

MICROEMULSIONS, LIQUID CRYSTALS AND ENHANCED OIL RECOVERY

by

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INTRODUCTION

The recovery of oil from a reservoir can be divided into three stages. In the primary oil recovery process, oil is recovered due to the pressure of natural gases which force the oil out through production wells. When this pressure is reduced to a point where it is no longer capable of pushing the oil out, water is injected to build up the necessary pressure to force the oil out. This is generally called the secondary oil recovery or water flooding process. The average oil recovery during the primary and secondary stages is about 30 percent of oil-in-place. The purpose of the tertiary oil recovery process is to recover at least part of the remaining 70 percent oil-in-place. Various techniques proposed for this stage are carbon dioxide injection, steam flooding, or surfactant flooding by either micellar or microemulsion solutions. This topic has been recently reviewed by Bansal and Shah (1).

The process of using surfactants for improved oil recovery can be divided into two groups. In the first, a solution containing a low concentration of a surfactant in the form of micellar solution is injected. In the second, the surfactant concentration is relatively high and the injected slug is formulated with three or more components and is known as microemulsion. The basic components of the microemulsion are hydrocarbon, surfactant, water, alcohol and salt. In the second process a relatively small pore volume (about 3 to 20 percent) as compared to the first (15 to 60 percent) is injected. This paper describes various phenomena occurring in both low and high surfactant concentration systems in relation to improved oil recovery.

The micellar solution flooding process is an immiscible-type displacement process. Two basic well configurations--the "five spot" pattern or the "line drive" pattern--are used for the micellar flooding process. In the "five spot" pattern (Figure 1), four production wells are drilled at the corners of a square, and the injection well through which micellar solution is pumped is at the center of this square. In the "line drive" pattern, production and injection wells are drilled in alternate rows. In both cases, the injected micellar solution tends to displace the oil towards the producing wells. Although considerable work has been done on the oil recovery process under both laboratory and field conditions, our basic understanding of the process and

mechanism of oil displacement is far from clear.

MOLECULAR AGGREGATES IN SURFACTANT SOLUTIONS

When a surfactant is dissolved in water, it tends to adsorb at the gas-liquid interface. The adsorption of surfactant at the interface results in a greater concentration at the interface as compared to that in bulk solution. Above a critical concentration, depending upon the structure of surfactant molecules as well as physicochemical conditions, the surfactant molecules form aggregates called micelles (Figure 2). This characteristic concentration is called the critical micelle concentration (CMC). Micelles are spherical aggregates of surfactant molecules containing 20 to 100 molecules. The formation of micelles in aqueous solution creates local nonpolar environments within the aqueous phase. Any oil soluble materials such as dyes, pigments or nonpolar oils can dissolve within the micelles (Figure 2D). Using ionic and nonionic surfactants, one can produce mixed micelles which are often larger in size and in the number of molecules within a micelle (Figure 2C). If a surfactant solution contains a surface active polymer, then a mixed adsorbed film of polymer and surfactant occurs at the interface. The polymer surfactant interaction can also occur at the micellar surface (Figure 2E). The solubilization of oil within micelles can also occur when such micellar solutions are injected into the oil fields.

THE ROLE OF VARIOUS INTERFACIAL PARAMETERS IN A CONCEPTUAL OIL DISPLACEMENT MECHANISM

As we visualize, four interfacial parameters are responsible for enhanced oil recovery by micellar flooding. These parameters are: (1) interfacial tension, (2) interfacial viscosity, (3) interfacial charge, and (4) contact angle. It has been established (2-4) that for the success of tertiary oil recovery process interfacial tension should be of the order of 10^{-3} dynes/cm. Foster (5) explained on the basis of capillary number (N_{ca}) that interfacial tension should be reduced 10,000 times to recover a larger amount of oil. Such low interfacial tensions reduce the work of deformation necessary for oil droplets to emerge from the narrow neck of pores (Figure 3). It is then necessary for these displaced oil droplets, usually referred to as oil ganglia, to coalesce and thereby form an oil bank (Figure 4). For this coalescence to occur, a very low interfacial viscosity is desirable. The moving bank coalesces with more oil ganglia (Figure 5) and causes further displacement of residual oil toward the producing wells. For a hydrodynamically stable system (for mobility control), it is necessary that the micellar solution be followed by a mobility control polymer solution (Figure 6).

