

UNIVERSITY OF FLORIDA RESEARCH PROGRAM  
ON CHEMICAL OIL RECOVERY SYSTEMS

by

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ABSTRACT

The improved oil recovery research program at the University of Florida is a multidisciplinary research program designed to elucidate various interactions occurring between injection fluids, such as surfactant and polymer solutions, and reservoir components, such as clays, minerals and oils. The following are the five major areas of research in this program.

- 1) Interfacial Phenomena
- 2) Bulk, Surface & Porous Media Rheology
- 3) Rock-Fluid Interactions
- 4) Polymer Rheology and Fluid Mechanics
- 5) Thermodynamic Phenomena and Phase Equilibria

The research program is designed to establish a broad framework of knowledge about the microstructure of injection fluids and their behavior in porous media in relation to oil displacement efficiency. It is hoped that the development of the basic framework of knowledge and the quantitative relationships among various parameters of the process will assist industry in designing and optimizing chemical oil recovery systems for reservoirs under varying conditions. This paper reviews our accomplishments of the past one year in each of these areas.

INTRODUCTION

Two semi-annual reports (June, 1977 and December, 1977) have been prepared detailing the results of several experiments in each research area. The reports have been sent to the Department of Energy laboratories, consortium members of oil and chemical industry and academic institutions involved in oil recovery research. The following are a few highlights of our research in each area of the research program.

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## INTERFACIAL PHENOMENA

### The Effect of Divalent Cations on the Optimal Salinity of Petroleum Sulfonate (Petrostep-465) and Ethoxylated Sulfonate (EOR-200 Mixtures)

Most reservoir brines consist of various mono-, di-, and trivalent cations. In this study we chose only two important divalent cations ( $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ ) which are predominantly present in the reservoir brine. The effect of  $\text{Ca}^{++}$  ions on the optimal salinity value was reported by Reed and Healy (1976) and it was found that in the presence of  $\text{CaCl}_2$  the optimal salinity decreases. The ratio of  $\text{CaCl}_2/\text{NaCl}$  was kept 0.1 in their study.

The systems we chose to study had a high salt tolerance (8.5% NaCl) and a high optimal salinity (8.1% NaCl). This allowed us to study the effect of higher ratios of  $\text{CaCl}_2/\text{NaCl}$  on optimal salinity. The surfactant formulation studied consisted of Petrostep-465 (3%), ethoxylated sulfonate EOR-200 (2%) and n-Pentanol (2%). n-Decane was used as the oil for all phase-behavior and interfacial tension measurements. The effect of  $\text{Ca}^{++}$  on optimal salinity was studied at three different ratios ( $\text{NaCl}/\text{CaCl}_2 = 1, 5, 10$ ).

The effect of  $\text{CaCl}_2$  on the stability of surfactant formulation is shown in Figure 1. The stability range of the surfactant formulation decreases upon increasing the amount of  $\text{CaCl}_2$  in the surfactant formulation. Though the initial effect of  $\text{CaCl}_2$  on the stability range of surfactant formulation is not significant, the salt tolerance (NaCl concentration wt.%) decreases from 8.5 to 8.0 and 7.0 when  $\text{NaCl}/\text{CaCl}_2$  ratio is 10 and 5 respectively. But the salt tolerance decreases (3.5% NaCl) drastically when  $\text{NaCl}/\text{CaCl}_2$  ratio decreases to 1. This system is capable of tolerating such high concentration of  $\text{CaCl}_2$  without any precipitation or phase separation up to 3.5% NaCl (or 7.0% wt. total solid).

Figure 2 shows the effect of  $\text{NaCl}/\text{CaCl}_2$  ratio on the interfacial tension and interfacial optimal salinity ( $S_Y$ ) of the surfactant formulation. It is evident that upon increasing the amount of  $\text{CaCl}_2$  in the surfactant formulation the optimal salinity ( $S_Y$  or  $S_\phi$ ) decreases. The optimal salinity ( $S_Y$ ) at different ratio of  $\text{NaCl}/\text{CaCl}_2$  and the corresponding ionic strength are given in Table I.

Table I

The Effect of  $\text{NaCl}/\text{CaCl}_2$  Ratio on the Optimal Salinity

Graph No. (Figs. A15-16)	$\frac{\text{NaCl}}{\text{CaCl}_2}$	Optimal Salinity ( $S_Y$ ) (wt.% NaCl)	Ionic Strength (I)* at optimal salinity
1.	No $\text{CaCl}_2$	8.0	1.37
2.	10	6.9	1.32
3.	5	5.85	1.32
4.	1	2.5	1.1

$$*I = \frac{1}{2} \sum C_i Z_i^2$$

From the calculated ionic strength it is evident that though the optimal salinity decreases drastically from 8.0 to 2.5 upon increasing the amount of  $\text{CaCl}_2$  in the surfactant formulation, the decrease in ionic strength value is not very much (1.37 to 1.1).

From the results presented here it seems that the surfactant formulation consisting of petroleum sulfonate and ethoxylated sulfonate can tolerate a sufficient amount of  $\text{CaCl}_2$  in the surfactant formulation without any precipitation or phase separation up to the appropriate concentration of  $\text{NaCl}$ . Moreover, these surfactant formulations still produce very low interfacial tension (in the range of millidyne) even in the presence of high concentration of divalent cations. We believe that appropriate mixtures of petroleum sulfonate and ethoxylated sulfonate are very promising for tertiary oil recovery because of their improved salt tolerance and ability to produce ultra-low interfacial tension. The effect of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  on salt tolerance, optimal salinity and dielectric properties of mixed surfactant formulations have been reported by Bansal and Shah (1978 a,b,c).

#### The Effect of Mixed Alcohols on the Phase Behavior of Surfactant/Alcohol/Oil/Brine Systems

Gogarty and Tosch (1968) used isopropanol (IPA) as the fourth component to form oil-external microemulsions for use in tertiary oil recovery. More recently, Jones and Dreher (1975) studied the effect of alcohols on the phase and viscosity behaviors of systems potentially useful for tertiary oil recovery. They found that water-soluble alcohols, such as IPA, were capable of increasing the solubilization capacity for water, while oil-soluble alcohols, such as n-hexanol, increased the solubilization capacity for oil. In a given range of salinities, however, neither type of alcohol can, by itself, increase the solubilization capacity for both oil and water.

For the three equilibrium phases of a surfactant/alcohol-oil-brine system,  $\gamma_{om}$  (or  $\gamma_{mw}$ ) decreases whenever  $V_o/V_s$  (or  $V_w/V_s$ ) increases. It would therefore be interesting to study the effect of mixed alcohols because of the possibility of increasing the solubilization capacity for oil and water simultaneously, and hence decreasing both  $\gamma_{om}$  and  $\gamma_{mw}$  in the corresponding multi-phase region of such systems.

It has been proposed (Healy and Reed, 1977) that, for such systems, the lowest interfacial tension in the multi-phase region occurs for the system with the lowest binodal curve in its corresponding pseudoternary phase diagram. The approach of this study was hence to investigate, for variable combinations of surfactant-alcohol mixtures, the height of the binodal curve in the phase diagrams at a 1:1 (v/v) brine/oil ratio. The solubilization and interfacial tension behavior in the multi-phase region of one particular system were also studied.

The surfactants used were Petrostep 465 (Stepan Chemical Company, 60% active, denoted as P-465). Three alcohols (Chemical Samples Company, 99.5% pure) were used: isopropanol (IPA), paramethyl cyclohexanol (PMCH) and n-pentanol (NAA). The oils used here were octane and benzene (Chemical Samples Company, 99% pure). Salinity refers to %  $\text{NaCl}$ , w/v in distilled water.

A known weight of a surfactant and alcohol mixture (single phase solution) was simultaneously titrated with oil and brine (1:1 v/v) in a 5 ml tube. By trial and error, the volume of oil and brine that just causes phase separation was determined. The solution was considered to be a single phase if it appeared to be a single phase if it appeared to be transparent after shaking. In most cases, the surfactant concentration was high enough so that phase separation, if any, occurred within an hour after titration. The height of the binodal curve, expressed as the minimum overall surfactant and alcohol concentration required to form a single phase of oil-brine mixture, was calculated from

$$100\% \times \frac{\text{gm surfactant and alcohol}}{\text{gm surfactant and alcohol} + \text{ml oil and brine just causing phase separation}}$$

This concentration unit is confusing, but can be considered to be close to the volume fraction, because the densities of the surfactant and alcohol mixtures varied between only 0.9, and 1.0 gm/ml. The high viscosity of the surfactant and alcohol mixtures made it difficult to measure their volume with any accuracy, and hence the reason for the above units.

