From Proceedings of ERDA Symposium on Enhanced Oil, Gas Recovery and Improved

Drilling Methods Vol. 1, A 11/1-19

August 30-September 1,1977

UNIVERSITY OF FLORIDA RESEARCH PROGRAM ON CHEMICAL OIL RECOVERY SYSTEMS

bу

D.O. Shah, R.D. Walker, Jr., J.P. O'Connell, R.J. Gordon and H.E. Schweyer
Department of Chemical Engineering
University of Florida
Gainesville, Florida 32611

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, oils and sand. The following are the five major areas of research of this program: 1) Interfacial Phenomena, 2) Bulk, Surface and Porous Media Rheology, 3) Adsorption and Ion Exchange Phenomena, 4) Polymer Rheology and Fluid Mechanics, and 5) Thermodynamic Phenomena and Phase Equilibria. The research program is designed to establish a broad framework of information relating the microstructure of injection fluids and their behavior in porous media to oil displacement efficiency. It is hoped that the development of the basic framework of new information and the quantitative relationships among various parameters of the process would assist industry in developing, optimizing and fine tuning of injection fluids for reservoirs of varying conditions. This paper reviews our accomplishments of the past one year in each of these areas.

INTRODUCTION

Tertiary oil recovery by surfactant and polymer flooding involves the displacement of oil by a surfactant slug which is followed by a polymer slug for mobility control. Our research program includes five major areas relevant to this process as follows:

(1) Interfacial Phenomena: The interfacial phenomena area involves the study of interfacial properties of stable surfactant formulations, and the elucidation of the microstructure of fluids responsible for their bulk and surface properties.

(2) Bulk, Surface and Porous Media Rheology: Such a study is necessary in order to relate the properties of complex surfactant solutions to their behavior is porous media. Rheological properties of the surfactant solutions have determined in order to control the mobility of the process. It is the theological properties can be correlated with the microstructure of the solutions.

Prepared for Energy Research and Development Administration under Contract No. EY-77-S-05-5341

- (3) <u>Polymer Rheology</u>: The main reason for the use of polymer solution in the process is to control the mobility of the process. For the flow of polymer through porous media, the extensional viscosity, zero shear viscosity, and degradation of the polymer are important parameters to be studied.
- (4) Adsorption and Ion Exchange Phenomena: Adsorption of surfactant on the porous media is one of the loss mechanisms in the process, and could be detrimental to the efficiency and economics of the process. A better understanding of the mechanisms of adsorption to various clays and minerals, and the techniques to reduce the surfactant and polymer losses are the main objectives of this research.
- (5) Thermodynamic Phenomena and Phase Equilibria: Theoretical aspects of this research involves the prediction, from molecular parameters, of solubilization, critical micelle concentration (CMC) and the effect of temperature and pressure on the surfactant solution properties. The experimental program involves the study of properties of surfactant solutions at elevated temperatures and pressures.

This paper is the summary of results obtained recently in each of these areas and reported elsewhere (1-11).

INTERFACIAL PHENOMENA

Microstructure of Surfactant Formulations and Middle Phase Microemulsions by Freeze-etching Electronmicroscopy

Our results on the microstructure of a birefringent surfactant solution and of the middle phase microemulsion at optimal salinity are reported here. Figure 1 shows the electronmicrograph of TRS 10-410 (5%) + IBA (3%) formulation in 2% NaCl at 17,100 magnification. Figure 2 shows the electronmicrograph of the same formulation fractured at a different angle at 36,000 magnification. This formulation exhibited a strong birefringence when placed between polarizing These electronmicrographs reveal that this birefringent formulation consists of a foam-like structure in which the surfactant and alcohol molecules are presumably present in the membranes whereas the aqueous phase is trapped inside the bubbles. These electronmicrographs clearly show a continuous membranous structure. In Figure 2 one can see the walls between adjacent compartments or bubbles. Each bubble is about 2-3 microns in diameter. It was established from other electronmicrographs (not reported here) that the membranes are made up of several bilayers of surfactant molecules. It was shown that each wall is made up of several bilayers of surfactant molecules. We would like to refer to such birefringent surfactant solutions as "Birefringent Cellular Fluids" since they consist of cells or compartments surrounded by membranes. We believe that this structure represents an intermediate phase before the surfactant molecules are totally squeezed out of water when the salt concentration is increased. It is very interesting that, in spite of its foam-like character, this formulation exhibits an extremely low viscosity.

Since the realization of the importance of the middle phase formation in tertiary oil recovery using concentrated surfactant formulations at the optimal salinity value (same amount of oil and water solubilized in the middle phase), the elucidation of the structure of the middle phase is one of the major objectives of the research in the field of tertiary oil recovery. Theoreticians

