SOME PHYSICOCHEMICAL ASPECTS OF MICROEMULSION FLOODING: A REVIEW

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I. ABSTRACT

Injection compositions for a variety of microemulsion and surfactant floods can be represented on equilibrium ternary diagrams with coordinates surfactant-cosolvent, brine, and oil. That portion of such a diagram having economic significance, divides into a single-phase region and a multiphase region. Within the single-phase region, micellar structure is studied in relation to effects of salinity and cosolvent on viscosity, optical birefringence and electrical resistivity. Within the multiphase region, effects on phase behavior, interfacial tension and solubilization parameter are determined as functions of salinity, brine composition, temperature, surfactant structure, cosolvent, and oil aromaticity. Correlations are found between interfacial tension and solubilization parameter that are useful in preliminary screening of surfactants for oil recovery potential. When, by any means, extent of the multi-phase region is reduced, a circumstance favorable to displacement in the miscible mode; a concomitant effect is that interfacial tensions are also reduced, favoring displacement in the immiscible mode.

II. INTRODUCTION

Oil remaining within the interstices of porous rock in the regions contacted by a waterflood can exist in a variety of configurations, determined by wettability that may vary from completely water-wet to preferentially oil-wet. At least in the preferentially water-wet case, this oil is discontinuous. Since capillarity is responsible for resistance to further displacement, a large reduction of interfacial tension may be the only practical way to recover additional oil. One method of achieving this is through injection of surface-active chemicals, a procedure technically feasible for application to reservoirs in any wettability state; however, our attention will primarily focus on the preferentially water-wet case.

Regardless of specific formulations injected, once within a reservoir the fluid system has three primary constituents: oil, water and surfactant; so it becomes useful to represent compositions on a ternary diagram.
Also, functions of composition can be so represented, as, for example, micellar structure, interfacial tension, and dilution paths. Since the ternary diagram divides into miscible and immiscible regions, a corresponding dichotomy of flooding regimes can be expected, and does, in fact, occur.

Accordingly, this chapter commences with discussion of the occurrence of residual oil and the phenomena responsible for its displacement by fluids containing surface-active agents (Section III). The next two sections review a sequence of four papers dealing with the miscible (Section IV) and immiscible (Section V) aspects of microemulsion flooding (1-4).

One goal of this work has been to develop screening procedures that identify the member of a family of surfactants preferred for a given application (i.e., a given temperature, brine composition and crude oil), primarily through simple "test-tube" experiments that collectively serve as a guide to reduce the number of long-core floods required. Emphasis here is on alteration of hydrophile-brine and lipophile-oil interactions through variation of surfactant and cosolvent structural parameters, salinity and temperature. Others (5) have emphasized the oil-lipophile interaction and show how to select the best hydrocarbon for a given surfactant, brine and temperature.

Although these advances have obvious utility, they pre-suppose a set of surfactants possessing parameterized functionality. In the event none of these surfactants is sufficiently good, there exists no theory or empiricism for construction of new surfactants with improved functionality to serve a specified purpose.

III. DISPLACEMENT OF RESIDUAL OIL

Oil, saline water and gas occur naturally within, for example, sandstone porous media usually consolidated with a variety of cementing materials deposited over long periods of time (6); often in configurations where water preferentially wets the rock, gas does not, and oil plays an intermediate role. With this model, it is evident that water will fill the smallest pores and gas the largest (7). If no gas is present, oil will fill the largest pores, but will, nonetheless, occupy a distribution of pore sizes, depending on wettability of the oil-water-rock system and on rock lithology. In case of extensive cementation of sand grains, the porous medium resembles a bundle of interwoven and intersecting tubes having bulges and constrictions, rather than the more easily visualized and popular but often misleading random or ordered packed beds of spheres or unconsolidated sands of narrow size distributions.
Waterflooding is a widely used secondary recovery technique wherein water is injected into the porous rock, thereby displacing all of the resident brine (8) and part of the oil in the contacted regions. If the rock-oil-water system is preferentially water-wet, the oil that remains is in the form of discontinuous globules or ganglia surrounded by rock and isolated by water (9, 10). This oil is trapped by capillarity and is referred to as residual oil.

It is generally recognized that during the waterflooding process, water and oil flow simultaneously but through separate porous networks (11), so it is not expected to find both water and oil within a single capillary; except, perhaps, where one phase is adsorbed on rock to the extent of a few molecular layers, or within minute crevices (7) where it was trapped by invading oil during a past displacement event. It follows that pores where residual oil occurs do not contain water to any significant extent. A scanning electron micrograph of residual oil ganglia appears in Figure 1. Impressions of the irregular confining rock on the ganglion surface are clear and augment evidence that water is substantially excluded.

Formation of residual oil ganglia during the waterflooding process is dependent on pressure gradient (12), oil-water interfacial tension (12), pore geometry (13), and possibly, on interfacial film properties (14). As water invades the porous rock, an oil-water transition zone is created where increasing water saturation causes rupture of the continuous oil filaments. It follows that points of rupture, and hence pore constrictions adjacent principal ganglion terminii, must communicate directly with water-saturated flow channels (see Figure 2). The essential problem of tertiary oil recovery is to replace water flowing through pores adjacent to the trapped ganglia with a different fluid that will interact with the oil, cause part of it to be displaced and subsequently coalesce with other similarly displaced oil or with other trapped ganglia, thus causing them to flow as well. In this way a continuous oil bank is created, caused to flow, and can be recovered.

A. Role of Interfacial Tension

The simplest model of trapped oil consistent with the above discussion is illustrated in Figure 3. Water flowing through adjacent and communicating capillaries establishes a pressure gradient across the trapped drop. The drop moves in the direction closest to the gradient direction, subject to pore wall constraints, until a pore constriction is met that is too small to permit further advance.