Figure 3 shows the total concentration of surfactant and alcohol required to make a single phase of 50:50 mixture of oil and brine. It was observed that at 1% NaCl, much lower concentration of surfactant and mixed alcohols was required as compared to formulations containing individual alcohols.

Figure 4 illustrates the effect of P-465/alcohol ratio in the formulation on the solubilization of oil and water. The alcohol mixture used was PMCH/IPA (1:4, w/w). The oil used was a mixture of octane/benzene (9:1, w/w). For this system, the effect of surfactant/alcohol ratio was drastic and the higher surfactant/alcohol ratios were found to be much more favorable in terms of solubilization capacity. In particular, when this ratio is 5:1 and the salinity is 0.5% NaCl, one can produce a single phase oil-brine mixture (1:1 v/v) with a surfactant and alcohol concentration as low as 9%. Since the surfactant was 60% active, this value would actually be 6% if one used a 100% active surfactant.

#### The Ultra-Low Interfacial Tension Attainment By Pure Surfactants

The unified theory of ultra-low interfacial tension reported elsewhere (Chan and Shah, 1978) can also explain the attainment of ultra-low interfacial tension by pure surfactant solution. Wade et al. (1977) used a pure alkyl benzene sulfonate,  $\text{R-C}_{16}\text{S}$ , synthesized in their laboratory to study the effect of surfactant concentration on ultra-low interfacial tension. They measured the interfacial tension of this surfactant in 1% NaCl solution against dodecane and found that interfacial tension continued to decrease after the CMC in aqueous phase was reached. This system provides an excellent case to test the validity of our proposed theory for ultra-low interfacial tension.

Pure 8 phenyl hexadecane Na sulfonate (100% active) was supplied by Conoco Chemicals in solid powder form and was used as received. The surfactant was dissolved in 1% NaCl solution and successively diluted. Then the diluted solutions were equilibrated with dodecane oil in 2:1 volume ratio. Three sets of interfacial tension data were obtained. The upper curve in Figure 5 is for equilibrated oil phase against 1% NaCl (no surfactant) solution. The continuous decrease of the interfacial tension with the increase of total surfactant concentration shows clearly that, for this system, the contribution of surfactant monomers in equilibrated oil phase to the lowering of interfacial tension is very significant. The middle curve in Figure 5 is for fresh dodecane (no surfactant) against equilibrated aqueous phase whereas the lower curve in the same figure is for the equilibrated system. It can be seen from these two curves that the interfacial behavior of the equilibrated aqueous phase is dictating the overall interfacial tension of the equilibrated system. The break points in both curves are at the same 0.0018% initial surfactant concentration (aqueous phase surfactant concentration before equilibration).

It is very interesting to see that the surface tension measurements reveal, as shown in Figure 6 that at 0.0018% initial surfactant concentration the equilibrated aqueous phase is at CMC.

Figure 7 shows that below the CMC, the surfactant is more soluble in oil. But after the CMC, the solubility of surfactant in brine, which is enhanced by the formation of micelles, increases. The partition coefficient passes through unity value at the CMC of the equilibrated aqueous phase. Figure 8 shows that the partition coefficient decreases as the total surfactant concentration increases. It can be concluded that as more and more micelles are formed in the equilibrated aqueous phase, the solubility of surfactant in this brine phase increases.

From the interfacial behavior, micellization and partition studies of this pure surfactant system, the following conclusions can be made:

- (1) Since the surfactant,  $8\phi C_{16}S$ , is more oil soluble, more surfactant molecules can be found in the oil phase when the aqueous phase concentration is below CMC.
- (2) Partition unity and interfacial tension breakpoint occur at the initial surfactant concentration of the aqueous phase where the surfactant concentration of equilibrated aqueous phase is CMC.
- (3) The decrease of the interfacial tension beyond this CMC is due to increasing number of monomers available for the interfacial adsorption from the oil phase.

The difference between a pure surfactant system (such as  $8\phi C_{16}S$ ) and a petroleum sulfonate system (such as TRS 10-80) is that there is no mixed micelle formation in a pure surfactant system. Consequently, no surfactant molecules which should have partitioned into the oil would be incorporated into the micelles in the equilibrated aqueous phase, and thus the monomer concentrations in both phases would not decrease after CMC. Therefore, no interfacial tension minimum can be observed in any pure surfactant system.

## The Effect of Dissolved Oils on Effective CMC of Micellar Solutions

The effect of salt and alcohol concentrations on the shifting of CMC in aqueous surfactant solutions had been extensively studied and reported in the past. There is a great deal of work devoted to these two effects on CMC contributed by so many distinguished scholars and scientists such as Shinoda, Mysels, Mukerjee etc. Comparatively, very little information had been collected about the effect of dissolved oils on the CMC. In the evaluation of various methods for measuring CMC, Ginn and Harris (1958) found that neutral oil dissolved in the surfactant solution reduced the CMC of the commercial dodecyl benzene sodium sulfonate. But no further information regarding the structure and composition of the free oil used was reported.

Light scattering  $I_{90}$  measurement for determination of CMC was introduced in our semi-annual report (June 1977). This technique was used in this study and the CMC's determined were cross-checked by electrical resistivity measurements. All the measurements were done at a constant temperature of 25°C. Occasionally, surface tension measured by Wilhelmy plate method was used to further support the CMC determination of the two methods mentioned above.

The CMC of SDBS solutions determined for the two sets of experiments as a function of hydrocarbon chain length of oils is shown in Figure 9. For the first set of experiments, the distilled water was pre-saturated with oil and then used to prepare surfactant solution. Thus, for a certain hydrocarbon oil under study, the amount of oil dissolved in each surfactant solution was the same, regardless of the surfactant concentration. For this type of study, the effective CMC of SDBS increases with the increase of the length of the hydrocarbon chain of the oil used. For the second set of experiments, surfactant solutions were first prepared and then equilibrated with oil. For this type of study, the amount of oil is smaller below the CMC and is larger beyond the CMC. The exact amount would be governed by the solubilization capacity of micelles and other interactions concerning the formation of the micelles. For this set of experiments, the effective CMC decreases linearly with the increase of hydrocarbon chain length of oils in the semi-log plot. The extrapolation of this linear curve to zero carbon chain length gives 0.04% as CMC for SDBS in distilled water without any oil dissolved which is a little bit lower than 0.06 determined experimentally.

### BULK AND POROUS MEDIA RHEOLOGY

#### A Correlation of Interfacial Tension with Oil Displacement Efficiency under Equilibrium and Non-equilibrium Conditions

In general, one would expect those surfactant formulations which produce ultra low interfacial tensions (in the range of millidynes) to be the most promising for the tertiary oil recovery process by surfactant flooding. Oil displacement studies were performed for an equilibrated and non-equilibrated surfactant system to study the effect on oil displacement efficiency under equilibrium and non-equilibrium conditions.

Figure 10 shows the percent oil recovery as a function of TRS 10-80 concentration in 1% NaCl. It was observed that 94% oil was recovered at 0.05% TRS 10-80 concentration as compared to 65% at both 0.005% and 0.5% concentrations. This maximum oil recovery at 0.05% TRS 10-80 corresponds to the minimum interfacial tension observed at this concentration. The oil recovery data shown in Figure 10 was obtained for the pre-equilibrated system (equilibrated oil phase displaced by equilibrated aqueous phase). To study the effect on oil recovery when the injecting fluids were not pre-equilibrated, the sand pack was saturated with non-equilibrated n-octane and it was flooded to the residual oil level. A fresh surfactant slug of TRS 10-80 (0.05%) in 1% NaCl was then pumped through the sand pack. It was interesting to note that in this case even after injection of 10 PV surfactant slug no oil was produced.

Figure 11 shows the effect of salt concentration on the oil recovery efficiency of the system TRS 10-410 (0.1%) + IBA (0.06%). It was observed that the maximum oil recovery (95%) is obtained at 1.5% NaCl concentration. This maximum oil recovery also corresponds to the minimum interfacial tension observed in this system. The calculated values of the capillary number  $N_c (= \frac{\mu v}{\gamma})$  at different salt concentrations are also plotted in Figure 11. As expected, a good correlation between capillary number and oil recovery efficiency was observed.