as well as experimentalists have suggested various structures for the middle phase. Scriven (12) has suggested that the middle phase is bicontinuous in nature, with a continuous surfactant layer separating water and oil. surfactant layer divides the volume into two multiply connected, interpenetrating subvolumes, each of which is physically continuous. Friberg et al. (13) proposed a structure for the middle phase, as a mixture of spherical aggregates and planer surfactant layers. Miller (14) also stated that the structure of the middle phase is probably "bicontinuous" when the middle phase exhibits ultra low interfacial tension with oil and water simultaneously. However, they did not rule out the possibility that the middle phase may be an oil or water external microemulsion at salinities different from the optimal salinity. Based upon the many similarities between the physico chemical properties of the middle phase and that of a microemulsion, as described by Schulman and his co-workers (15-20), the structure of the middle phase was proposed by Hsieh and Shah (21) to be a water external microemulsion with monodispersed oil droplets suspended in a continuous aqueous phase. The conclusion that the water is the external phase was based on the low electrical resistance of the middle phase, namely, 50 to 300 ohm/cm. To strengthen the view that the middle phase is a water-external microemulsion, electron micrographs of the middle phases at different salt concentrations for the Exxon system (surfactant formulation) were obtained using freeze-etching electronmicroscopy at 60,000 magnification. The electronmicrograph of the middle phase at 1.2% NaCl (optimal salinity) concentration is shown in Figure 3. This electronmicrograph clearly indicates that the middle phase is composed of spherical oil droplets dispersed in a continuous aqueous phase. The spherical droplets are of almost uniform size and are arranged in an almost regular arrangement. Very similar observations were made for other salt concentrations and it was also found that the size of these dispersed oil droplets decreased as the concentration of salt increased. This decrease in the size of oil droplets to almost micellar size appears to facilitate the inversion of the water-external microemulsion to oil-external microemulsion upon further increase in the salt concentration. Though the electronmicrograph clearly indicates that the middle phase is composed of dispersed spherical oil droplets in a continuous aqueous phase, further investigation to determine the size of these droplets by small angle x-ray scattering and the surface charge and shape of the droplets by impedence measurements at radio frequencies is under way and we plan to report these studies in our subsequent semi-annual

The Effect of Oil Chain-length on Optimal Salinity

In view of the fact that different crude oils can be considered having different equivalent carbon numbers, it was thought that the effect of chain length of oil on the optimal salinity value of a particular surfactant formulation should be of importance in tailoring surfactant formulations for different crude oils. The study presented in this section was designed to elucidate the effect of chain-length of oil on interfacial tension optimal salinity (S_{γ}) and phase behavior optimal salinity (S_{φ}) by measuring the solubilization parameters and interfacial tension of the surfactant formulation containing 5% TRS 10-410 + 3% isobutanol at various salinities. The optimal salinity values obtained for different oils via measurement of solubilization parameters and interfacial tensions (7) are shown in Figure 4. It is evident from Figure 4 that as the

chain length of the oil increases the optimal salinity value (S_{γ} or S_{φ}) also increases. The values of S_{γ} and S_{φ} are very close to each other for these oils. This observation is very similar to the observations of Reed and Healy (22) for values of S_{γ} and S_{φ} for their system. It was also found that, at the optimal salinity, interfacial tension, γ_{om} or γ_{mw} , increases and the solubilization of brine or oil decreases as the chain length of oil increases. The increase in the interfacial tension at optimal salinity upon increasing the chain length of oil might be relevant to determining a suitable surfactant formulation for the higher equivalent carbon number crude oils.

Molecular Mechanism for Achieving Ultra Low Interfacial Tension in Low Concentration Surfactant Systems

In the past few years, achievement of ultra low interfacial tension by using dilute aqueous solutions of petroleum sulfonates has been reported in literature (23-25). This phenomena, however, occurs in a very narrow range of surfactant concentration. Interfacial tension first decreases with an increase in surfactant concentration, and at a critical concentration, the interfacial tension reaches its minimum value. Beyond this critical concentration, the interfacial tension increases with increasing surfactant concentration. This sharp minimum in interfacial tension can make the tertiary oil recovery by low surfactant concentration solution difficult. Unfortunately, there is no explanation offered for the molecular mechanism for the generation of the ultralow interfacial tension. We believe that a broad interfacial tension minimum can be produced only after we understand the molecular mechanism governing the sharp minimum in interfacial tension.

Based on the surfactant partition and surface tension data, the molecular mechanism for the effect of three major variables, namely, surfactant concentration, salinity, and the chain length of oil, on the ultra-low interfacial tension have been proposed (5,11).

Effect of Surfactant Concentration on Interfacial Tension and Partitioning in Oil

For the effect of surfactant concentration on interfacial tension, it was shown (5,11) that as the surfactant concentration increases, the number of surfactant monomers in brine and oil increases. When the monomer concentration in the brine reaches the <u>Critical Micelle Concentration</u> (CMC) both the interfacial tension and surface tension show minima. The number of surfactant molecules in the oil phase also reaches a maximum at this concentration. We have proposed that the concentration at which the minimum interfacial tension and surface tension as well as the maximum amount of surfactant partition in the oil phase occur is the true CMC.

Figure 5 schematically illustrates the proposed molecular mechanism for the interfacial tension minimum observed in the system. At very low surfactant concentrations (e.g., C_1 , C_2 below CMC), the surfactant would partition in three different regions, namely, brine, interface and oil. As one increases the surfactant concentration, the concentration in each region increases. The increase

in surfactant concentration at the interface will cause a decrease in the interfacial tension as well as an increase in the amount of surfactant in the oil phase. Both of these predictions were confirmed experimentally. However, if the micelles just begin to form in the aqueous phase at the concentration C_3 then there will be a maximum number of monomers in the aqueous phase at this concentration. If the surfactant concentration is increased, more micelles will be formed (e.g., C4, C5). It is generally assumed that the number of monomers of surfactant remains constant above CMC. If this was indeed true, we should have seen the same amount of surfactant in the oil phase beyond CMC. In fact, the total amount of surfactant in the oil phase decreases after CMC. This suggests that the number of monomers in the oil phase (since the surfactant concentration in the oil phase is very low, we can assume that it is essentially in monomeric form) decreases, the number of monomers at the interface and in the aqueous phase also decreases, and this will cause an increase in interfacial tension. The decrease in the number of monomers in the aqueous phase beyond CMC was confirmed experimentally from the osmotic pressure and light scattering measurements (26).