For simplicity, assume the oil-water-rock system is completely water-wet, advancing and receding contact angles, $\theta_2$ and $\theta_1$ respectively, are zero, interfacial tension is the same at all oil-water interfaces, and capillaries are sufficiently small that these interfaces are spherical.
Fig. 1. Electrosan micrograph of a residual "oil" ganglion. A Berea sandstone core was saturated with water and paraffin at elevated temperature and water flooded to the residual state. The entire core was then quick-frozen in liquid N₂ and the sandstone matrix was subsequently dissolved in HF. (Technique developed by J. J. Taber; these ganglia prepared by R. A. Humphrey.)
Fig. 2. Approximate configuration of trapped oil ganglion, showing exclusion of water and accessibility of water to ganglion terminii

Fig. 3. Model of an elementary oil ganglion trapped by capillarity and a pore constriction
Laplace’s Equation can then be used to calculate the pressure decrement, or capillary pressure, \( P_c \), across the curved interface, i.e., with reference to Figure 3:

\[
p_{c1} = p_o - p_{w1} \approx \frac{2\gamma}{r_1}
\]

and

\[
p_{c2} = p_o - p_{w2} \approx \frac{2\gamma}{r_2}
\]

It follows that a pressure difference in excess of

\[
\Delta P = p_{w2} - p_{w1} \approx 2\gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right)
\]

(1)

will be required to exceed the capillary force retaining the drop, and cause it to flow (15,16).

It is instructive to calculate the pressure gradient necessary to move the drop shown in Figure 1, using a typical oil-water interfacial tension of 30 dyne/cm, \( r_1 = 9 \times 10^{-5} \) cm, \( r_2 = 4 \times 10^{-3} \) cm, and the drop length = 4 x 10^{-2} cm, all dimensions estimated from the largest drop in the electroscan micro-graph. The result is the aqueous phase must develop \( \sim 573 \) psi/ft to displace this residual oil ganglion, whereas a practical limit achievable in real field situations is two orders of magnitude less, about 1-2 psi/ft (2, 17). Consequently, an interfacial tension reduction to about 0.1 dyne/cm is needed for incipient residual oil production. *Substantial oil production may require less than 0.01 dyne/cm.*

B. Capillary Number

It follows that for a system of length \( L \), a critical value of pressure drop across that length must be exceeded before residual oil can be displaced. More generally, Taber (16) showed there is a critical value of \( \Delta P/L\gamma \) for each porous medium, and these critical values increase with decreasing permeability (18). Two consequences are that, in a preferentially water-wet system, all of the residual oil can be recovered by waterflooding at a sufficiently high pressure gradient; and no matter how low a non-zero inter-facial tension may be, there is always a positive gradient sufficiently small that no oil is displaced.

\( \Delta P/L\gamma \) can be made dimensionless by including \( K \), the effective permeability to the displacing phase, and in other ways (12, 19-21). In fact, many pertinent groups can be obtained through dimensional analysis.

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* Definitions of terms can be found in "Nomenclature".
Among these are
\[ \frac{(\Delta P/L)K}{\gamma}, \frac{|v| \mu}{\gamma}, \text{ and } \cos \theta; \]

where \( \Delta P/L \) is the pressure gradient measured over the finite length \( L \) at the displacement front, and \( |v| \) is the magnitude of the average displacing phase velocity there. Although the first and second groups are equivalent in the case of steady flow, so that the integral form of Darcy's law obtains, the first and third are phenomenologically related to the displacement process; and hence we prefer to define the capillary number as

\[ N_c = \frac{(\Delta P/L)K}{\gamma \cos \theta}. \]

Caution must be exercised in judging which of two floods has the larger value of \( N_c \). Thus, in Figure 4, flood (a) has the larger value if \( N_c \) is calculated for the total core length whereas flood (b) has the larger value if \( N_c \) is calculated, as it should be, over the displacement front, other variables being the same.

\[ \text{Fig. 4. Simplified pressure vs distance functions for two core floods of differing character} \]

Adsorption must also be considered. If adsorption is significantly different for two floods, capillary number effects may be obscured.

A practical observation is: a necessary but not sufficient scaling criterion is that laboratory velocities and pressure gradients must be comparable in magnitude to those expected in the reservoir, presuming invariance of rock and resident fluids.
C. Oil Bank

In the case of anionic surfactants, once residual ganglia are effectively mobilized, a continuous oil bank is observed to form ahead of the flood front and flows at an oil saturation that depends primarily on the ultimate saturations and the fractional flow curve for the resident oil-brine-rock system (22, 23). Although details of the mechanism of oil bank formation are unknown, once formed, the oil bank gathers up residual ganglia at its front, continually extending its length. This coalescence of disjoint ganglia apparently requires establishing a temporal oil saturation considerably in excess of the residual oil saturation, which may account for the spike in fractional oil flow often observed at the leading edge of the oil bank. Fortunately, criteria for mobilizing residual ganglia are sufficient to maintain and propagate an oil bank; however, the converse is not true (24).

From the onset of oil bank formation, the function of the surfactant is to maintain continuity of the flowing oil filaments to as low a saturation as possible before they rupture and are irretrievably trapped.

Since the ultimate residual saturation is established within an interfacially active environment, oil remaining behind may contain surfactant (2, 25), and this loss, in addition to that lost through adsorption, contributes to total surfactant retention.

D. Polymer Bank

Since economics severely limits the total quantity of surfactant that can be injected, it is necessary to displace a surfactant containing bank with a much less expensive fluid. Ordinary brine is precluded in view of mobility considerations; i.e., integrity of the surfactant bank requires that the mobility, $K/\mu$, of each bank be less than that of its predecessor (26). This is usually achieved by displacing the surfactant bank with water containing a high molecular weight polymer at low concentration. This provides the necessary mobility reduction through increase in viscosity, $\mu$, and decrease in effective permeability, $K$. Although a variety of polymers are available, all we have studied suffer from one or more of the following: mechanical (27, 28), chemical (29), thermal (30), or bacterial (31) degradation, injection face plugging (32, 33), excessive adsorption or entrapment (34), excessive inaccessible pore volume (35, 36), or undesirable phase behavior when mixed with surfactants (2, 37). Suffice it to say there is need for considerable improvement in polymers for use in oil recovery.
E. Total Flooding System  Oil saturation, \( S_o \), for the total flooding system is graphed in Figure 5 and the various banks identified. Often

![Figure 5](image_url)

*Fig. 5. Oil saturation is graphed as a function of distance from the injection point, and the various banks and characteristic regions identified*

A preflush is used to condition the reservoir and provide an environment more nearly optimal for the surfactant system that follows. However, it must be remarked that, in view of heterogeneity, changes in conformance attendant mobility reduction of successive banks, and uncertainties regarding ion exchange between injected chemicals and interstitial clays; it has not been established that a preflush is a practical way to substantially and sufficiently reduce total salinity (38-43).