#### Oil Displacement Efficiency of High Salt Tolerant Formulation

It was shown previously (Figure 2) that a low-tension but high salt tolerant formulation (> 20% NaCl) can be achieved by mixing petroleum sulfonate with ethoxylated sulfonate and cosolvent in presence of electrolyte solutions. Here a similar system is employed to test the ability of such formulations to displace oil in porous media.

Figure 12 shows tertiary oil recovery as a function of salinity of 8.0% NaCl concentration and above. For each run, 0.05PV slug of 7% surfactant concentration was injected, so that the result obtained can be compared with the literature values. Viscosity measurements of each injecting fluid are listed in Table 2. The polymer concentration of the mobility buffer was chosen in order to have a favorable mobility ratio during flooding process. The sand pack oil displacement result obtained thus far is encouraging. At 9.0% NaCl concentration, 76% residual oil was recovered.

#### POLYMER RHEOLOGY

##### The Effect of Molecular Weight on Screen Factor, Viscosity and $\Delta P/L$ of Polymer Solutions

The main objective of the research in this area has been to correlate the molecular weights of the potential polymers to be used for mobility control in tertiary oil recovery process with the corresponding rheological parameters. In order to achieve this aim, we undertook measurements of

Table 2

Viscosity of 2.5% TRS 10-410 + 2.5% EOR 200 + 3% IBA in Variable NaCl Solutions

NaCl, wt. %	Viscosity, cP
8.0	7.38
8.5	4.01
9.0	5.09
9.5	3.09
10.0	5.96

2000 ppm Polymer 340 in 8.0% -10% NaCl 3.37

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several parameters such as intrinsic viscosity, screen factor,  $\Delta P/L$ , viscosity, etc. for polyacrylamides of different degree of hydrolysis in solutions of different ionic strengths. We obtained these parameters as a function of age of polymer solution and as a function of time over which constant shear was applied to the solution. Figure 13 shows the effect of percent change in viscosity average molecular weight as a function of percent change in screen factor,  $\Delta P/L$  and viscosity for an experiment in which polymer solution (500 ppm Calgon P815) was subjected to constant shear in a blender over a period of time. Samples were collected at different intervals in order to evaluate these parameters. Viscosities were measured using Cannon-Fenske viscometer (no. 100). Intrinsic viscosity was obtained by interpolating reduced viscosity vs concentration plots to zero concentration, which is in effect a measure of viscosity average molecular weight. Since the appropriate Mark Houwink constants were not available for this system from the literature, we have plotted the intrinsic viscosity instead of molecular weight. Though a system as complex as this, cannot be characterized fully by measuring one moment of the distribution. However, it was not practical to obtain the rest of the averages of the molecular weight distribution of these polymer samples. In spite of this restraint, we observed a very strong dependence of screen factor, and  $\Delta P/L$  ( $\Delta P/L$  was measured over a column 6" x 3/8" packed with silica gel EM-Gel SI 1000A°, Particle Size 230-400 mesh) on the intrinsic viscosity. It is quite clear from Figure 13 that about 20-25% decrease in the intrinsic viscosity of the original sample causes about 80% loss in screen factor, whereas shear viscosity is reduced only about 20%.



The above mentioned experiments indicate a strong dependence of these parameters on the molecular weight of the polymer. At present we are investigating the effect of change of molecular weight on these parameters as a function of age, concentration of sodium and calcium, temperature, degree of hydrolysis etc. and these findings will be reported in the coming semi-annual report.

### Surfactant-Polymer Interaction

Surfactant and polymer, when dissolved in water, have been shown to form aggregates. It has been shown that such interactions can strikingly influence the interfacial and rheological properties of surfactant formulations (Noronha and Shah, 1976) and that they may lead to phase separation.

In the present investigation, the system studied was 8-phenyl hexadecyl sulfonate supplied by the University of Texas and Calgon-835, a partially hydrolyzed polyacrylamide from Calgon Corporation. In an attempt to identify any surfactant-polymer interactions in this system, prior to studying the consequences of such interactions and the nature of the associations, the electrical conductivity of surfactant solutions containing fixed amount of the polymer was measured, as a function of the surfactant concentration. The water used was double distilled and had a specific conductance of  $1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  at 23°C. The conductance measurements were made with a Beckman Instrument Conductivity Bridge RC-16B2 at a frequency of 1000 Hz. All measurements were made at room temperature (23°C). The conductance of the polymer solutions were significant and were:

100 ppm polymer:	Specific conductance	$38 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$
250 ppm polymer:	Specific conductance	$74 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$
500 ppm polymer:	Specific conductance	$154 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$

These conductances were subtracted from all the measurements of solutions containing both the surfactant and polymer. The results are shown in Figure 14. These data show that with polymer present, the specific conductance remains substantially constant up to a transition point when it shows a rapid rise. Also shown is the data for the surfactant alone. If we take these transition points to be the new CMC's it may be observed that the surfactant concentration at these points increases with increasing polymer concentration.

The new CMC's, the shifts from that of pure surfactant and the binding values for each polymer concentration are shown in Table 3. It is seen that the CMC is shifted to higher concentrations as the polymer concentration is increased. Similar studies are in progress using surface tension and interfacial measurements for polymers with different degrees of hydrolysis.

TABLE 3

The Shift In CMC (wt.%) And The Binding Ratio of Surfactant (8 $\phi$ C<sub>16</sub>NaS) To Polymer for Various Concentrations of The Polymer (Calgon-835)

Polymer Concentration

Cp wt.%	CMC wt.%	$\Delta \text{CMC} \cdot \text{wt.}\%$	$\Delta \text{CMC}/\text{Cp}$
0	.0015	-	-
.01	.004	.0025	0.25
.025	.010	.0085	0.34
.050	.020	.0185	0.37

\* $\Delta \text{CMC} = (\text{CMC}) - (\text{CMC with no polymer})$ .

## ROCK/FLUID INTERACTIONS

It has long been known that a micellar/polymer slug interacts both with reservoir fluids and the reservoir rock, frequently with a resulting loss of surfactant. These losses are usually attributed to adsorption, multivalent cation precipitation, and to electrolyte precipitation or salting-out. Both of the latter processes may confuse adsorption measurements with the result that the apparent adsorption loss may be considerably greater than the actual adsorption loss. Moreover, there is evidence that all of these loss processes are affected by the presence of oil.

The existence of both multivalent cation precipitation and surfactant salting-out have been recognized in several adsorption experiments, and these results led initiation of a small scale investigation of electrolyte salting-out and multivalent cation precipitation of surfactants.

### Salting-Out of Anionic Surfactants

Aqueous stock solutions of purified (desalted and deoiled) anionic surfactants were prepared; in all cases these solutions were quite clear. NaCl, alcohol, and EOR-200 (an ethoxylated surfactant made by Ethyl Corp.) were added to aliquots of the surfactant stock solutions to make the desired final composition. The container was capped, the solutions were mixed, and they were then stored in an air bath at 35°C. Periodic observations were made for about 24 hours. The results of these tests are summarized in Table 4.

These data indicate that neither SDBS nor SLS are particularly sensitive to salting-out. For the range of salt concentrations anticipated in adsorption experiments all solutions of these two surfactants remained clear. However, cloudiness or precipitation was observed for Aerosol-OT, SPBS, and TRS-10-410 for most conditions tested. The addition of short chain alcohols was relatively ineffective in inhibiting salting-out (especially for the higher equivalent weight materials), and the addition of the ethoxylated surfactant, EOR-200, was less effective than anticipated in view of the very promising earlier results in oil displacement tests with sand packs. It seems reasonable to conclude—at least tentatively—that surfactant salting-out is likely to occur when one is working with purified anionic surfactants with equivalent weights greater than 350 and when the salt content exceeds one wt. %. On the other hand, if oil is present, entirely different salt tolerances may be observed.