The relationship between interfacial charge and interfacial tension has been established for the brine/oil system and it has been found that the electrophoretic mobility and interfacial tension curves are inverse images of each other (6,7). The importance of interfacial charge in the crude oil/aqueous phase system suggests that the nature and magnitude of the charges on solid surfaces are also important variables in determining the efficiency of the oil displacement process. Wagner and Leach (8) and Leach, et al. (19), suggested that reversing wettability of a porous material (from oil-wet to water-wet) during a water flood will result in

DISPLACEMENT OF OIL IN PETROLEUM RESERVOIRS
BY WATER OR CHEMICAL FLOODING (FIVE-SPOT PATTERN)

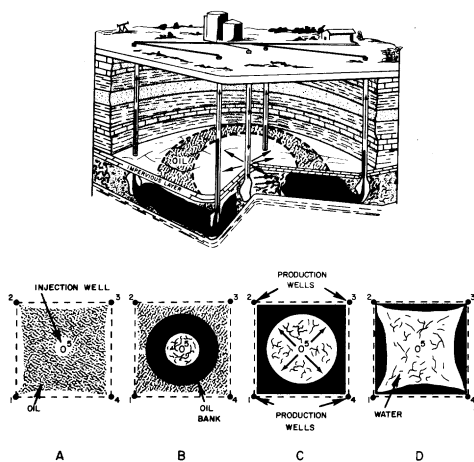


Figure 1. A three-dimensional view of a petroleum reservoir section showing a five-spot pattern for injection and production wells. A, B, C, and D show the injection of water, formation of oil bank, production of oil, and water breakthrough, respectively.

ADSORPTION, MICELLE FORMATION, SOLUBILIZATION
AND INTERACTIONS AT THE MICELLE SURFACE

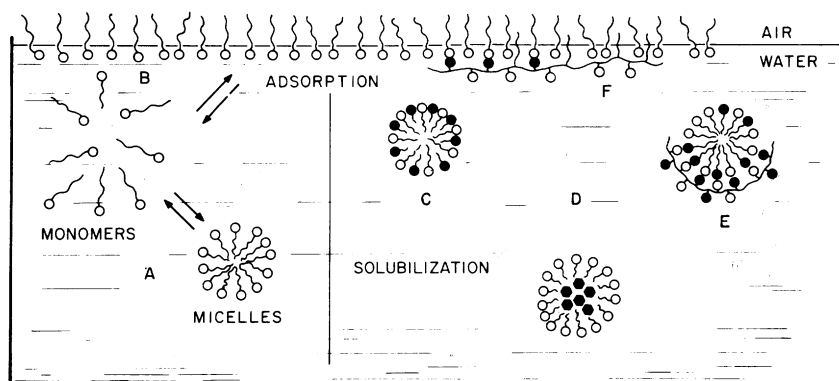


Figure 2. Micelle formation (A), adsorption (B), mixed micelles (C), solubilization (D) and polymer-micelle association (E), and surfactant monolayer-polymer association (F) in aqueous surfactant solution.

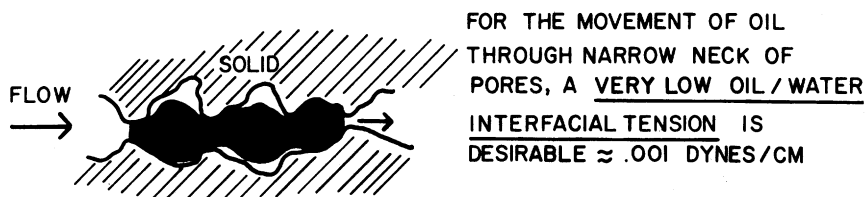
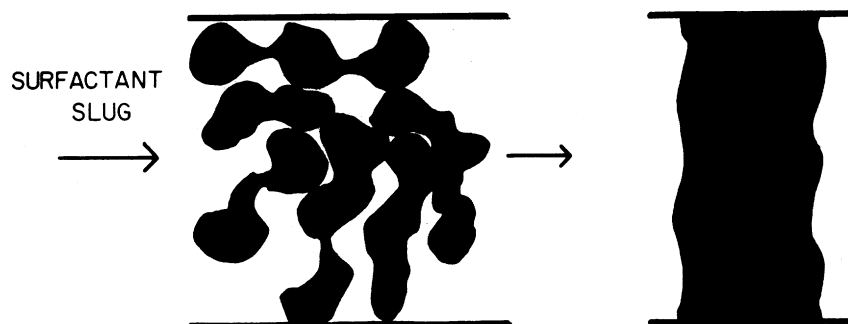
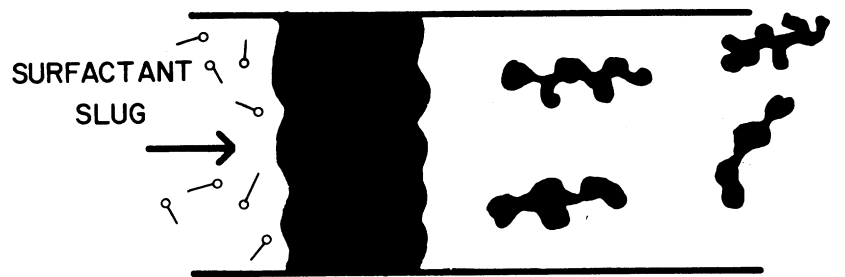