In this chapter attention will be confined primarily to phase behavior, micellar structure, interfacial tension and optimal properties of the surfactant bank, where the surfactant is contained in a microemulsion.

F. Ternary Diagram

There are a variety of interfacially active liquids that will displace residual oil from a porous medium. Independent of what type of surfactant system is injected, once within the porous medium, the liquid system can be considered composed of three components: oil, water and surfactant. The "oil" can be a pure hydrocarbon or as complex as a crude oil; the "water" can vary from fresh water to an oilfield brine containing a dozen or so different ions, and it may additionally contain chemicals injected in a preflush; and the "surfactant" can be a pure compound, a distribution of homologues (3), a petroleum sulfonate (45-48), etc., and include cosurfactants such as ethoxylated alcohols (49, 50), sulfated ethoxylated alcohols (51,52), etc., and cosolvents such as alcohols, ethers, glycols, etc. The variety is endless, but properties of all of these can be usefully represented as functions on a pseudo-ternary diagram (53) such as shown in Figure 6.
The dashed line is an upper bound for injection compositions having economic significance; and, therefore, surfactant concentrations in excess of about 15% are, for the most part, of no interest in relation to tertiary oil recovery.

The binodal curve divides the diagram into a single-phase region above, and a multiphase region below. Although micellar structure varies, no interfaces can be observed when following any path lying entirely within the single phase (miscible) region or along the binodal curve. In the multi-phase region there are always at least two phases, commonly three, and on one occasion seven phases were observed in equilibrium.

Shading along the coordinate axes distinguishes areas where concentrations of one or two components are so low the fluid takes on a different character in some respect. On the bottom there is, in some circumstances, a change in character of phase behavior and there is the question of achieving a CMC. On the left or right sides there may be insufficient oil or water, respectively, to stabilize the system. Phase behavior in these areas has not yet been studied in detail. However, see Reference 54 in regard to the region of low surfactant concentration.
G. Types of Floods

Examples of injection compositions for all reported surfactant flooding systems are indicated by the letters A, M, S and I in Figure 6.

_Aqueous surfactant flooding_ (55, 56) (A), the oldest of these processes, has no oil in the material injected except for that unreacted and not separated from the surfactant during manufacture. _Conventional microemulsion floods_ (57, 58) (M), variously called _micellar_ (23), _miscible-type_ (59), _Maraflood_ (60,61) and _high concentration_ (62), may have an injection composition anywhere considerably above the binodal curve and away from the shaded areas. Usually, _soluble oil floods_ (63, 64) (S), comprise a substantially anhydrous composition, high in surfactant content. _Uniflooding_ (65) includes floods of type S, but may also involve injection compositions that include a significant quantity of water (47), in which case they would be indistinguishable from floods of type M. _Immiscible microemulsion flooding_ (4,66) (I) refers to any injection composition on or in the neighborhood of a binodal curve. In this chapter, only microemulsions such as those designated I or M will be considered.

_Idealized_ paths for flooding compositions at the front and rear of a surfactant bank can be constructed on a ternary diagram. Thus, if the phase diagram has the character illustrated in Figure 7, and the composition injected is X, then the overall composition at the front of the surfactant bank will follow the dilution path XOB, where OB is the composition of the oil bank. The displacement will be locally miscible (2) along XC and immiscible along COB. In view of tie line behavior the separate phases are oil and a sequence of micro-emulsions along CW, as shown. At the back of the surfactant bank, displacement will be locally miscible everywhere along the dilution path XW. A great variety of other path configurations obtain as phase behavior and injection compositions change.

_Two criteria for a microemulsion composition of type M to effectively recover oil are now evident: The multiphase region should be minimal so as to prolong locally miscible displacement, and interfacial tensions in the multiphase region should be low so as to enhance immiscible displacement (1, 2)._ 

IV. MICROEMULSIONS: THE SINGLE-PHASE REGION

As remarked earlier in connection with Figure 6, emphasis will be placed on compositional points above and below the binodal curve but excluding the shaded regions. In this section we will study some properties of the miscible region above the binodal curve.
Any injection composition within the miscible region has the advantage of locally miscible displacement until dilution causes the bank to deteriorate into multiphases. During the locally miscible regime 100% of the residual oil can be recovered, even at very low flooding rates (2).

A. Definition

The term "microemulsion" is a misnomer, as pointed out by Winsor (67) and others (68, 69), but is in common use and will be retained. In the chemical literature various authors have pointed out attributes they felt a fluid must have in order to qualify as a microemulsion. For example, in addition to oil, water and surfactant, a microemulsion has been required to be transparent (70-72), thermodynamically stable (73), has almost always included a cosolvent (an alcohol, for example); and salt has been specified as essential to existence of an upper-phase microemulsion in equilibrium with an aqueous phase (74). However, in spite of these qualifications, no concise definition of a microemulsion was found. The authors introduced the definition that a microemulsion is a stable, translucent, micellar-solution of oil, water that may contain electrolytes, and one or more amphiphilic compounds. Accordingly, a microemulsion need not be transparent, is not an emulsion (macroemulsion), and is not required to contain salts, cosolvents or cosurfactants.
Winsor (67) points out that certain non-transparent but translucent and often opalescent micellar solutions are stable. Further, we have found that many of the most interfacially active micellar solutions have these characteristics and have maintained them for two years. The degree of translucency is merely a measure of average micelle size and configuration and can be caused to vary continuously from completely transparent to nearly opaque simply by varying, for example, salinity. Although inclusion of the constraint that a microemulsion must be transparent is a matter of choice, it excludes the preponderance of systems that have utility for tertiary oil recovery. It is an experimental fact that when compositions lead to opaque fluids, these fluids are usually unstable, separate on standing and hence were macroemulsions; so translucency is an essential aspect.