### Calcium Tolerance of Anionic Surfactants

The calcium tolerance of several anionic surfactants has been reported earlier. It was shown in these experiments that the addition of  $\text{CaCl}_2$  to aqueous solutions of the surfactants resulted in development of a turbid solution after a certain threshold  $\text{CaCl}_2$  concentration;

TABLE 4

Salting-Out of Purified Anionic Surfactants by NaCl

Surfactant	Surf. Conc'n. wt. %	Alcohol, EOR-200 wt. %	NaCl Conc'n. wt. %	Observation	Remarks
Sodium Dodecylbenzene Sulfonate	0.1	None	1.0	Clear	Not pptd. up to 5 wt. % NaCl
Sodium Lauryl Sulfate	0.1	None	1.0	Clear	Not pptd. up to 5 wt. % NaCl
Sodium Penta-decylbenzene Sulfonate	0.1	n-C <sub>4</sub> ,3	1.0	Cloudy	
	0.1	n-C <sub>4</sub> ,5	1.0	Clear	
	0.4	no alc. E-200,0.1	0.4	Cloudy	Clear below 0.4 wt. % NaCl pptd. above 4 wt. % NaCl
	0.4	n-C <sub>4</sub> ,5 E-200,0.1	1.75	Clear	Above 1.8 wt. % NaCl, phase sepn. occurs(alc. soln. of SPBS)
	0.5	no alc. no E-200	0.1	Cloudy	
	0.5	n-C <sub>4</sub> ,5	1.25	Clear	Above 1.25 wt. % NaCl, cloudy or phase separation
Aerosol-OT	0.1	i-C <sub>3</sub> ,5	1.0	Cloudy	no short chain alcohol inhibited salting-out
	0.8	no alc. E-200,0.2	0.5	Ppt.	
	0.8	n-C <sub>4</sub> ,5 E-200,0.2	0.5	Cloudy	Cloudy but no ppt., phase sepn. starts at 2 wt. % NaCl
	1.0	no alc. no E-200	0.1	Cloudy	
	1.0	n-C <sub>4</sub> ,5 no E-200	0.2	Clear	Solns. cloudy between 0.3 and 1.2 wt. % NaCl, phase sepn. above 1.2 wt. % NaCl
TRS-10-410	0.1		1.0	Cloudy	Short chain alcohols did not inhibit salting-out

then a precipitate formed. At the suggestion of several industrial associates, this process was reversed, i.e., surfactant (sodium lauryl sulfate, chosen because of its large solubility, is the only one tested by this procedure to date) was added to  $\text{CaCl}_2$  solutions of fixed concentration. These results are shown in Figure 15.

From Figure 15 one can see that when surfactant (SLS) was added to dilute  $\text{CaCl}_2$  solution (20 ppm), no turbidity was noted until the surfactant/calcium ratio approached unity. The turbidity increased rapidly to a maximum value (but no precipitate formed) and it remained<sub>+2</sub> relatively constant as the S/Ca ratio increased. However, when the  $\text{Ca}^{+2}$  concentration was greater (200 ppm or larger), the solution became turbid almost as soon as the addition of surfactant was begun. The turbidity passed through a maximum when the S/Ca ratio ranged between 1 and 2, then it decreased and the precipitated surfactant redissolved as the S/Ca ratio reached a value of 3-4.

The low solubility of the purified higher equivalent weight sulfonates (i.e., above 350) makes it very difficult to study the calcium tolerance for a wide range of conditions. For many of the materials of greatest interest for micellar/polymer flooding, it does not appear likely that S/Ca ratios above unity can be achieved for  $\text{Ca}^{+2}$  concentrations greater than about 100 ppm.

It is interesting to compare these data with those obtained by Meister et al. (paper prepared for presentation at the Colloid Symposium, June, 1978). These authors studied the calcium tolerance of a considerable number of commercial anionic surfactants. In general, the surfactants in their study contained oil, and the calcium tolerance found is about ten times that found in our experiments for the same surfactant (but deoiled). It appears, therefore, that the presence of oil reduces the sensitivity of anionic surfactants to calcium ions (probably by means of dissolution of the calcium sulfonate in oil).

#### Dynamic Adsorption of Anionic Surfactants

To supplement the studies on equilibrium adsorption, a small effort in dynamic adsorption was initiated. A small packed bed apparatus was assembled and several step-change and pulse experiments conducted. The details of the procedure are described in the Fifth Semi-annual Report on this project (December, 1977). A set of typical breakthrough curves for a step-change experiment are shown in Figure 16 and for pulse experiments in Figures 17 and 18.

In these experiments a one wt. % KCl solution is displaced from a bed of crushed Berea sandstone by a solution containing one wt. % NaCl, 0.001 wt. % Eosin (a dye marker), and 0.1 wt. % SDBS. The step-change breakthrough curves of Figure 16 reveal 1) symmetry of displacement of KCl by NaCl, 2) correspondence of NaCl and Eosin breakthrough, and 3) lag of SDBS breakthrough because of adsorption. The breakthrough curves in the pulse experiment shown in Figure 17 show 1) essentially complete recovery of Eosin (~ 90%), and 2) lag, slug dispersion, and incomplete recovery of SDBS (generally < 25%). Those in Figure 18 to which a

mobility control polymer was added, show 1) less surfactant lag, 2) reduced slug dispersion, and 3) substantially improved surfactant recovery (~ 50% vs < 25% without polymer).

One important result of these fixed bed experiments has been to demonstrate very conclusively the necessity of eliminating salting-out, cation exchange and surfactant precipitation, and clay deflocculation if one is to obtain precise estimates of surfactant losses by adsorption. On the other hand, if-as is the case in most core tests-oil is present, the oil may exert an overriding influence on all of these processes.

#### THERMODYNAMIC PHENOMENA

Research in the area of Thermodynamic Properties has focused on two theoretical and two experimental endeavors. One theoretical aspect deals with the nature of aqueous solutions involving nonpolar species and surfactants. We have previously shown that the large entropy change associated with micellization could be explained as an "excluded volume" effect where, after a micelle is formed, the small water molecules have access to regions of space previously occupied by the surfactant chains. While the volume is essentially the same, the entropy effect is mostly determined by the area of the excluded volume. This is much larger for the monomers than for the micelle. Our idea is generally applicable for aqueous solutions since the entropic "hydrophobic effect" dominates all nonpolar solubilities and makes water a poor solvent for many organic species. We have thus begun establishing a general approach to this phenomenon based on the modified scaled particle theory for water by Stillinger (1973). At present we have established the most sensitive water structure parameters, with values being determined for all solutions by using a combination of x-ray scattering data for water and precise solubilities and entropies of solution of the noble gases (He, Ne, Ar, Kr, Xe) and pseudospherical gases ( $\text{CF}_4$ ,  $\text{SF}_6$ , Neo- $\text{C}_5\text{H}_{12}$ ). We can describe these data substantially within experimental error using empirical values of fundamental molecular quantities and shall proceed next to describe nonspherical species such as paraffins.

The other theoretical investigation is for microemulsion formation using statistical mechanical information not heretofore applied. The theory of Reiss (1975) has no short-range electrostatic force included, so it is not valid for finding the mean size of the dispersed phase. However, it does provide a suitable framework for the entropic driving force for microemulsion formation and we are modifying the theory to use information available from the thermodynamic properties of ionized plasmas and dispersed latex spheres.

The experimental efforts involve work at elevated pressures. Both apparatuses are completed and preliminary testing is underway. In one, we shall study the effect of temperature, pressure and dissolved gas (such as  $\text{CH}_4$  and  $\text{CO}_2$ ) on the transition from anisotropic to isotropic surfactant-oil-water fluids<sup>2</sup> will be detected by transmission through crossed polarizers. Preliminary evidence is that while pressure up to 700 bar often yields relatively small effects on this transition, dissolved solutes stabilize the anisotropic form to relatively high temperatures.

In the other apparatus, careful PVT measurements of the phase volume behavior of concentrated surfactant solutions particularly including the middle phase, will be made as a function of temperature and pressure up to 200 bar. The influence of dissolved gas on the bubble point and volumetric behavior of these solutions are also to be measured quantitatively.