Figure 3. Movement of oil ganglia through a narrow neck of pores; a very low interfacial tension (10^{-3} dynes/cm) is desirable for its displacement in porous media.



DISPLACED OIL GANGLIA MUST COALESCE TO FORM A CONTINUOUS OIL BANK: FOR THIS A VERY LOW INTERFACIAL VISCOSITY IS DESIRABLE

Figure 4. Formation of a continuous oil bank through coalescence of displaced oil ganglia: for this a very low interfacial viscosity is desirable.



**COALESCENCE OF OIL GANGLIA WITH OIL
BANK CAUSES FURTHER DISPLACEMENT OF OIL**

Figure 5. Coalescence of additional oil ganglia with a moving oil bank.

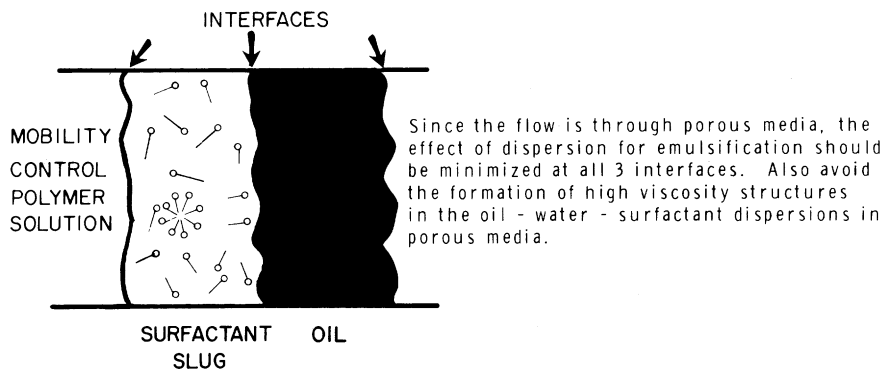


Figure 6. Formation of three interfaces in porous media during tertiary oil recovery by surfactant and polymer flooding.

an increase in oil recovery. With a proper choice of surfactant, one can selectively alter the contact angle (wettability) of oil on solid surfaces (Figure 7), thus creating more favorable conditions for oil displacement. Melrose and Brandner (2) and Morrow (10) concluded that for optimal recovery of residual oil by a low interfacial tension flood, the rock structure should be water-wet. Slattery and Oh (11) suggested that for the most efficient displacement of residual oil, the porous structure should be water-wet. Intermediate wettability may be less desirable than either oil-wet or water-wet behavior.

The success of the above approach for improved oil recovery will depend on the proper choice of chemicals in formulating the optimum micellar slug. The composition of the micellar slug influences the properties of the micellar solution (e.g., viscosity, salt tolerance, temperature stability, etc.).

INTERFACIAL PROPERTIES OF MICELLAR SOLUTIONS

It has been established that for the success of a tertiary oil recovery process, the capillary number (ratio of viscous to interfacial forces) should be in the region of 10^{-2} . During an ordinary water flooding process, the capillary number is of the order 10^{-6} and the residual oil at this capillary number is about 50 percent pore volume. To recover a larger amount of oil, i.e., to minimize the residual oil to near zero, requires a capillary number four orders of magnitude larger than this. In practice, this can be accomplished only by reducing the interfacial tension at the oil/brine interface, which has values of the order of 10 dynes/cm. Reducing this interfacial tension to a value of 10^{-3} dynes/cm will produce a capillary number in the desired range. Recently, studies have been conducted on aqueous solutions of petroleum sulfonate which demonstrate that such low tensions can be obtained with the use of relatively small concentrations of surfactants (5,12-14).