The proposed definition requires a micellar-solution, and this will survive, but the notion of a micelle has become broader with time and study. Thus, according to Winsor (67), there were initially but three kinds: spherical water-external (Hartley micelles), spherical oil-external, and lamellar, all shown in dynamic equilibrium in Figure 8.

![Fig. 8. Winsor's concept of intermicellar equilibrium between spherical and lamellar micellar structures. “It should be (re-) emphasized that the conception of intermicellar equilibrium does not mean that perfect $S_1$, $S_2$, and $G$ micellar forms are present in equilibrium, but rather that a fluctuating micellar form may be regarded as resolved into $S_1$ and $S_2$ forms in equilibrium with $G$ micelles.”... Winsor (67), p. 56](image-url)
Later Winsor (75) revised and expanded his intermicellar equilibrium concept to include spherical micelles in cubical array and cylindrical micelles in hexagonal array as shown in Figure 9. The lamellar micelle is at once the most interesting and also the most difficult to visualize as coextensive with an entire phase, and can evidently exist in many forms consistent with bilayer and multilayer substructures (76).

![Fig.9. Winsor's intermicellar equilibrium among spherical, cylindrical and lamellar micelles (75)](image)

**B. Stability**

Although to date all investigators have agreed that a microemulsion should be thermodynamically stable, it has not been customary to experimentally validate the fact; rather, it seems to have been taken for granted or confused with the notion of equilibrium alone. There is some difficulty with an experimental approach, because, although stability is well defined in terms of differentials of thermodynamic functions, how this is applied when it is desired to ascertain, in the absence of any such functions, whether or not a specific translucent micellar solution is stable, may not be obvious. The authors have discussed this problem in Reference 1 and the result is largely reproduced in what immediately follows.

What is implied by "stable" is stable equilibrium. An isolated system has reached equilibrium when no further macroscopic changes occur (77). This statement raises questions: What are the macroscopic variables? How long does one wait? Among the variables that can be checked are temperature, pressure, number and volumes of phases, color, pH, translucency, viscosity, electrical conductivity, and optical birefringence. If several of these were measured as functions of time and found to be convergent, probability of an equilibrium state would be high, but stability would not be established.
From a practical view there are two questions. Is there a chemical reaction occurring? Will there be a change in the number or volumes of phases in the course of time? It may not be possible to establish stability in a rigorous thermodynamic sense; however, it is important to make clear what is meant by stability in this discussion; and this will, of necessity, be arbitrary. In the case at hand, the surfactant-oil-water system is sealed within a rigid container and placed in contact with a heat reservoir so as to maintain a constant temperature. Under these constraints the natural thermodynamic function is the Helmholtz free energy. Necessary and sufficient conditions for a minimum of this function determine criteria for stable equilibrium. A consequence is Le Chatelier’s principle (78), according to which “the criterion for stability is that the spontaneous processes induced by a deviation from equilibrium be in a direction to restore the system to equilibrium.”

A convenient way to cause deviation from equilibrium is to increase the temperature. If there are chemical reactions occurring, their rates will increase, chemical potentials will change, and the probability of large local density fluctuations will increase, thereby improving the likelihood for nucleation of a new phase (78). Further, in view of temperature gradients, properties that were independent of time and position at equilibrium, become dependent on both. Nevertheless, upon return to the original temperature, the same equilibrium values of all the properties should be resumed had the state been a stable one.

It seems reasonable then to specify that if after a temperature cycle the system returns to its original equilibrium state, that state is stable. As a practical matter, we shall mean an increase in temperature of 10°C for 1 day, and the state will be determined by number, volume, translucency, and optical birefringence of phases measured at least 3 days after returning the system to its original temperature. There is nothing special about the temperatures or times selected. In fact a fluid may appear metastable to a 10°C perturbation, but stable to a 1°C increment. This will be discussed further later.

C. Intermicellar Equilibrium

Winsor’s original concept of intermicellar equilibrium is illustrated in Figure 8. Spherical water-external micelles with oil cores are labelled $S_1$; spherical oil-external micelles with water cores are labelled $S_2$ and bilayer or multi-layer lamellar micelles are designated G. In case a phase is composed of lamellar micelles it may not be possible to identify an external phase.

Since these micellar structures are considered in equilibrium they can coexist within a single phase; thus $(S_1, G)$ represents a phase having some attributes of $S_1$ and some of G. Further discussion appears later.
D. Micellar Structure Maps

The system studied was:

Surfactant: Monoethanol amine salt of C\textsubscript{N} o-xylene sulfonic acid (MEACNOXS), vol. %; N = 9, 12, 15.

Cosolvent: Tertiary amyl alcohol (TAA), vol. %.

Oil: 90% Isopar-M plus 10% Heavy Aromatic Naptha (90/10 I/H), vol. %.

Brine: Distilled water plus X% NaCl, where X = (gm NaCl/100 ml solution) x 100.

Molecular weight distribution of the surfactant alkyl chain and other properties of chemicals used are found in Reference 3.

For each ternary system studied, over 100 compositions were prepared at intervals of 2% surfactant and 10% brine or oil, sealed in glass vials with teflon lined caps and equilibrated at constant temperature. Phase boundaries were drawn mid-way between adjacent samples that proved single-phase vs multiphase. This procedure will be called the grid-point method.

Viscosity, electrical resistivity and optical birefringence were measured for every single-phase sample. Procedural details are given in Reference 1. Examples of data obtained are given in Figures 10, 11 and 12.

Viscosity data when the brine component is 2% NaCl are shown in Figure 10. Since the oil component has a viscosity of only 2.5 cp, a remarkable feature is that high viscosities appear everywhere except toward the right corner, and there is a completely gelled region toward the left. This suggests predominantly lamellar structures and transitions to other configurations as oil content increases. Samples corresponding to points labeled "gel" are translucent (sometimes transparent), thus qualifying as microemulsions (in this case, microgels).