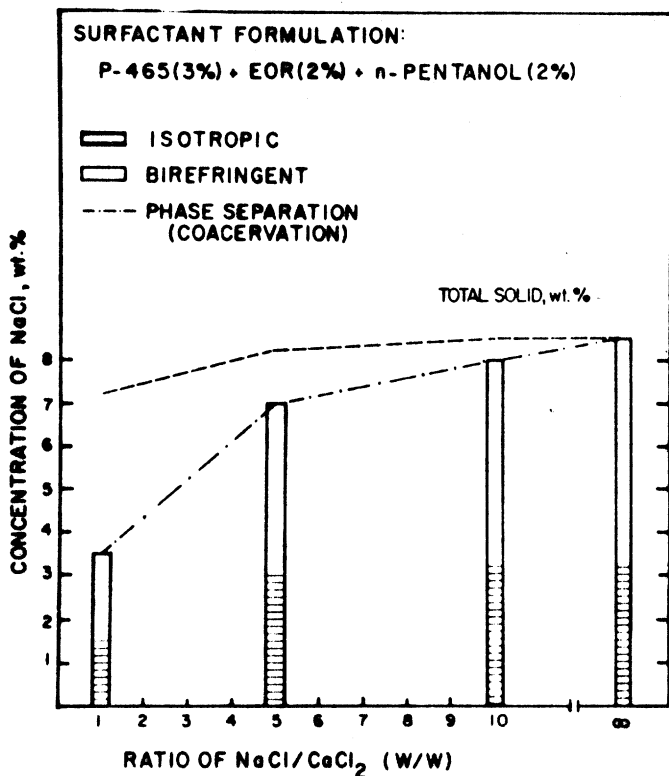
#### ACKNOWLEDGEMENTS

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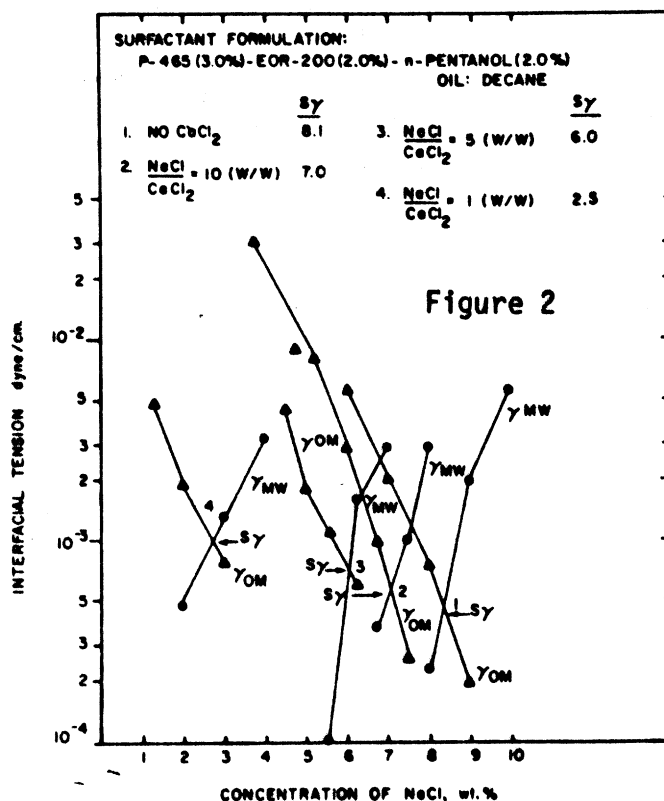
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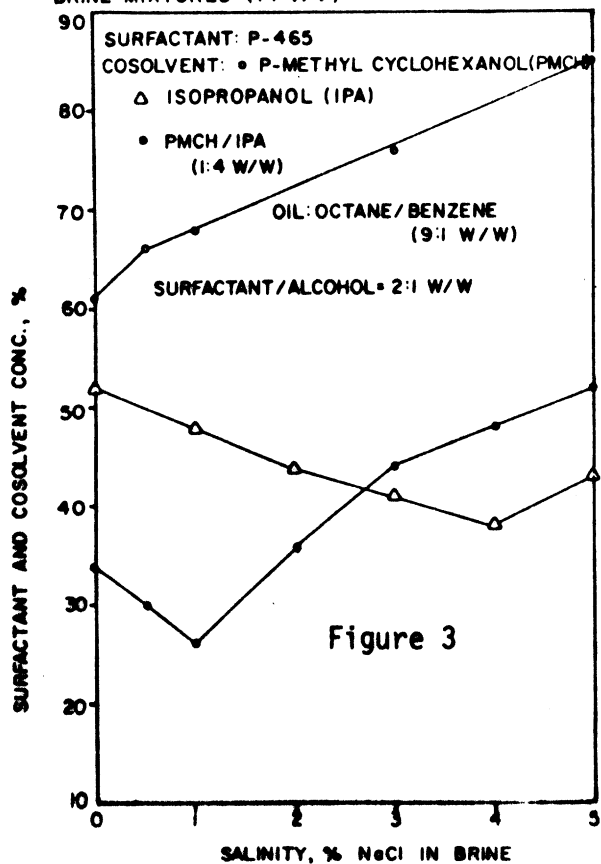
Figure 1 The effect of NaCl/CaCl<sub>2</sub> ratio on the optical appearance of a surfactant formulation



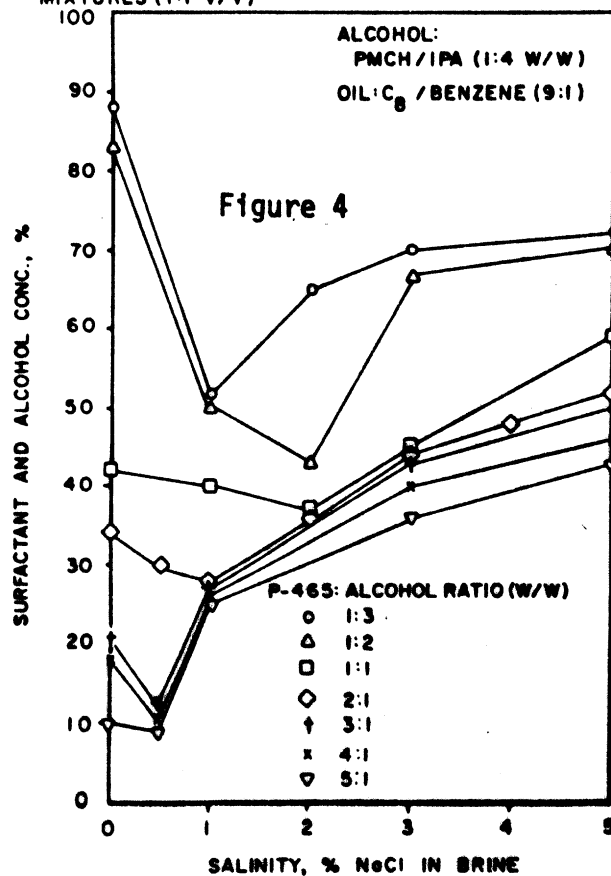
EFFECT OF CaCl<sub>2</sub> ON INTERFACIAL TENSION AND OPTIMAL SALINITY.



THE EFFECT OF P-METHYL CYCLOHEXANOL AND ISOPROPANOL MIXTURES ON FORMATION OF SINGLE PHASE OF OIL-BRINE MIXTURES (1:1 V/V)



THE EFFECT OF SURFACTANT/ALCOHOL RATIO ON THE FORMATION OF A SINGLE PHASE OF OIL-BRINE MIXTURES (1:1 V/V)