Effect of Salinity on Interfacial Tension and Partition Coefficient

Surfactant partitioning in oil and brine is extremely sensitive to salt concentration. By adding salt to the aqueous phase, the solubility of the surfactant in the aqueous phase decreases. When the solubility of the surfactant in oil and the aqueous phase become equal, a maximum number of monomers can be expected to be present at the interface, and thus the interfacial tension should be a minimum at this salt concentration. The proposed molecular mechanism for the effect of salt concentration on interfacial tension and partition coefficient is schematically shown in Figure 6. At zero salt concentration, most of the surfactant remains in the aqueous phase, and hence very little of it partitions into the interface or oil phase. As the salt concentration increases, the surfactant preferentially dissolves in the oil phase. At optimal salinity, the surfactant concentration is the same in both oil and brine phases. This presumably results in the highest interfacial concentration of surfactant, and hence the lowest interfacial tension. It is interesting to note that if one measures the surface tension of equilibrated brine phase, the minimum surface tension occurs at the same salt concentration (Broken curve in Figure 6). The partition coefficient at the same concentration is unity.

Effect of Chain-length of Oil on Interfacial Tension

The proposed molecular mechanism for the effect of oil chain length on interfacial tension is illustrated schematically in Figure 7. It was established (5,11) from partition coefficient data that as the chain length of oil increases, the solubility of the surfactant in the oil phase decreases. Therefore the number of monomers of surfactant in the oil phase decreases with an increase in the chain length of oil, as shown in the upper part of Figure 7. Consequently, the concentration of surfactant in the brine phase must increase as the oil is changed from C₆ to C₁₆. It appears from interfacial tension and surface tension

results that the concentration of surfactant in the aqueous phase equilibrated with C6 and C8 is below CMC. The surfactant concentration in the aqueous phase equilibrated with decane is at the CMC and with higher chain-lengths of oil, the surfactant concentration in the aqueous phase is above the CMC. As mentioned earlier, the monomer concentration decreases as the surfactant concentration increases beyond the CMC. This would increase both interfacial tension and surface tension as was confirmed experimentally. The molecular mechanism proposed in Figure 7 takes the mystery out of the oil chain-length effect reported by various investigators. It appears to us that a sharp chain-length dependence is not due to any specific interaction between oil and surfactant molecules, but due to partitioning (or solubility) in the oil phase and a critical micelle concentration phenomena.

The molecular mechanisms proposed for the effect of surfactant concentration (Figure 5), the effect of salt concentration (Figure 6) and the effect of oil chain-length (Figure 7) account for all experimental studies carried out by us as well as by others (27,28) on these aspects of ultra-low interfacial tension. The explanations proposed here are valid for those surfactants which exhibit minimum in interfacial tension as a function of surfactant or salt concentration. The synthetic sulfonates (isomeric or very narrow equivalent weight distribution) do not show a sharp minimum as a function of surfactant concentration. This suggests that in such systems monomer concentration may not decrease beyond CMC. This unified understanding of the molecular mechanisms for achieving ultra-low interfacial tension will assist in designing and manipulating desirable surfactant systems for tertiary oil recovery.

Enhancement of Salt Tolerance and Optimal Salinity of Surfactant Formulations

From the existing literature on petroleum sulfonates, it appears that surfactant formulations based upon petroleum sulfonates exhibit relatively low salt tolerance and low values of optimal salinity. This section reports our results on the effect of blending an ethoxylated sulfonate (EOR-200) with a petroleum sulfonate (Petrostep 465) on various properties of the mixed surfactant systems. Figure 8 illustrates the effect of salt concentration on the surfactant formulation consisting of Petrostep 465 + n-Pentanol + EOR-200.

The surfactant formulation passes through different regions, namely, stable, precipitation, birefringent, and finally to phase separation (Figure 9.) It is evident that as the amount of EOR-200 in the surfactant formulation increases, the salt tolerance of each region increases. The surfactant formulation remains stable with the addition of up to 24% salt when EOR-200 is 4% in the surfactant formulation. As compared to the salt tolerance of the two individual surfactants (Petroleum sulfonate or ethoxylated sulfonate) the mixed surfactant system exhibits a much higher salt tolerance than either of the pure surfactants, suggesting a synergistic effect by blending of these surfactants. It was also found for these mixed surfactant systems that as the fraction of ethoxylated sulfonate increases (up to 1:4 ratio of petroleum sulfonate/ethoxylated sulfonate), the optimal salinity increases. It was interesting to note that the pure EOR-200 system as such is not able to produce an ultra-low interfacial tension but the addition of Petrostep 465 to the system drastically reduces the interfacial tension.