Resistivity data for the same system are shown in Figure 11. Resistivities are low and fairly constant throughout the region of high viscosity. These data also show a transition occurring at high oil concentration. Each sample was tested for optical birefringence. If birefringence was exhibited while the sample was stationary, the point was labeled B. If birefringence was not exhibited while the sample was stationary, but was evident during agitation (streaming birefringence), the point was labeled S.
Fig. 10. Viscosity, cp @ 48 sec⁻¹, 2% NaCl

Fig. 11. Resistivity, ohm-meters, 2% NaCl
If birefringence was not exhibited in either case the point was labeled N. B indicates a lamellar structure coextensive with the entire phase and therefore implies a G-phase. S shows that lamellar structures are present, but shear is needed to induce the required degree of anisotropy. It is inferred that S is in a transition region corresponding to (S₁, G) or (G, S₂). N implies no crystalline structure and corresponds to S₁, S₂, or (S₁, S₂). Results are shown in Figure 12. Photomicrographs of birefringent microemulsions appear in Reference 1.

Birefringence and resistivity data were combined to define the micellar structure map shown in Figure 13. Noteworthy features are disjoint pairs of water-external, gel, and multiphase regions. Structural transitions of large variety appear. In particular, it is possible to move from an oil-external phase to a water-external phase without passing through an intervening gel region.

1. Salinity

Reducing salinity to 1% NaCl drastically alters configuration of the multiphase region, increases viscosity everywhere, increases resistivity somewhat, and expands the region of birefringence. The resulting micellar structure map (Figure 14) is dominated by G, and S₁ has disappeared.
Fig. 13. Micellar structure map, 2% NaCl; showing disjoint G, S₁, and multiphase regions.

Fig. 14. Micellar structure map, 1% NaCl -- dominated by G, and S₁ is absent.
2. Cosolvent

The very high viscosities that can occur in the G and (G, S) regions of the 1- and 2-percent NaCl ternary diagrams would prohibit application of these compositions to tertiary oil recovery. One way to adjust viscosity is to add a co-solvent, such as an alcohol, to the surfactant (79). Effects of adding 37% TAA to the surfactant for the case of 1% NaCl are to dramatically improve phase behavior, and reduce viscosity. Resistivity is reduced except for an abrupt jump to very high values at high oil content. The structure map (Figure 15) is dominated by S₁ and provides a second instance of $S_1 \neq S_2$ without an intervening G. We conclude therefore that although it is possible for the transition from $S_1$ to $S_2$ to pass through lamellar and cylindrical forms (70), it is by no means essential. Indeed Winsor's diagram of intermicellar equilibrium (Figure 8) makes it clear there are two routes between $S_1$ and $S_2$; one of them passes through G; the other does not.

![Micellar structure map](image)

**Fig. 15.** Micellar structure map, 1% NaCl, 37% TAA, showing simplified phase behavior dominated by $S_1$; and a direct $S_1 \neq S_2$ transition without intervening G. Also shown are injection compositions A-E used to evaluate the effect of external phase on flooding results.
3. Optimal Salinity

As remarked earlier, locally miscible displacement is favored by a ternary diagram having the largest possible miscible region, i.e., a minimal multiphase region. Since salinity is one of the variables that can strongly affect the ternary diagram it is reasonable to introduce the following definition: **optimal salinity for miscibility**, $C_m$, is the salinity that minimizes height, $C_s$, of the multiphase region at 50/50 water oil ratio (WOR). In Figure 16, $C_s$ is graphed vs salinity for the 63/37 surfactant/cosolvent system. Evidently, $C_m = 1.25\%$ NaCl. A micellar structure map at optimal salinity appears in Figure 17, where it can be seen that only $S_1$, $S_2$ and $G$ remain, and the multiphase region is small.

![Fig. 16. Determination of optimal salinity for the system 63/37 surfactant/TAA cosolvent](image)

4. Divalent Ion

When $Ca^{++}$ was added to the NaCl brine in the ratio 0.91 NaCl/0.09 CaCl$_2$, optimal salinity was reduced from 1.25\% NaCl to 1.1\% total dissolved solids (1.0\% NaCl, 0.1\% CaCl$_2$), as might be expected; but there was very little effect on the micellar structure map (1).

E. Biopolymer

Since it is necessary to add a polymer to drive water that displaces a microemulsion bank (see III.D), polymer will mix with the microemulsion to an extent that depends, among other things, on the distance traveled.
The average polymer concentration in the polymer bank may vary from a few hundred ppm to one thousand ppm or more, depending on the application and the type of slug grading used (80). If the concentration were 1000 ppm of XC Biopolymer, then some consequences of interaction with the microemulsion are illustrated in Figure 18 where this concentration of polymer was added to the brine. The effect is drastic. Any economic injection composition of type M will separate out another liquid phase or a solid precipitate. In the former case, local regions of low mobility may be generated in situ; in the latter case, the possibility of partial plugging must be considered.

F. Temperature

The system 63/37 MEAC12OXS/TAA, 90/10 I/H, 1% NaCl was studied as a function of temperature to determine effects on extent of the miscible region. The multiphase boundary was located using the grid-point method (see IV.D) at temperatures of 75, 120, 150 and 180°F. Figure 19 shows the miscible region is extensively reduced at 120°F and reduced somewhat further at 150 and 180°F. Had the temperature been lowered sufficiently below 75°F (if freezing did not intervene), the multiphase region would again expand thereby defining an optimum temperature analogous to \( C_m \).
**Fig. 18.** Addition of 1000 ppm of XC biopolymer to the 63/37 surfactant/cosolvent system at 1% NaCl diminishes the miscible region.

**Fig. 19.** Increasing temperature diminishes the miscible region. A sufficient reduction in temperature would have a similar effect.
G. Micellar Structure and Flooding

Simplicity of phase behavior and the rather sharp $S_1 \leftrightarrow S_2$ transition makes the system illustrated in Figure 15 ideal to study the effect of external phase on oil recovered from microemulsion flooding of type M. Accordingly, a sequence of floods in 4 ft Berea cores was conducted using the injection compositions A, B, C, D and E (Figure 15), all containing 15% of 63/37 surfactant/TAA, but with varying oil content. A, B and C were $S_1$; D and E were $S_2$. Table I shows final oil saturation, $S_{of}$, accounting for injected oil, for each flood. $S_{of}$ varied somewhat with oil content; however, there appears to be no obvious advantage attributable to either oil-external or water-external microemulsions. Complete descriptions of these floods and all pertinent data can be found in Reference 2.