It has been shown (15) that a petroleum sulfonate with an equivalent weight distribution that is relatively narrow and/or symmetrical about the median is the most effective in lowering interfacial tension. A minimum in interfacial tension can also be obtained through an adjustment of the electrolyte content of the aqueous phase. Sodium chloride was shown to be more effective than sodium sulfate, carbonate or tripolyphosphate in increasing the interfacial activity of a petroleum sulfonate. It was pointed out that the production of low interfacial tensions for different types of oils might require different optimum electrolyte concentrations and a different equivalent weight of petroleum sulfonates.

Much of the work done on interfacial tension does not have a systematic approach for evaluating the effect of different variables on the interfacial tension at a micellar solution-oil interface. Recently, however, a systematic study has been performed (16,17) to evaluate the effects of several variables on the interfacial tensions of a homologous series of hydrocarbons. The variables examined were: (1) salt concentration, (2) surfactant concentration, (3) average equivalent weight of petroleum sulfonate, (4) surfactant concentration, and (5) aging.

It has been found (16,17) that, for a given concentration of salt and surfactant, there is a definite affinity for a particular hydrocarbon

and a pronounced minimum in interfacial tension at a particular value of R (number of carbon atoms in the oil). In some cases the interfacial tension of the two adjacent alkanes is one or two orders of magnitude larger than the minimum value. The preferred value of R varies inversely with the surfactant concentration and directly with the salt concentration. It has also been established (17) that production of a low interfacial tension requires an optimal electrolyte concentration for a given surfactant concentration, and an optimal surfactant concentration for a given electrolyte concentration. At a given salinity and surfactant concentration, the value of R corresponding to the minimum tension is the same for alkylbenzenes and alkanes. However, the absolute value of the interfacial tension at the minimum is lower for alkylbenzenes as compared to alkanes. The correlations for surfactant and electrolyte concentrations are basically the same for both the alkylbenzenes and alkanes. However, the minimum tension achieved with the alkanes seems to occur at higher surfactant and salt concentrations than with the alkylbenzenes.

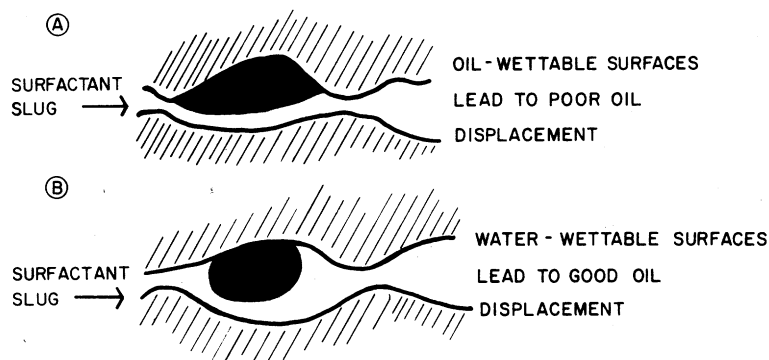
The effect of the equivalent weight of petroleum sulfonate on the position of the minimum has also been studied. The main conclusion reached was that as the equivalent weight of the surfactant increases, the preferred value of R (corresponding to the interfacial tension minimum) also increases. The mechanisms responsible for this shift have not been identified, but prediction of the direction of the shift of the minimum by a mixture of two surfactants is possible if the general trends of each surfactant on a homologous series is established. It has also been found that the ammonium ion shifts the minimum to higher values of R for alkanes. As the molecular weight of the cation is increased, the minimum tension is again shifted to larger R values. As has been discussed, such a shift is also characteristic of an increase in the surfactant equivalent weight. This suggests a strong association and formation of ion pairs between the cation and surfactant (17).

The effect of different alcohols on the value of R at the tension minimum has also been investigated (17). It was found that an increase in the molecular weight of the alcohol shifted the tension minimum to larger values of R . Changes in interfacial tension with time has also been investigated and the "aging" effect has been observed both in the presence and absence of co-surfactants (alcohols). The interfacial tension measured against a variety of hydrocarbons tends to change with time. The direction of change is most often toward higher interfacial tension, the magnitude of these changes being dependent on the surfactant concentration and the alcohols used as cosolvents.