The effect of divalent ions (Ca and Mg) on the salt tolerance and optimal salinity of this mixed surfactant system was also studied. The system chosen for this study consisted of Petrostep 465 (3%) + EOR-200 (2%) + n-Pentanol (2%) and this formulation has a salt tolerance limit of 8.5% NaCl and its optimal salinity value with n-decane is 8.1%. It was found that the formulation consisting of petroleum sulfonate and ethoxylated sulfonate can tolerate a sufficient amount of CaCl2 and MgCl2 in the surfactant formulation without any precipitation of phase separation up to the appropriate concentration of NaCl, and the surfactant formulation still produced very low interfacial tensions (in the range of millidynes/cm). It was also found that the optimal salinity value decreases from 8.1% to 2.5% when the CaCl2/NaCl ratio in the surfactant formulation increases from 0 to 1:1(w/w) in the surfactant formulation.

BULK, SURFACE AND POROUS MEDIA RHEOLOGY

Effect of the Structure of Alcohol and of Dilution on the Viscosity of a Surfactant Formulation

The objective of this research was to investigate the effect of dilution of a surfactant formulation on its bulk viscosity and apparent viscosity as measured by flow through a porous medium and to correlate these viscosities with the microstructure of the surfactant formulation. The rationale for this study was that if an aqueous surfactant formulation is injected into the reservoir, it will be diluted by reservoir brine and subsequently would change its properties. The system investigated was 5% TRS 10-410 + 3% Butanol + 2% NaCl. The formulation was gradually diluted by addition of 2% NaCl. It was found that as the aqueous surfactant formulation was diluted by brine, while keeping surfactant/cosolvent ratio fixed, a maximum in bulk viscosity occurred at a specific surfactant concentration. Furthermore, this maximum in viscosity correlated well with the maxima observed in measurements of screen factor, NMR half-band width and apparent viscosity in Berea sandstone. Figure 9 shows the effect of molecular structure of butanol on the viscosity of the surfactant formulation. Up to 5% surfactant concentration, n-, iso- and 2-butanol systems exhibit a maximum in viscosity at a specific surfactant/cosolvent concentration. Based upon this study it was concluded that for alcohols, their brine solubility plays a predominant role in influencing the micellar structure as compared to their molecular areas.

The significance of this study is twofold. First, it is established that there is a correlation between rheology and flow through porous media for this surfactant formulation. One can, hence, simply use any one of the parameters measured (screen factor, NMR half-band width, relative viscosity) to screen the surfactant formulation before any extensive flow through porous media investigation is undertaken. Secondly, this study also has implications for injection of such formulations into an oil reservoir. As the concentrated surfactant formulation is injected into the ground, there will be not any injectivity problems because of the low viscosity of the formulation. However, once into the ground, it will be diluted with the field brine and will exhibit a higher viscosity presumably more appropriate for the mobility control of the surfactant slug and the

process. Such formulations, which at the injection point exhibit a low viscosity and upon subsequent dilution increase their viscosity, might have certain advantages. However, if the viscosity peak is very high then it may create a conformance problem.

Oil Displacement Tests

Figure 10 shows the efficiency of tertiary oil recovery as a function of salinity for a 0.05 PV slug of 5% TRS 10-410 + 3% IBA in brine displacing n-dodecane oil. The capillary number at each salinity was calculated and these are also shown on the same graph. It is evident from Figure 10 that there is an excellent correlation between tertiary oil recovery and capillary number or "controlling" interfacial tension. A maximum oil recovery of 72% was obtained at 1.5% NaCl where $\gamma_{mo} = \gamma_{mw}$ (optimal salinity value). The recovery was greatly improved, however, when a longer sand pack of 15" was used in place of 6.63" length used for results observed in Figure 10, and a final recovery of 82% was obtained. Still, this recovery is much less than the 92% recovery reported by Beneau and Clampitt (29). The difference in the recovery values can be attributed to the 300 md, 3 ft. long Berea core and 0.1 PV surfactant slug used by them and the 3000md. 1.2 ft. long sand pack and 0.05 PV surfactant slug used in our experiment.

POLYMER RHEOLOGY AND FLUID MECHANICS

Because of the small average shear rates (1-10 sec⁻¹) encountered by the injection fluids in tertiary oil recovery, one would not expect extensional flow behavior to be of importance. However, when one isolates a portion of the field, one would find a maze of converging-diverging channels that could create large instantaneous shear rates that would certainly be strongly dependent upon extensional flow. The purpose of this research is to determine those rheological parameters that are important in polymer flow through porous media and also to determine the effect of physico-chemical variables upon them.

Various rheological properties, e.g., shear viscosity, screen factor, extensional viscosity, etc., of Dow "Pusher" series as well as other polymers were studied at different CaCl₂ concentrations. For all the Dow Pusher polymers and experimental Dow polymer, the effect of CaCl₂ was found to be similar. This was also observed in the presence of sodium chloride.

In general, capillary viscometry measurements were more sensitive to salt addition than either screen factor or extensional viscosity. Relative changes in screen factor and extensional viscosity following salt addition corresponded closely to one another. It was also observed that shear viscosity is sensitive to mechanical degradation at low salt concentration, while at higher concentrations changes in viscosity following shearing were negligibly small. Figure 11 schematically summarizes current achievements and future goals in this research area.