**TABLE I**

**EFFECT OF EXTERNAL PHASE ON FINAL OIL SATURATION**

<table>
<thead>
<tr>
<th>Slug Composition</th>
<th>External Phase of Injected Slug</th>
<th>$S_{of}$ (percent PV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Water</td>
<td>7.4</td>
</tr>
<tr>
<td>B</td>
<td>Water</td>
<td>8.0</td>
</tr>
<tr>
<td>C</td>
<td>Water</td>
<td>11.1</td>
</tr>
<tr>
<td>D</td>
<td>Oil</td>
<td>6.4</td>
</tr>
<tr>
<td>E</td>
<td>Oil</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Significance of the external phase has been a matter of interest (81, 82), but to our knowledge, no other studies of oil recovery in relation to micellar structure have been published.

V. MICROEMULSIONS: THE MULTIPHASE REGION

As a microemulsion flood of Type M (see III G) progresses, surfactant adsorption, as well as mixing with brine and oil at the front and with polymer-water at the rear, cause gradual deterioration of the bank. Eventually, even the highest surfactant concentration present in the bank will fall below the multiphase boundary, one or more phases will break out; and thereafter the displacement assumes an immiscible character. In this section we will consider properties of the multiphase region that bear on a microemulsion flood of Type M or an immiscible microemulsion flood of Type I. Overall compositional points below the multiphase boundary correspond to multiple phases comprising microemulsions of various kinds, excess oil and excess water; and therefore opaque macroemulsions of these are observed upon mixing.
Under some circumstances these macroemulsions completely separate into distinct phases very rapidly, and under other circumstances they are resistant to separation, sometimes requiring many years to separate in the gravitational field alone. It should be evident that understanding the microemulsion displacement process requires comprehension of phase behavior. Establishing equilibrium phase behavior seems a logical first step.

A. Phase Behavior and Micellar Structure

A system will be called simple when it behaves as though composed of three pure components having ternary diagrams similar to those illustrated in Figure 20.

![Ternary Diagrams](image)

**Fig. 20.** Illustration of simple phase behavior, and Winsor's type I, III, and II systems

Part (a) of this figure shows a two-phase region wherein microemulsions along the binodal curve are in equilibrium with oil containing molecularly dispersed surfactant (excess oil). This is Winsor's Type I system (67). Part (c) shows a two-phase region wherein microemulsions along the binodal curve are in equilibrium with excess water, i.e., Type II. More recently, Type II systems have been considered by Adamson (83), and by Tosch, Jones and Adamson (74). Usually a Type I multiphase region is skewed to the right and a Type II region is skewed to the left, as illustrated. Part (b) shows Type II in the upper-left node, Type I in the upper-right node, and Type III in the lower triangle. Any composition within this triangle equilibrates into three phases: microemulsion corresponding to compositional point M, excess water, and excess oil. In this chapter, Winsor's Type I, II, and III systems will be called lower-phase, l, upper-phase, u, and middle-phase, m, respectively.
Among the variables that affect the type of diagram observed are salinity, oil composition, surfactant molecular structure, alcohol cosolvent, and temperature.

Not all microemulsions qualitatively conform to simple multiphase behavior; it sometimes happens that where one phase was expected, two or more immiscible microemulsion phases appear. However, these extra phases frequently occur in minor quantities, and so the expected phases predominate. Therefore simple behavior appears to be a good approximation for numerous microemulsion systems having utility for tertiary oil recovery.

1. Equilibration

In Section IV D, the multiphase boundaries were determined using the grid-point method. A different method involves preparation of several multiphase samples having constant overall surfactant concentration but varying water-oil ratios. The assumption of negligible surfactant concentration in excess water and oil phases allows calculation of equilibrium microemulsion compositions from equilibrated phase volumes, and construction of a binodal curve (3). If the overall surfactant concentration of the samples is changed, the phase diagram will change, reflecting the multicomponent nature of surfactant, cosolvent, brine, and oil used. Figure 21 shows binodal curves at two different overall surfactant concentrations for a lower-phase microemulsion system.

2. Real Systems

Figure 22 exhibits phase diagrams for a real system that approximates simple behavior. Increasing salinity causes successive appearance of lower-, middle-, and upper-phase diagrams. A notable difference between real and simple behavior is the locus of middle-phase compositions rather than a single point (Figure 20). As the base surfactant concentration is increased, lateral extent of this locus should decrease.

Figure 23 is a photograph of samples having identical overall compositions except that salinity varies from 0.5 to 2.5% NaCl. At this writing, all phase volumes have been constant for over a year. These samples illustrate the effect of salinity on phase behavior when water-oil ratio is maintained constant at 1/1, and surfactant concentration is also held constant. Evidently, increasing salinity causes the microemulsion system to undergo the transitions \( l \rightarrow m \rightarrow u \). This remarkable, systematic behavior of complex, multicomponent microemulsion systems is essential to all that follows.

3. Micellar Structure

Micellar structure of microemulsion phases that undergo the transition \( l \rightarrow m \rightarrow u \) was studied using the approach of Section IV D, and results are shown in Figure 24.
Since none of the microemulsions was birefringent or streaming birefringent, and since resistivity increased continuously, neither of these properties identifies $l \rightarrow m$ or $m \rightarrow u$. However, viscosity changes abruptly at these transitions and is related to microemulsion phase volume (Figure 24b). Winsor’s model would imply $S_1$ at low salinity, $S_2$ at high salinity and ($S_1$, $S_2$) for the middle phases. A continuous shift from $S_1$ to $S_2$ is supported by birefringence and resistivity, but does not appear to account for the abrupt changes in viscosity. These latter phenomena suggest $l \rightarrow m$ and $m \rightarrow u$ are, in a sense, sharp transitions. We accept that $S_1$ and $S_2$ predominate in $l$ and $u$ phases, respectively, but are uncertain concerning the middle phase. However, the following middle-phase properties are evident from the data:

1. If there is an external phase it is neither oil nor water
2. If there are micelles, they are not, on the average spherical, cylindrical or lamellar.
B. Stability Revisited

A microemulsion was defined in a way that seems satisfactory for compositions well into the miscible region; but suppose the composition is very close to, or on the multi-phase boundary; and let us then look into the question of stability (see IV B) again.