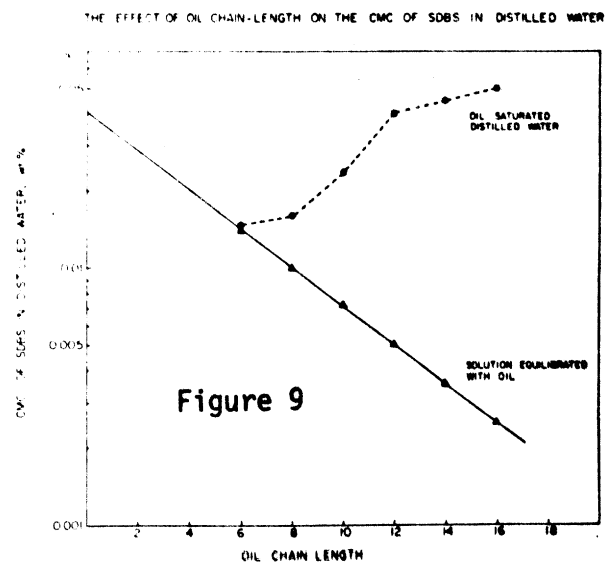
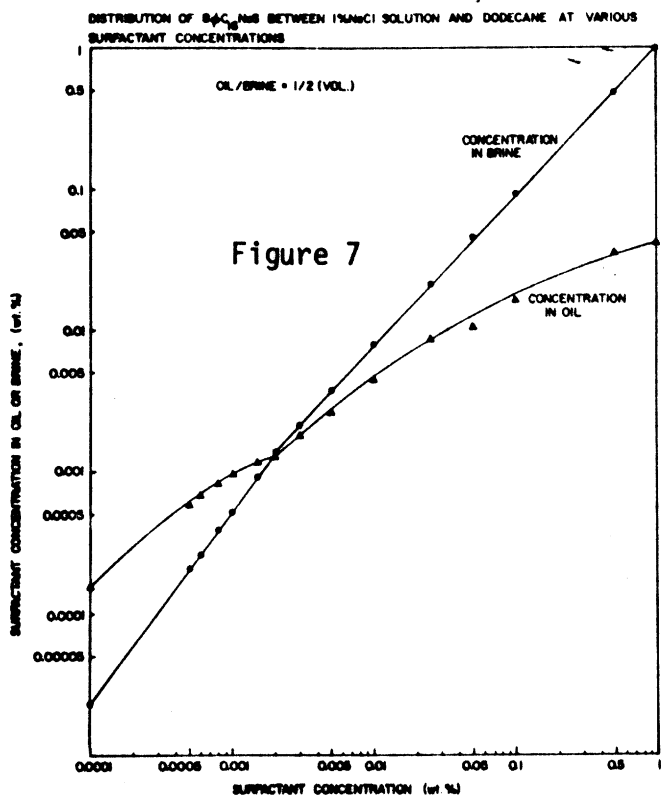
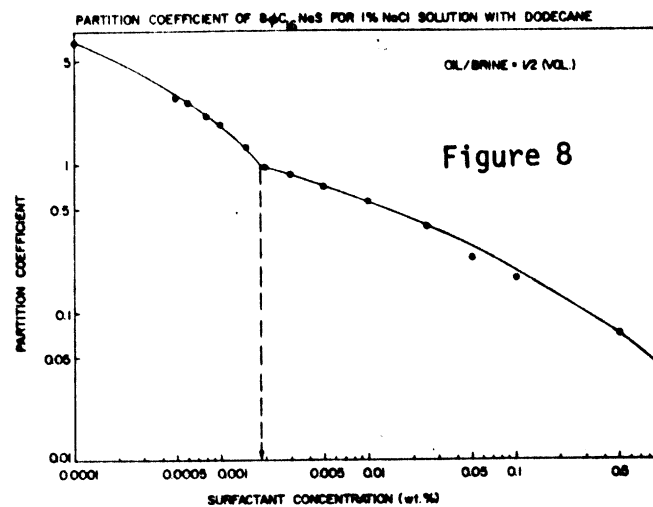
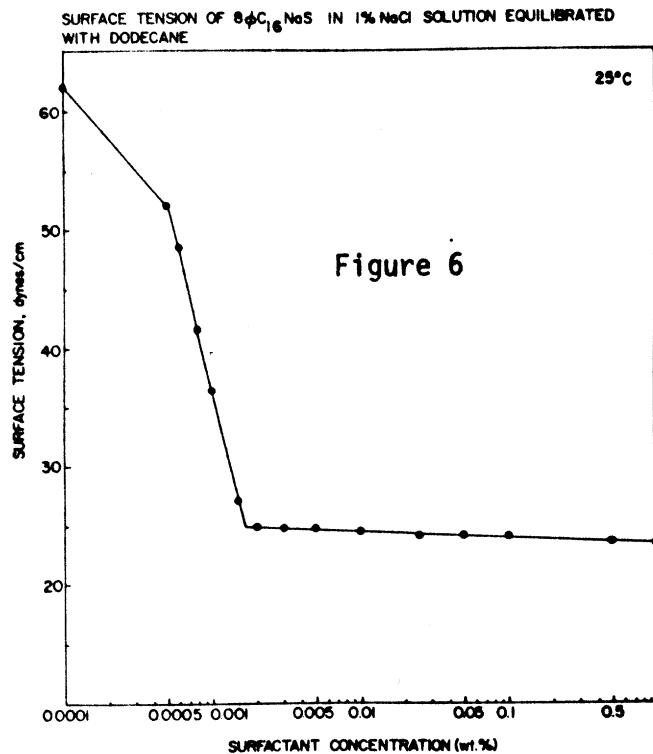
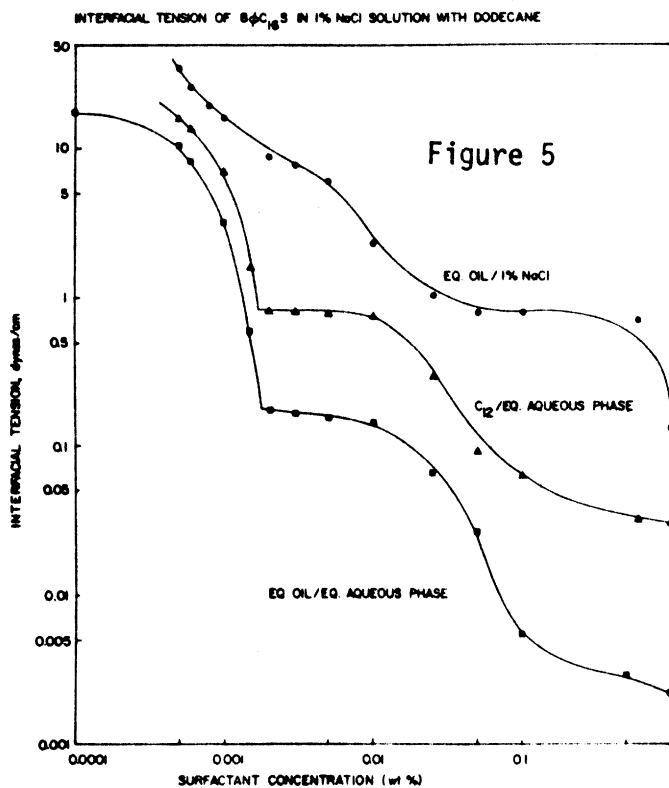


Figure 10

THE EFFECT OF CONCENTRATION OF TRS 10-80 ON n-OCTANE  
EQUILIBRATED AQUEOUS PHASE DISPLACING EQUILIBRATED OIL PHASE

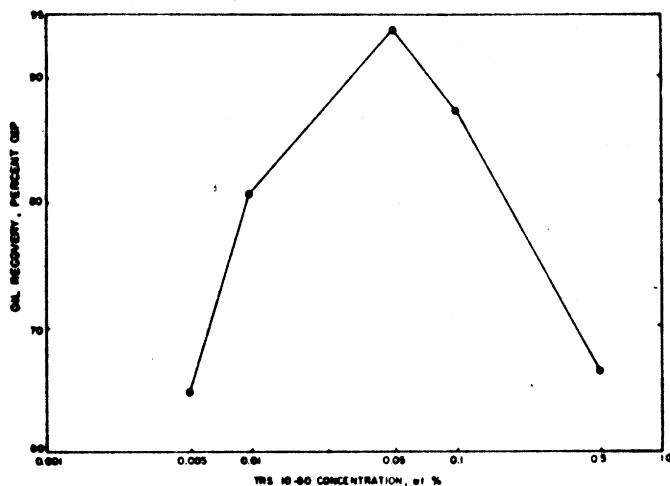


Figure 11

PERCENT OIL RECOVERY BY 0.1% TRS10-410 + 0.06 %  
IBA ON n-DODECANE; CONTINUOUS INJECTION OF  
EQUILIBRATED AQUEOUS PHASE TO DISPLACE  
EQUILIBRATED OIL PHASE