A CORRELATION OF INTERFACIAL TENSION WITH ELECTROPHORETIC MOBILITY

The salt or surfactant concentration in a micellar solution is one of the most important and effective variables in manipulating the interfacial tension between the micellar solution and oil, although the molecular mechanism of this process is not elucidated. It is known that the salt concentration in a micellar solution affects both the interfacial charge and micellar size. In our laboratory, the relationship between interfacial charge and interfacial tension (7,18) has been studied extensively by measurements of the interfacial tensions and electrophoretic mobilities of various systems. It has been established

WETTABILITY, CONTACT ANGLE, AND OIL DISPLACEMENT



PROPER CHOICE OF SURFACTANT CAN CHANGE (A) TO (B)

Figure 7. Effect of rock-wettability on oil displacement.

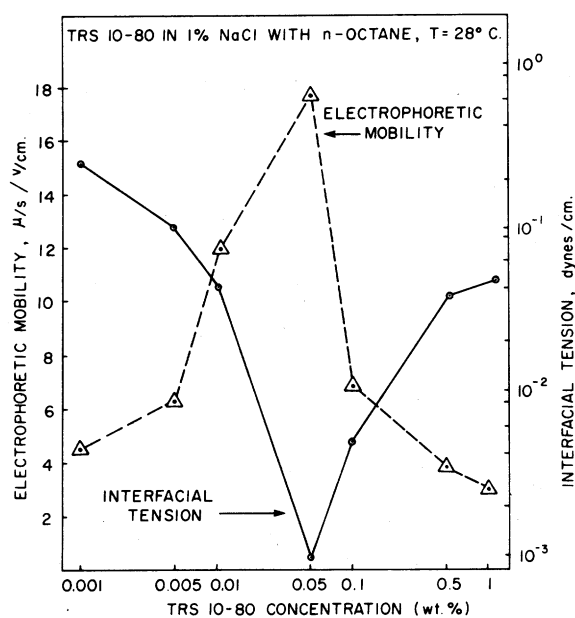


Figure 8. Effect of surfactant concentration on interfacial tension and electrophoretic mobility of oil droplets.

for the brine/oil system that the electrophoretic mobility and interfacial tension curves are inverse images of each other. The micellar system used for these measurements consisted of TRS-10-80 (surfactant) + 1% NaCl + n-octane (oil) and the results obtained are shown in Figure 8. The results of interfacial tension measurements obtained by Chan and Shah (18) are in agreement with those reported by Cash, et al. (16). The above system exhibits an unusual minimum in interfacial tension at 0.05% TRS-10-80. At the same concentration, the electrophoretic mobility exhibits a striking maximum. From the results reported previously (7,18), it is clear that the electrophoretic mobility, which is an indirect measurement of interfacial charge density, has a strong correlation with the interfacial tension for the oil/brine or oil/surfactant solution system. These results also demonstrate that the electrophoretic mobility and interfacial tension curves are almost inverse images of each other. We have shown (19) a similar correlation between interfacial tension and electrophoretic mobility for various crude oils in the presence of NaOH solutions. These results indicate that perhaps a detailed study of the electrochemistry of the oil/water interface in the presence of a surfactant may provide a better insight into how the ultra-low interfacial tension is achieved.

We believe that a greater emphasis on interfacial charge as compared to interfacial tension is highly desirable. If one considers only the ultra-low interfacial tension in the oil displacement process, then the nature of the charge on the solid surfaces (rocks, minerals and clays) is of no consequence. However, if one considers the interfacial charge at the crude oil/surfactant formulation interface, then the nature and magnitude of the charges on the solid surfaces become extremely important in determining the efficiency of the oil displacement process.

MICROSTRUCTURE OF A SURFACTANT FORMULATION USING FREEZE-ETCHING ELECTRONMICROSCOPY

Our results on the microstructure of a birefringent surfactant solution are shown in Figures 9-11. Figure 9 shows the electronmicrograph of TRS 10-410 (5%) + IBA (3%) formulation in 2% NaCl at 17,100 magnification. Figure 10 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 glass plates. 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 10 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 (Figure 11) that the membranes are made up of several bilayers of surfactant molecules. It is evident 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" (20,21) 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 relatively