For the anionic surfactants studied, if a middle-phase system is heated, oil will be spontaneously rejected. At the elevated temperature the microemulsion is undersaturated with respect to water, but water will not spontaneously solubilize to any measurable extent, even with mild stirring of the microemulsion phase. If the system is then cooled to the original temperature, it will be undersaturated with respect to oil, but oil will not spontaneously solubilize to any measurable extent, even over extremely long periods of time, even with fairly rapid stirring of the microemulsion. Further, if the oil is slowly re-injected into the bottom of the microemulsion phase, it will thread its way back into the oil phase in a filament so minute as to be hardly visible, with only a very small loss of oil. If, however, the oil is rapidly flushed into the microemulsion it will mostly disappear; i.e., work is required.

Evidently, resistance to diffusion afforded by oriented layers of surfactant at the interface (84) and augmented by the gravitational field, permits only very minute net rates of oil and water transport.
Fig. 23. Effects of increasing salinity for the system 4% 63/37 MEAC120XS/TAA, 48% 90/10 I/H, 48% X NaCl, are shown here. The transitions \( \lambda \rightarrow m \rightarrow u \) are evident; a remarkably systematic result for a compositionally complex system.
Of course, if the system is thoroughly mixed and allowed to equilibrate after each perturbation, it will return to the appropriate state. We conclude that although immiscible microemulsions may be stable in the pure thermodynamic sense, they are not stable in a practical sense; i.e., once perturbed the system does not spontaneously return to its original state in a period of time that has practical utility. Nevertheless, these "immiscible microemulsions" are translucent micellar solutions and serve all the same purposes as the previously defined microemulsions (IV A), except they are saturated with oil and/or water. Accordingly, we introduce the operational definition: a microemulsion is a persistent translucent combination of oil, water that may contain electrolytes and one or more amphiphilic compounds. "Persistence" can then be defined according to requirements of the specific application.

C. Interfacial Tension and Solubilization Parameter

Figure 23 reveals there are two kinds of interfaces and hence up to three interfacial tensions can be measured depending on salinity: $\gamma_{mo}$ (microemulsion-oil), $\gamma_{mw}$ (microemulsion-water) and $\gamma_{ow}$ (excess oil-excess water)*; and further, the excess oil and water volumes, and hence volumes of oil and water within the microemulsion phase, $V_O$ and $V_W$, respectively, depend on salinity.

* $\gamma_{ow}$ was high, $\sim 0.1$ dyne/cm, and was not routinely measured.
Figure 25 relates interfacial tensions, $\gamma_{mo}$ and $\gamma_{mw}$, and solubilization parameters, $V_O/V_S$ ($V_S =$ vol. surfactant in microemulsion phase not including cosolvent), to salinity. As salinity increases, $\gamma_{mo}$ decreases and $\gamma_{mw}$ increases. As either tension decreases, the appropriate solubilization parameter increases: Hence in $l$ and $u$ phases low interfacial tensions correspond to micelles swelled with internal phase. This is consistent with Robbins' model (85, 86).

Recognition that volumes of oil or water solubilized in a microemulsion phase in relation to the amount of surfactant there are measures of interfacial activity will prove to have practical as well as conceptual value.
Although solubility of one aqueous or organic phase in another is quite different from the notion of water or oil solubilized within surfactant micelles, it is interesting to note some parallel, supporting developments.

It has long been recognized that solubility measurements provide a means of studying molecular interactions. Hansen's approach (87), using the solubility parameter concept of Hildebrand and Scott (88, 89), is well known. Other investigators of non-surfactant systems have reasoned that, for the liquid-liquid case, cohesional and adhesional molecular forces that determine the magnitude of interfacial tension, also determine the extent to which two liquids are soluble. In 1913, Hardy (90) showed that interfacial tension between aqueous and organic liquid phases may be reliably considered as a linear function of the log of the "degree of miscibility" of the liquids. More recently, Donahue and Bartell (91) made a further study of the relationship between $\gamma$ and solubility. None of these studies involved surfactants.

The salinity, $C_T$, where $\gamma_{mw}$ intersects $\gamma_{mo}$ is called the interfacial tension optimal salinity. Similarly, $C_\phi$, the phase behavior optimal salinity is defined by the intersection of $V_O/V_S$ with $V/V_S$. Puerto and Gale (92) have developed methods for predicting $C_\phi$ and $V_O/V_S$ at $C_\phi$ for mixtures of alkyl orthoxylene sulfonates.

Interfacial tension and solubilization parameter graphs (Figure 25) suggest the correlations shown in Figure 26. Although these correlations were obtained through variation of salinity alone, similar results obtain when overall composition is a variable (3). Data scatter implies there are additional parameters (see Reference 85 in this regard); nevertheless, correlations of this kind reduce the number of interfacial tension measurements required to evaluate a surfactant, and show that phase volumes can replace interfacial tensions as a preliminary measure of interfacial activity. This becomes particularly useful in the case of some black crude oils where equilibrated tension measurements are extremely difficult or impossible, but phase boundaries may be visible under ultraviolet light (93).

The curves shown result from fitting these data with the empirical equations:

\[
\log \left( \frac{\gamma_{mo}}{\gamma_{mo}^*} \right) = \frac{a}{m_o (V_O/V_S)} + 1 \tag{1}
\]

and

\[
\log \left( \frac{\gamma_{mw}}{\gamma_{mw}^*} \right) = \frac{b}{m_w (V_O/V_S)} + 1 ; \tag{2}
\]

using the parameters,
D. Optimal Salinity

Three optimal salinities have been so far defined, $C_m$ (see IV D3), $C_\gamma$ and $C_\phi$. For the system 3% 63/37 MEAC120XS/TAA, 48.5% 90/10 I/H, 48.5% X% NaCl, $C_m = 1.25\%$ (Figure 16), $C_\gamma = 1.4\%$, and $C_\phi = 1.5\%$ (Figure 25); i.e., they are about the same. All of these were determined using a constant WOR = 1. A natural question concerns the possible dependence of optimal salinity on WOR and $C_s$.