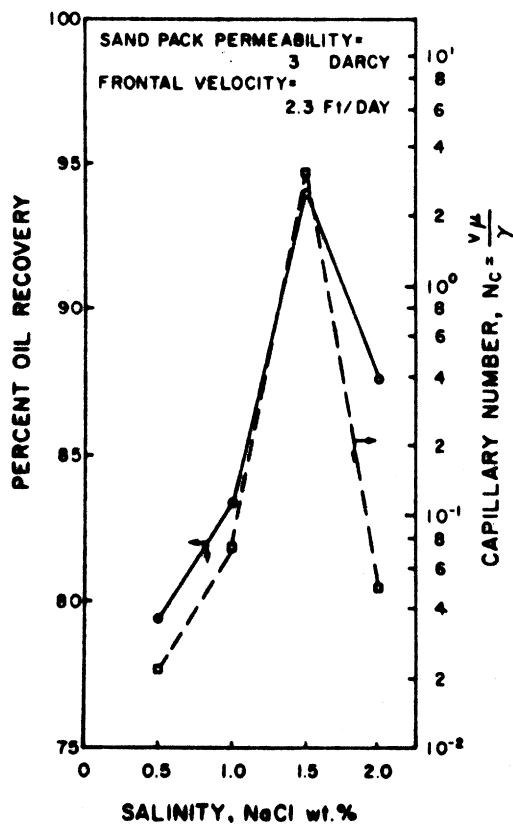
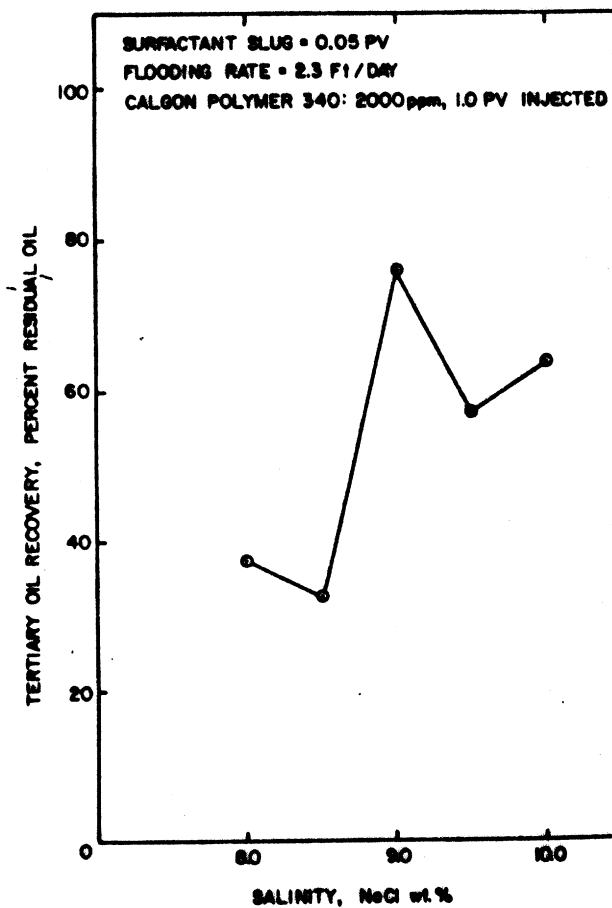
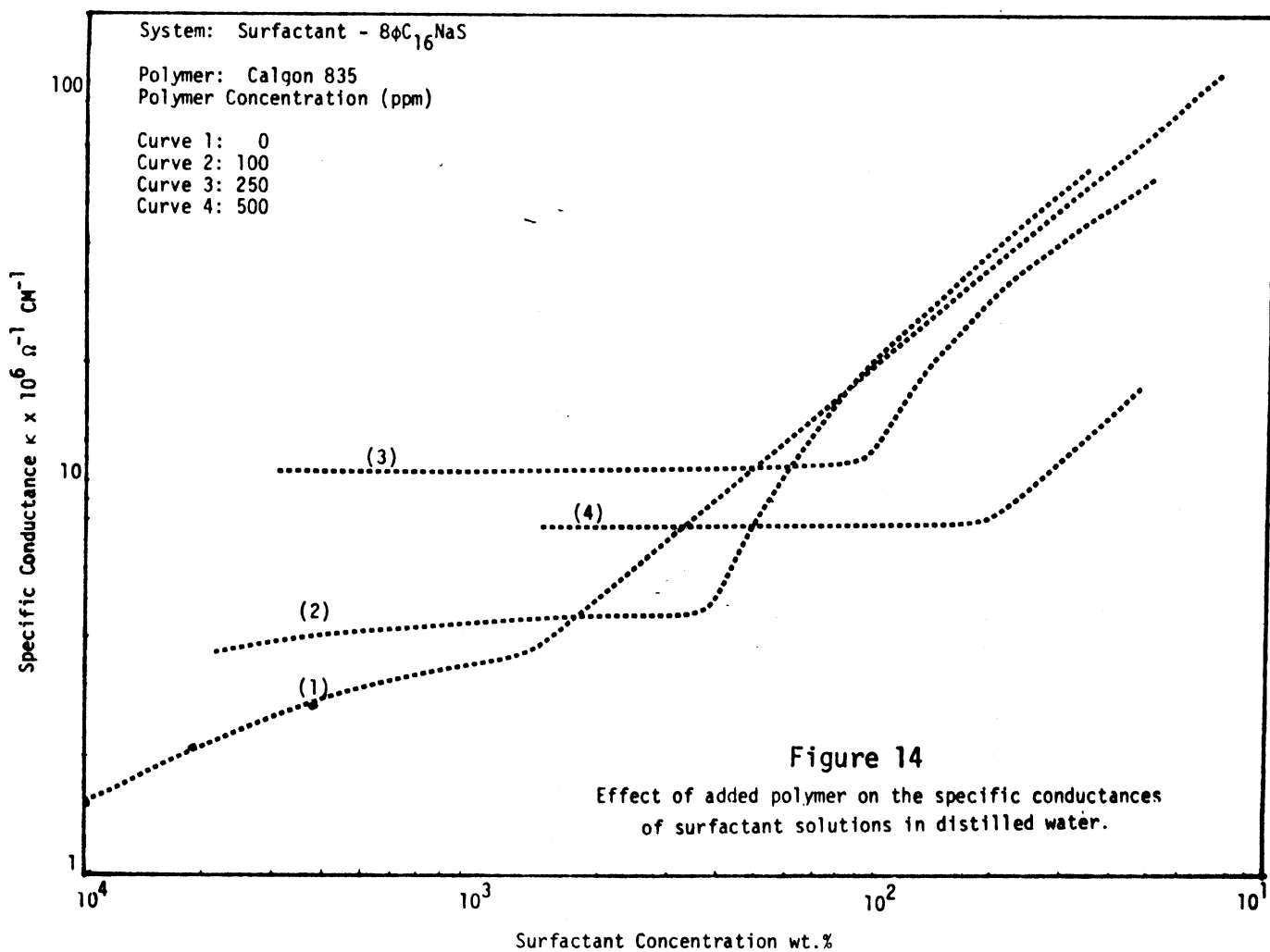
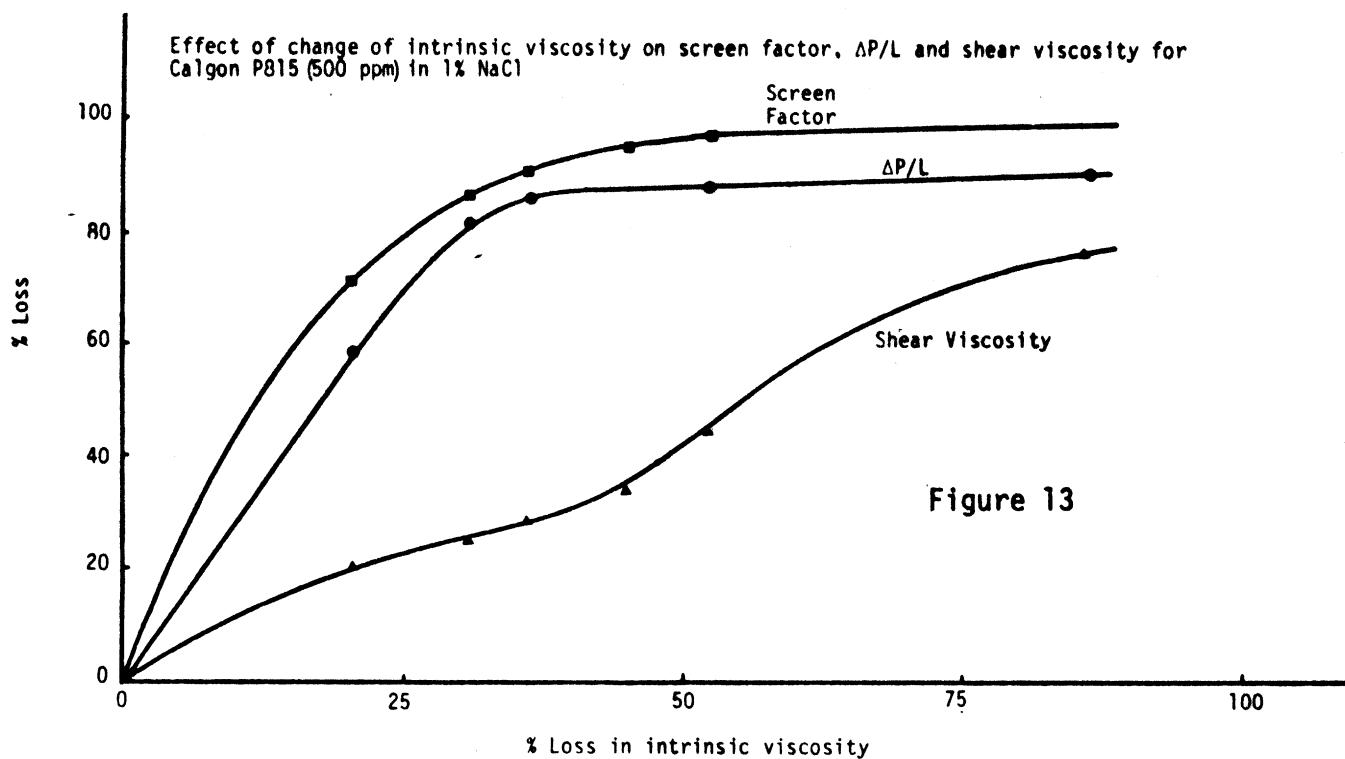