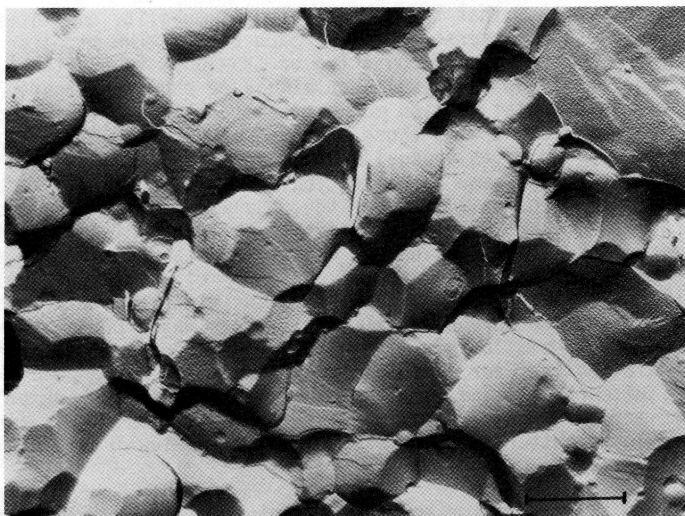


Figure 9. The freeze-fracture electronmicrograph of a surfactant formulation consisting of 5% TRS 10-410 + 3% isobutanol in 2% NaCl brine (17,100X, Bar = 2 microns).

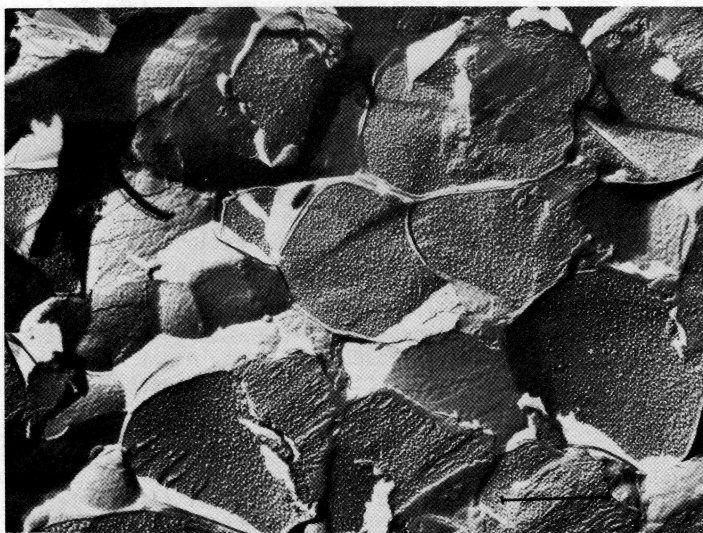


Figure 10. The freeze-fracture electronmicrograph of a surfactant formulation shown in Figure 9, fractured at a different angle (36,000X, Bar = 1 micron).

low viscosity (20,21).

THE EFFECT OF OIL CHAIN-LENGTH ON OPTIMAL SALINITY

Since different crude oils can be considered as oils of 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_Y) 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 (22) are shown in Figure 12. It is evident from Figure 12 that as the chain length of the oil increases, the optimal salinity value (S_Y or S_ϕ) also increases. The values of S_Y and S_ϕ are very close to each other for these oils. This observation is very similar to the observations of Reed and Healy (23) for values of S_Y 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. Hsieh and Shah (22) have reported the effect of various alcohols and the surfactant/alcohol ratio on the optimal salinity and the volume fraction of the middle phase microemulsion for a petroleum sulfonate formulation.

THE STRUCTURE AND COMPOSITION OF THE MIDDLE PHASE MICROEMULSIONS

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 microemulsion 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 (24) has proposed that the middle phase may be bicontinuous, with a continuous surfactant layer separating water and oil. The surfactant layer divides the volume into two multiply connected, interpenetrating subvolumes, each of which is physically continuous. Friberg, et al. (25) proposed a structure for the middle phase as a mixture of spherical aggregates and planar surfactant layers. Miller, et al. (26) also stated that the ultra-low interfacial tension can be produced when a micellar solution separates into a micelle-rich and a micelle-lean phase.

Based upon the many similarities between the physicochemical properties of the middle phase microemulsions and that of microemulsions described by Schulman and his co-workers (27-32), the structure of the middle phase was proposed by Hsieh and Shah (33) and Hsieh (36) to be a water external microemulsion with swollen micelles or their aggregates suspended in a continuous aqueous phase. The conclusion that water is



Figure 11. The freeze-fracture electronmicrograph of the surfactant formulation shown in Figure 9 at 60,000X magnification. The right hand side portion of the micrograph clearly indicate the multilayer structure for the lamelle surrounding the compartments or cells (Bar = 0.5 micron).