The work presented in this section summarizes our research in three 1) Methods of determining the cation exchange capacity (CEC) of clays and reservoir minerals were explored and a centrifugation technique for separation of solids from the residual liquid was found satisfactory. The cation exchange capacities of a select4d group of clay minerals of Berea sandstone were determined and were found to be within the normal limits for mineral species involved. 2) Surfactant precipitation by multivalent cations, either added to the brine or by cation exchange, was examined and found to be very substantial. Precipitation was shown to be a potentially significant surfactant loss mechanism. The effect of cation exchange on the adsorption of TRS 10-410 on the clay fraction of Berea sandstone was examined and found to be relatively small. The small effect noted may have resulted from surfactant precipitation by displaced calcium and magnesium ions. 3) The adsorption of sodium pentadecylbenzene sulfonate on kaolinite, halloysite, and montmorillonite was measured at 35°C and one wt.% NaCl. These adsorption isotherms differ in several respects from those obtained for crushed Berea sandstone and for its clay fraction. In the first place, no adsorption maxima were observed. Secondly, there is a possibility that the isotherm rises to a second plateau at higher SPBS concentrations.

Scanning electron microscopy and energy dispersive x-ray analyses of selective reservoir core samples, and of selected clay minerals have been carried out to learn more about the exact structure of porous media encountered by a surfactant slug in a typical reservoir situation, especially concerning the pore size and geometry, the distribution of clays and related materials, and the probable contact area between the surfactant solution and the rock constituents. A typical scanning electron micrograph of Berea sandstone is shown in Figure 12. The basic matrix of sand grains may be seen quite clearly, but it is obvious that much of the surface of the sand grains is covered by a very fine grained extraneous material which is revealed to be a mixture of clays in the other scanning electron micrographs at higher magnifications. As noted earlier, our main concern here was not to characterize the minerals in detail but to get a feel for the rock structure with which surfactant solution would come into contact. The electron micrographs make it clear that any solution injected into these formations would have access to most of the surface and that flow through passages lined with clay may often be occurring with a clearance of only a few hundred to a few thousand A. As one might expect, cation exchange and adsorption will be facilitated by these structures.

THERMODYNAMIC PHENOMENA AND PHASE EQUILIBRIA

The work in this area has attempted to establish some definite molecular concepts and macroscopic correlations for the properties of aqueous solutions. The rationale is that the myriad of solution phenomena observed in concentrated surfactant solutions (micellization, solubilization, interfacial adsorption and liquid crystal structures) are probably controlled in the most part by the unique structure and interactions of the aqueous phase rather than the nonaqueous and inter-

acial phases (unless the interfacial area is very large). Thus, for example, we view the phenomena of micellization (30), which we have demonstrated (31) to be driven by the increase of entropy of the water when the volume occupied by the hydrocarbon tails is aggregated from the monomer to the micelle, as being related both molecularly and thermodynamically to the solubility of gases in water (32,33). We are using statistical mechanical models for quantitative expressions so that we will cover not only these phenomena, but also so that the theory and its parameters will describe the PVT behavior, the incorporation of solutes into micelles, the influence of added electrolytes, the behavior of multicomponent surfactants, etc. We use scaled particle theory (34,35) as modified by Stillinger (36) for water and plan further modifications consistent with observed phenomena. We have shown (37) quantitative success for correlating the CMC of surfactants and the entropy of micellization; with a few more developments associated with the energetics of molecular interactions, we should be able to predict the CMC, the mean aggregation number and their dependence upon added salt and other surfactants. The theory is also being formulated so that such extensions as solubilization phenomena are clear.

All along, we attempt to incorporate in our work the observations of, as well as influence the conclusions about, the phenomena observed by others in the University of Florida effort. The recognition that equilibrium properties imply certain phase behavior and concentration dependence is an imput we make as well as suggest lines of experimentation which check assertions and point out features crucial to a physical picture or mechanism.

Finally, we are preparing experiments associated with PVTX behavior of oil recovery fluids and the influence of pressure, temperature and dissolved gas on the isotropic/anisotropic transitions in liquid crystals as observed by static optical birefringence. Initially we have found that anisotropic phases are stabilized by increased pressure, and, particularly, by the presence of dissolved methane. Further work to confirm this trend and establish quantitative relationships is being done.

ACKNOWLEDGEMENTS

The authors wish to convey their sincere appreciation and thanks to ERDA (Grant no. EY-77-S-05-5341) and the consortium of twenty one oil and chemical companies for their generous support of the improved oil recovery research program at the University of Florida. Authors are grateful to Professor D.W. Deamer of the University of California at Davis for carrying out the freeze-etching electronmicroscopy experiments of surfactant formulations. Last, but not least the authors convey their thanks to Drs. M.K. Tham, M.C. Lee, W.C. Hsieh and V.K. Bansal and to Messrs. K.S. Chan, J. Noronha, M. Chiang, R. Giordano, F. Consoli, C.S. Chou, R.J. Brugman, R.G. Cruz, N. Desai and C. Krishnamoorthy for their active and valuable participation in the research program.

