 5



SURFACE TENSION OF 8-PHENYL HEXADECANE SODIUM SULFONATE.

▲ in distilled water; ● in distilled water equilibrated with 0.5 vol. % n-dodecane (95 %).  
 ○ in distilled water equilibrated with 0.5 vol. % of n-dodecane (99%).

Figure 7