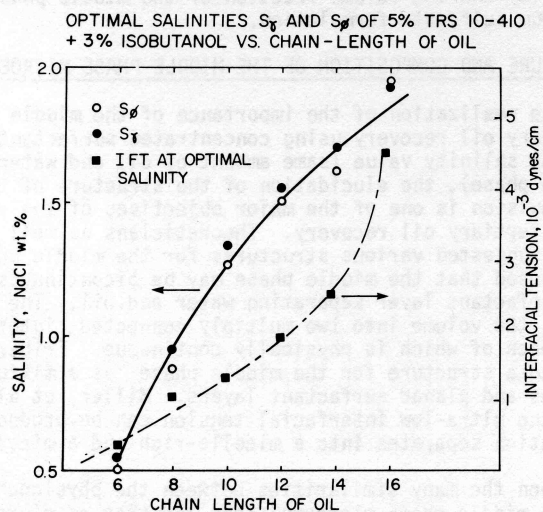


Figure 12. The effect of alkane (oil) chain length on the optimal salinity of the formulation 5% TRS 10-410 + 3% isobutanol. The interfacial tension at the corresponding optimal salinity for each alkane is also shown.

the external phase was based on the low electrical resistance of the middle phase and several other experimental observations (34).

Figure 13 schematically illustrates our proposed mechanism for the formation of the middle phase microemulsion. The formation of the middle phase microemulsion upon increasing salinity can be explained as follows. At low salinity, the oil phase is in equilibrium with the aqueous surfactant phase. The aqueous phase contains surfactant micelles with solubilized oil. As the salinity increases, the following phenomena are expected to occur.

- (1) The size of the micelles increases due to the increase in the amount of solubilized oil. This is presumably related to the increased micellar size upon addition of electrolytes.
- (2) With increasing salinity, the surfactant and oil present in the brine phase exhibit a greater tendency to come out of the aqueous phase due to "salting out" effect.
- (3) The electrical repulsion between the swollen micelles decreases due to the neutralization of the surface charges and the compression of the electrical double layer around these micelles. Hence, the droplets can approach each other more closely through the van der Waals attractive force between them.
- (4) The buoyancy force on the swollen micelles increases with increase in salinity due to the following factors: (a) a decrease in overall density of micelles due to further solubilization of oil, (b) increase in size of micelles due to further solubilization of oil, (c) increase in the density of brine with increase in salinity.

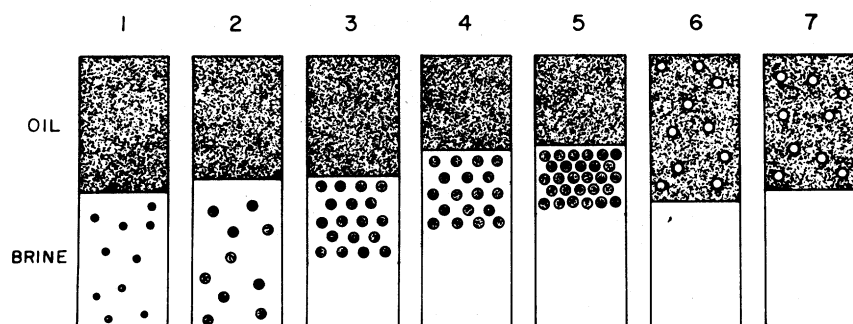
The combination of these effects drives the swollen micelles out of the bulk brine phase. And, consequently, a new phase containing swollen micelles is formed and separated from the brine phase. This phenomenon is similar to coacervate phase formation in a surfactant solution. It is known that many surfactant solutions upon addition of salts or a change in temperature, pH, etc., separate into a two phase system. One phase (coacervate phase) is surfactant-rich and the other phase is surfactant-lean. The external phase in the coacervate system is brine as suggested by the electrical conductance measurements (34). We believe that the main difference between the coacervate phase in a surfactant solution and the middle phase microemulsion in the oil/brine/surfactant system is that the latter contains excess oil phase, and therefore the micelles in the middle phase will be swollen with oil.

As illustrated in Figure 13, we believe that there is a distinct oil/water interface between oil and the middle phase microemulsion whereas between the middle phase microemulsion and the brine, there is no such discontinuity, and the brine is structurally continuous in the entire middle phase.

Figure 14 shows the freeze-fracture electron micrograph of the middle phase microemulsion (35) in the surfactant system reported by Reed and Healy (23). The system illustrated in Figure 14 consists of 4%

PHYSICAL SEPARATIONS

- ⊙ oil swollen micelles (microdroplets of oil)
- reverse micelles (microdroplets of water)



Schematic Representation of the Effect of Salinity on the Behavior of TRS-10-410/Isobutanol/Oil/Brine System

Figure 13. A proposed mechanism for the formation of the middle phase microemulsion upon increasing the salt concentration in the oil/brine/surfactant/alcohol systems.