REFERENCES

- M. Chiang, K.S. Chan and D.O. Shah, "A Laboratory Study on the Correlation of Interfacial Charge with Various Interfacial Properties in Relation to Oil Recovery Efficiency during Water Flooding," Colloid and Interface Science Vol. II, ed. M. Kerker, Academic Press Inc., (1976) 321.
- D.O. Shah, W.C. Hsieh and D. Deamer, "The Structure and Interfacial Properties of Birefringent Cellular Fluids" paper presented at AIChE Meeting, Chicago, Nov. 28-Dec. 2, 1976.
- 3. D.O. Shah, K.S. Chan, V.K. Bansal, "The Importance of Interfacial Charge vs. Interfacial Tension in Secondary and Tertiary Oil Recovery Process" paper presented at 83rd National Meeting of AIChE, March 20-24, 1977, Houston, TX, no.50C...
- 4. J. Noronha, V.K. Bansal and D.O. Shah, "Surfactant-Polymer Interaction in Relation to Tertiary Oil Recovery," paper presented at 83rd National Meeting of AIChE, March 20-24, 1977, Houston, TX,no. 6b
- 5. K.S. Chan and D.O. Shah, "The Molecular Mechanism for Achieving Ultra-low Interfacial Tension," paper presented at the 51st Colloid and Interface Science Symposium, Grand Island, NY, June 19-22, 1977.
- 6. V.K. Bansal and D.O. Shah, "Solubilization, Phase Behavior and Interfacial Tension of Ethoxylated Sulfonate + Petroleum Sulfonate Mixtures for Enhanced Oil Recovery"paper presented at the 51st Colloid and Interface Science Symposium, Grand Island, NY, June 19-22, 1977.
- 7. W.C. Hsieh and D.O. Shah, "The Use of High Resolution NMR Spectroscopy for Characterizing Petroleum Sulfonates," SPE no. 6600 presented at SPE-AIME International Symposium on Oilfield and Geothermal Chemistry at La Jolla, CA, June 27-28, 1977.
- 8. W.C. Hsieh and D.O. Shah, "The Effect of Chain Length of Oil and Alcohol as well as Surfactant to Alcohol Ratio on the Solubilization Phase Behavior and Interfacial Tension of Oil/Brine/Surfactant/Alcohol Systems," SPE no. 6594 presented at SPE-AIME International Symposium on Oilfield and Geothermal Chemistry at La Jolla, CA, June 27-28, 1977.
- 9. Improved Oil Recovery Research Program at University of Florida, Gainesville, Semi-annual Report, Dec. 1975.
- 10 Improved Oil Recovery Research Program at University of Florida, Gainesville, Semi-annual Report, June 1976.

- 11. Improved Oil Recovery Research Program at University of Florida, Gainesville, Semi-annual Report, Dec. 1977.
- 12. L.E. Scriven, "Equilibrium Bi-continuous Structure" Nature Vol. 263, p. 123-125, Sept. 2, 1976.
- 13. S.Friberg, I. Lapezynsra and G. Gilliberg, "Microemulsions Containing Nonionic Surfactants," Journal Colloid Interface Science, Vol. 56, No.1, p. 19-32, 1976.
- 14. C.A. Miller, R.N. Hwan, W.J. Benton and T. Fort, Jr., paper submitted to J. Colloid Interface Science (1976).
- 15. J.H. Schulman and T.S. McRoberts, "On the Structure of Transparent Water and Oil Dispersions," Trans. Far. Soc. 42-B- 165-170 (1946).
- 16. J.H. Schulman and D.P. Riley, "X-ray Investigation of the Structure of Transparent Oil-Water Disperse Systems I," J. Coll. Sci. 3, 383-405 (1948).
- 17. J.H. Schulman and J.A. Friend, "Light Scattering Investigation of the Structure of Transparent Oil-Water Disperse Systems II," J. Coll. Sci., 4, 497-509 (1945).
- 18. J.H. Schulman, W. Stoeckenius and L.M. Prince, "Mechanism of Formation and Structure of Microemulsions by Electron Microscopy," Jour. Physical Chemistry, 63, 1677, 1959.
- 19. J.E. Bowcott and J.H. Schulman, "Emulsions" Zetschrift fur Elektrochemie" Band 59, Heft 4,p. 283-290, 1955.
- 20. W. Stoeckenius, J.H. Schulman and L.M. Prince, "The Structure of Myelin Figures and Microemulsions as Observed with the Electron Microscope" Kolloid Zeitshrift, Band 169, Heft 1-2, p. 170-180, 1960.
- W.C. Hsieh and D.O. Shah, "Improved Oil Recovery Research Program," Semi-annual Report, Dec. 1976 University of Florida, p. A-112.
- 22. R.L. Reed and R.N. Healy, "Physico-chemical Aspects of Microemulsion Flooding," <u>Improved Oil Recovery by Surfactant and Polymer Flooding</u>, edited by D.O. Shah and R.S. Schechter, Academic Press, 1977.

- 23. J.C. Melrose and C.F. Brander, "Rule of Capillary Forces in Determining Microscopic Displacement Efficiency for Oil Recovery by Water-Flooding," J. Can. Petr. Tech., 13 (54) 1974.
- 24. W.R. Foster, "A Low Tension Water-Flooding Process" Jour. Pet. Tech. 205 1973.
- 25. J.L. Cayias, R.S. Schechter and W.H. Wade, "The Utilization of Petroleum Sulfonates for Producing Low Interfacial Tensions between Hydrocarbon and Water," Jour. Colloid. Interf. Sci. Vol. 59 No.1 p. 31-38, 1977.