Figure 12

THE EFFECT OF SALINITY ON PERCENT TERTIARY OIL  
RECOVERY BY 1.5% TRS10-410 + 2.5% EOR 200 + 3% IBA OF  
n-DODECANE IN SAND PACKS AT 27°C





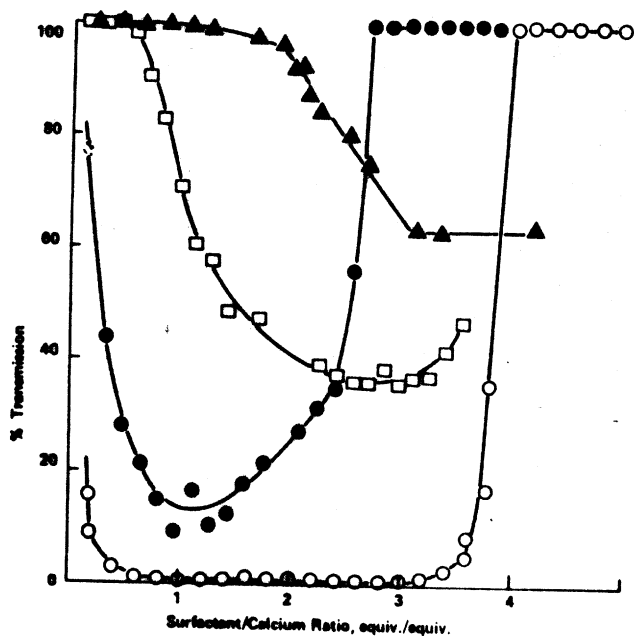


Figure 15. Calcium Tolerance of Sodium Lauryl Sulfate  
 $\Delta$  - 19 ppm  $\text{Ca}^{+2}$ ;  $\square$  - 46 ppm  $\text{Ca}^{+2}$ ;  $\bullet$  - 200 ppm  $\text{Ca}^{+2}$ ;  
 $\circ$  - 500 ppm  $\text{Ca}^{+2}$ .

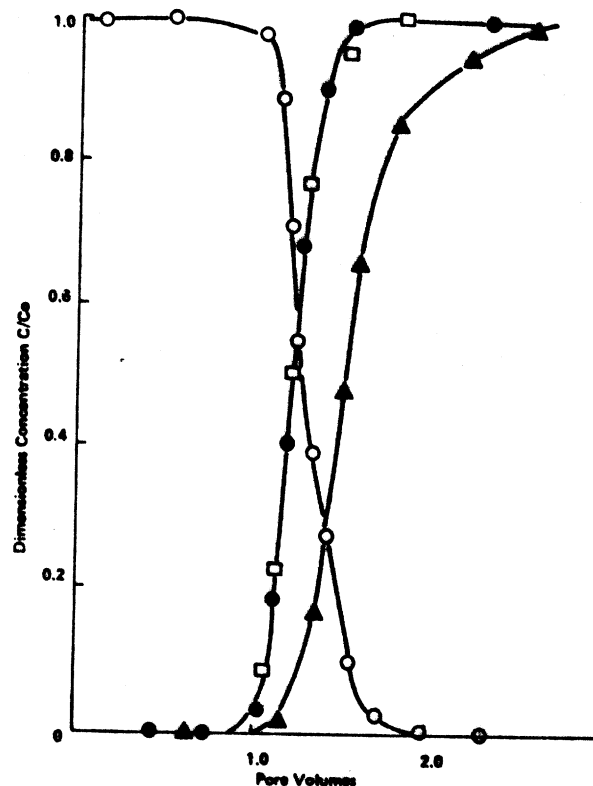


Figure 16. Concentration History of Solutes in Bed of Crushed Berea Sandstone with Step-Change Input. Bed Length = 6 in.  $V = 1.66$  ft./day.  
 $\circ$  - KCl ( $c = 1$  wt. %);  $\square$  - NaCl ( $c = 1.0$  wt. %);  $\bullet$  - Eosin ( $c = 0.001$  wt. %);  
 $\blacktriangle$  - SDBS ( $c = 0.1$  wt. %).

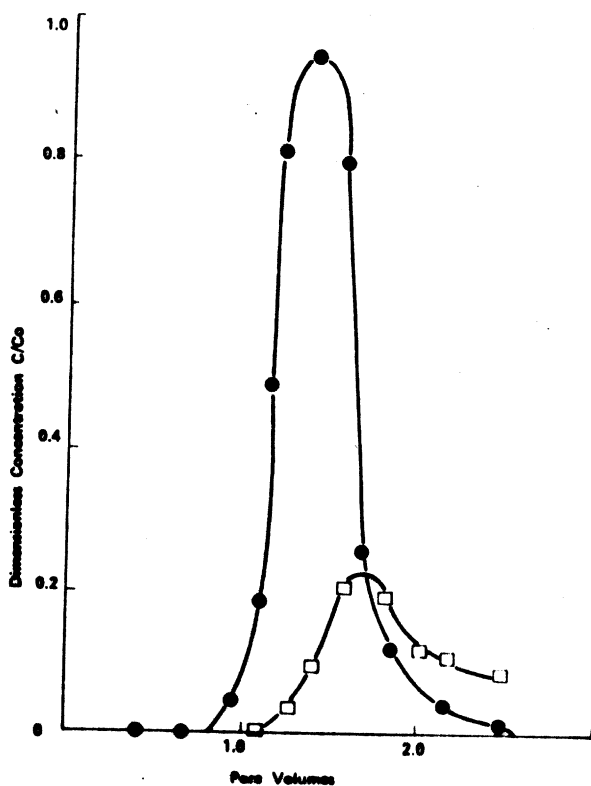


Figure 17. Concentration History of Solutes in Bed of crushed Berea Sandstone with 0.5 PV pulse input. Bed Length = 6 in.  $V = 1.66$  ft./day.  
 $\bullet$  - Eosin ( $c = 0.001$  wt. %);  $\square$  - SDBS ( $c = 0.1$  wt. %).

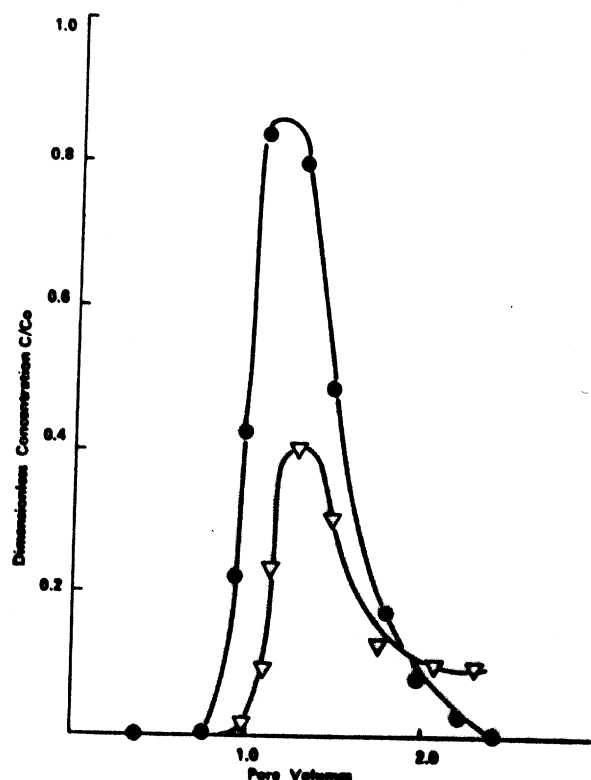


Figure 18. Concentration History of Solutes in Bed of Crushed Berea Sandstone with 0.5 PV Pulse Input. Bed Length = 6 in.  $V = 1.66$  ft./day.  
 $\bullet$  - Eosin ( $c = 0.001$  wt. %);  $\nabla$  - SDBS ( $c = 0.1$  with 500 ppm Calgon PAM 515 Polymer).