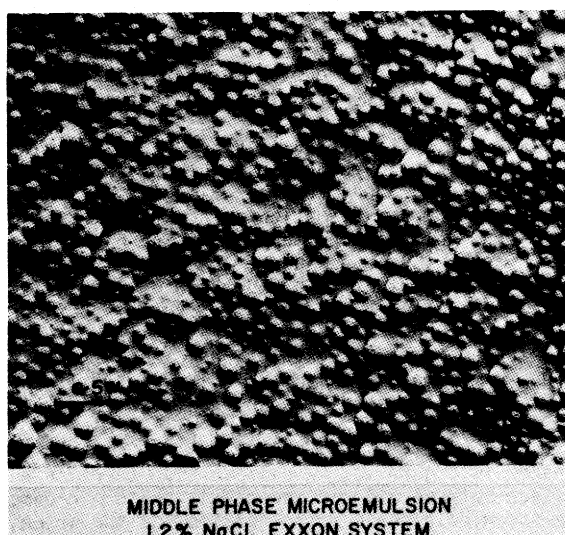


Figure 14. The freeze-fracture electronmicrograph of the middle phase microemulsion. The composition of the system given in the text (Bar = 0.5 micron).

TABLE I

Composition of the Middle Phase after Equilibration
of 5% TRS 10-410 plus 3% Isobutanol Formulation
with Equal Volume of Various Hydrocarbon Oils

Oil Chain Length	Salinity wt. %	Volume fraction of Middle Phase, %	Composition (moles)	
			TRS 10-410: Isobutanol: Oil: Water	
C ₆	0.50	46	1 : 2.85 : 43.9	: 336
C ₈	0.75	41.3	1 : 2.63 : 40	: 224
C ₈	0.875	34.7	1 : 2.36 : 38.8	: 131
C ₁₀	1.125	36	1 : 2.06 : 31.4	: 159
C ₁₀	1.25	32	1 : 2.03 : 30.5	: 110
C ₁₂	1.50	28	1 : 1.88 : 19.6	: 130
C ₁₂	1.50	28	1 : 1.85 : 17	: 156
C ₁₄	1.75	21.3	1 : 1.60 : 7.9	: 154
C ₁₆	2.00	19	1 : 1.40 : 7.4	: 154

Emulsifier (monoethanolamine Dodecyl orthoxylene sulfonate + tertiary amyl alcohol, 2/1 v/v) + 48% oil (Isoper M/HAN, 9/1 v/v) + 48% Brine (1.2% NaCl in D₂O). The system was made in D₂O in order to study it by NMR spectroscopy. Interestingly, the optimal salinity shifts to a lower value (from 1.6 in H₂O brine to 1.2 in D₂O brine) if one substitutes D₂O for H₂O. This is consistent with the idea that buoyancy is one of the factors influencing the phase separation of swollen micelles.

Using NMR spectroscopy, we determined the concentration of alcohol (isobutanol) in the middle phase microemulsion. From UV absorption measurements, the surfactant concentration was determined. From volume measurements of excess oil and brine phases, the volume of oil and brine in the middle phase microemulsion was determined. Table I shows the composition of the middle phase microemulsions at or near optimal salinity for systems containing various oils from C₆ to C₁₆. The molar ratio of each component with respect to surfactant is given in Table I (22). At corresponding optimal salinities, the middle phase microemulsion containing n-hexane has about 3, 44 and 366 alcohol, oil and water molecules per surfactant molecule whereas the middle phase microemulsion containing hexadecane has the corresponding number of molecules of about 1, 7 and 154. Therefore, as the oil chain length is increased, the number of moles of alcohol, oil and water per mole of surfactant in the middle phase decreases (36). This is consistent with the observation that the volume of the middle phase decreases as the chain length of oil increases.

FOOTNOTES

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ACKNOWLEDGMENTS

The authors wish to express their sincere thanks to the Department of Energy (Grant No. EY-77-S-05-5341) and the consortium of twenty-one major oil and chemical companies for their generous support of the Improved Oil Recovery Research Program at the University of Florida. The authors acknowledge the assistance of Professor David Deamer of University of California at Davis for freeze-fracture electron microscopy of the middle phase microemulsions and that of Dr. K.S. Chan for the electrophoretic mobility results presented in this paper.

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