不成成 多大大学 ときいうか

- 26. K.S. Chan and D.O. Shah, "Improved Oil Recovery Research Program,"
 University of Florida, Gainesville, Semi-annual Report, June 1977.
- L. Cash et. al. "The Application of Low Interfacial Tension Scaling Rules to Binary Hydrocarbon Mixtures," Jour. Colloid Interf. Sci., Vol. 59, No. 1 p. 39-44, 1977.
- 28. M. Banere, "Phase Diagram Optimization in Micellar Systems," SPE no. 6500 presented at 51st Annual Fall Technical Conference of SPE at New Orleans, Oct. 3-6, 1976.
- 29. D.F. Boneau and R.L. Clampitt, "A Surfactant System for the Oil-Wet Sandstone of North Burbank Unit," Jour. Pet. Tech. Vol. 29, 501-506 1977.
- 30. J.P. O'Connell and R.J. Brugman, "Thermodynamic Aspects of Interfacial Tension, Micelles, and Microemulsions," Improved Oil Recovery by Surfactant and Polymer Flooding, ed. D.O. Shah and R.S. Schechter, Academic Press, Inc. 1977.
- 31. Improved Oil Recovery Research Program, University of Florida, Gainesville, Semi-annual Report, Dec. 1976.
- 32. D.M. Hinmelblan, "Solubilities of Inert Gases in Water," J. Chem. Engg. Data. 5, 11, 1960.
- 33. B.B. Bensen and D. Krause, "Emperical Laws for Dilute Aqueous Solutions of Monopolar Gases," J. Chem. Phys. 69, 68, 1976.
- 34. H. Reiss, "Scaled Particle Methods in the Statistical Thermodynamics of Fluids," Adv. Chem. Phy. 9, 1, 1965.
- 35. R.A. Pierotti, "The Solubility of Gases in Liquids," Jour. Physical Chem. 67, 1840, 1963.
- 36. F.H. Stillinger, "Structure in Aqueous Solutions of Monopolar Solutes from the Standpoint of Scaled-Particle Theory," J. Solution Chem. 2, 141, 1973.
- 37. R.J. Brugman and J.P. O'Connell, "A Thermodynamic Model for Ionic Micelle Formation," presented at AIChE Meeting, Chicago, IL, Dec. 1976.

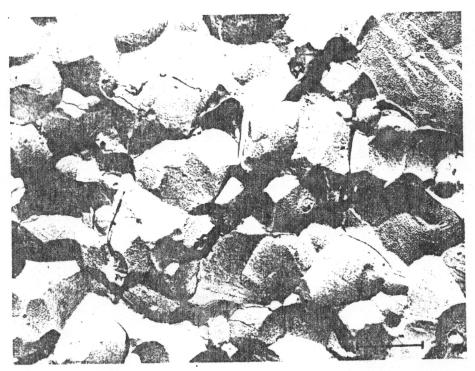


Figure 1. Freeze-etching Electron Micrograph of a Surfactant Formulation (TRS 10-410 + Isobutanol) in 2% NaCl (17,100X)

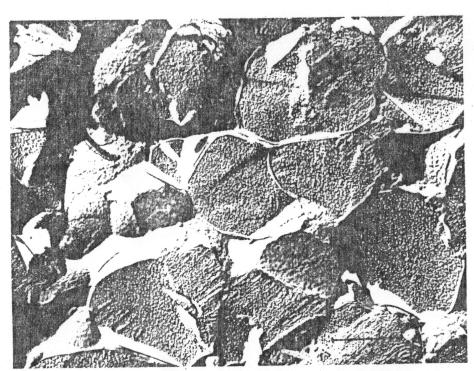
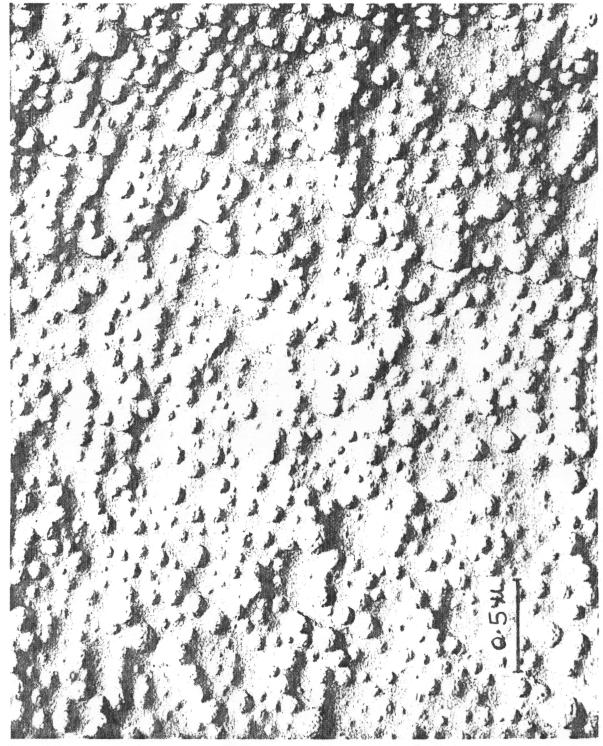


Figure 2. Freeze-etching Electron Micrograph of a Surfactant Formulation (TRS 10-410 + Isobutanol) in 2% NaCl (36,000X)



Freeze-etching Electron Micrograph of Middle Phase Microemulsion of Exxon System at 1.2% NaCl Concentration

OPTIMAL SALINITIES $S_{\overline{\nu}}$ AND $S_{\overline{\rho}}$ OF 5% TRS 10-410 + 3% ISOBUTANOL VS. CHAIN-LENGTH OF OIL

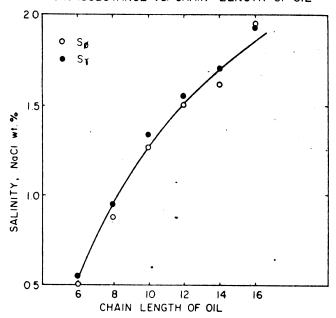


Figure 4. Effect of Chain-Length of Oil on Optimal Salinity Value

THE MOLECULAR MECHANISM FOR THE EFFECT OF SURFACTANT CONCENTRATION

ON INTERFACIAL AND SURFACE TENSIONS

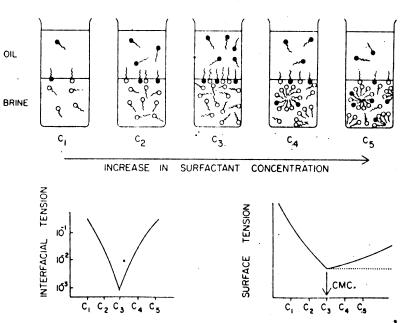


Figure 5. The Molecular Mechanism for the Effect of Surfactant Concentration on Interfacial Tension and Surface Tension

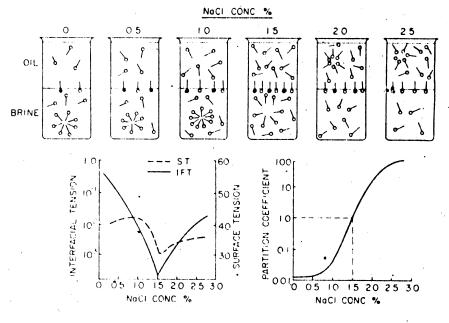


Figure 6. The Effect of Salt Concentration on Interfacial and Surface Tensions

THE EFFECT OF CHAIN-LENGTH OF OIL ON INTERFACIAL AND SURFACE TENSIONS

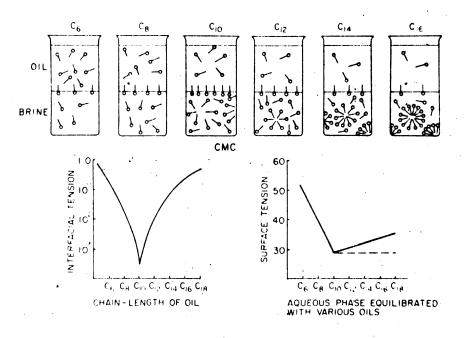


Figure 7. The Effect of Chain-Length of Oil On Interfacial and Surface Tensions

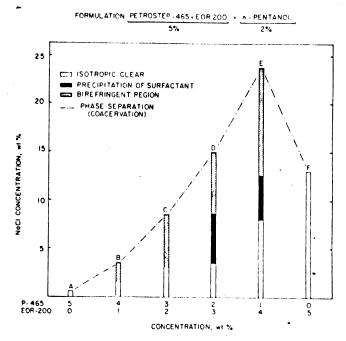


Figure 8. Effect of Ethoxylated Sulfonate on Salt Tolerance of . Petroleum Sulfonate

EFFECT OF NoCI CONCENTRATION ON PERCENT TERTIARY OIL RECOVERY BY 5% TRS 10-410+3% IBA OF n-DODECANE IN SAND PACKS

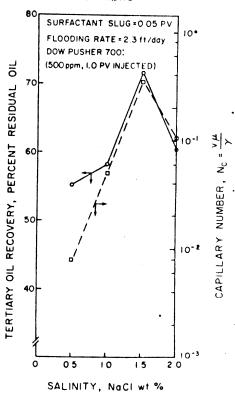


Figure 10. Effect of NaCl Concentration on Percent Tertiary Oil Recovery by 5% TRS 10-410 + 3% IBA of n-Dodecane in Sand Packs

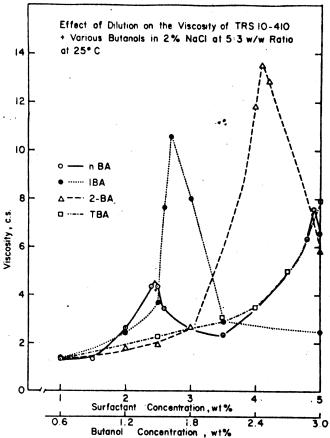


Figure 9. Effect of Dilution on the Viscosity of TRS 10-410 + Varian Butonels in 2% NaCl at 5:3 w/w Ratio at 25°C

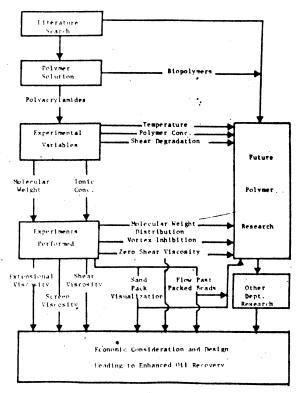


Figure 11. Research Achievements and Goals in Polymer Rheology and Fluids Mechanics

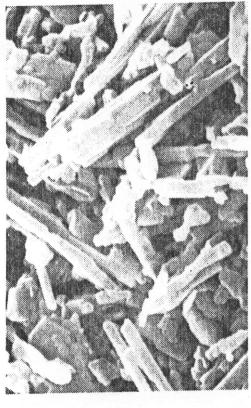


Platelet Stack on Quartz Crystal. 1,400X

Fracture Surface. 150X



Platelets on Quartz Crystals. 11,000X



Rods and Platelets. 22,000X

Figure 12. Scanning Electron Micrographs of Berea Sandstone