An unusual ternary diagram appears in Figure 27 where in-creasing WOR results in $l \to m \to u$. Behavior of $C_\phi$ in relation to WOR and $C_s$ was determined for this system and results appear in Figure 28. Dependence of $C_\phi$ on $C_s$ is moderate except for $C_s < 3\%$. Dependence on WOR is also moderate. These results provide an explanation for the complex phase behavior illustrated in Figure 27. At high water-oil ratios on the left side of the diagram, salinity is less than $C_\phi$; and hence surfactant will reside in an aqueous phase ($l$). In the center, salinity is near optimal so the expected middle-phase appears there.
Fig. 27. The unusual behavior shown here, i.e., $l + m + l$ results from the dependence of optimal salinity on water-oil ratio.

Fig. 28. The dependence of $C_\phi$ on $C_S$ is moderate except for $C_S < 3\%$. $C_\phi$ is almost linear in log WOR. Qualitative character of these effects depends on the system.
At low water-oil ratios, salinity is still close to optimal; hence the expected lower-phase microemulsions are found. Although there are insufficient data to analyze a complete flooding situation, it is evident that dependence of optimal salinity on surfactant concentration and water-oil ratio could have important effects.

E. Cohesive Energy Ratio

Winsor viewed interfacial activity in terms of the cohesive energy ratio, \( R = E_{1o}/E_{hw} \), where \( E_{1o} \) and \( E_{hw} \) are the lipophile-oil and hydrophile-water interaction energies, respectively. High interfacial activity occurs when \( E_{1o} \) and \( E_{hw} \) are both large and, in addition, \( R \sim 1 \). When \( R \ll 1 \), \( S_1 \) is favored; and when \( R \gg 1 \), \( S_2 \) is favored.

The concept of optimal salinity can be interpreted in terms of \( R \) and the salinity dependence of \( E_{hw} \) and \( E_{1o} \). It seems reasonable to assume \( E_{hw} \) is a monotonically decreasing function of salinity, whereas \( E_{1o} \) is independent of salinity. Then \( C_\gamma \) corresponds to the salinity where \( E_{1o} \sim E_{hw} \); i.e., \( R \sim 1 \).

F. Interfacial Tension Optimal Salinity

Interfacial tensions between microemulsions and equilibrated excess oil or excess water phases were determined as functions of salinity, temperature, surfactant structure, co-solvent structure, oil composition, and composition of dissolved solids in the aqueous phase.

1. Surfactant Structure

Figure 29 shows interfacial tension vs. salinity graphs for three alkyl chain lengths, all measured at 112°F. Similar graphs were obtained at 74 and 150°F (3). Increasing \( N \) from 9 to 15 decreases \( C_\gamma \) from 4.4 to 0.2% and \( \gamma(C_\gamma) \) from 0.01 to 0.001 dyne/cm. Although increasing \( N \) decreases \( \gamma(C_\gamma) \), the range of salinity over which the surfactant is effective is also decreased.

These results can be interpreted in terms of cohesive energy ratio. Since \( E_{hw} \) is a decreasing function of salinity, and \( E_{hw} \sim E_{1o} \) at \( C_\gamma \); both \( E_{hw} (C_\gamma) \) and \( E_{1o} (C_\gamma) \) increase as \( C_\gamma \) decreases, resulting in higher interfacial activity and hence lower \( \gamma \). Increasing \( N \) at constant salinity causes \( \gamma_{mo} \) and \( V_w/V_s \) to decrease, \( \gamma_{mw} \) and \( V_o/V_s \) to increase, and phase behavior to move in the direction \( l \rightarrow m \rightarrow u \).

2. Temperature

Figure 30 shows, for \( N = 12 \), interfacial tension as a function of salinity at three temperatures. Similar graphs were obtained for \( N = 9 \) and 15 (3). Both \( C_\gamma \) and \( \gamma(C_\gamma) \) increase with temperature. Increasing temperature causes \( \gamma_{mw} \) and \( V_o/V_s \) to decrease, \( \gamma_{mo} \) and \( V_w/V_s \) to increase, and phase behavior to change in the direction \( u \rightarrow m \rightarrow l \).
If the data of Figure 30, augmented with solubilization parameter data (3), are graphed as functions of temperature at constant salinity, Figure 31 is obtained. Here it can be seen that optimal temperature can be defined analogously to optimal salinity. In the case at hand, optimal temperature is 118 or 130°F depending on $\gamma$ or solubilization parameter, respectively.

A convenient summary of relations among $C_\gamma$, optimal interfacial tension, temperature and the surfactant structural parameter, N, appears in Figure 32. An application of these results is selection of a surfactant structure that gives $\gamma_{mo} = \gamma_{mw}$ at a given temperature and salinity, and estimation of the value of interfacial tension there; thus providing a guide for surfactant structure required to be effective in a particular reservoir environment.

3. Cosolvent

Changing the cosolvent from TAA to tertiary butyl alcohol (TBA) causes optimal salinity, interfacial tension at optimal salinity, and the range of salt tolerance to increase (see Figure 33). Another interesting feature is the symmetry between the $\gamma_{mo}$ and $\gamma_{mw}$ curves. Symmetry is further reflected in Figure 34 where all $\gamma_{mo}$ and $\gamma_{mw}$ data are correlated with a single curve, and in phase behavior (Figure 22), which is nearly simple.
Fig. 30. Dependence of interfacial tension on salinity for the system 3% 63/37 MEAC120XS/TAA, 48.5% 90/10 I/H, 48.5% X% NaCl showing an increase in optimal salinity and in the value of \( \gamma \) at optimal salinity as temperature increases.

Fig. 31. Interfacial tension and solubilization parameter determine optimal temperatures for the system 3% 63/37 MEAC120XS/TAA, 48.5% 90/10 I/H, 48.5% 2% NaCl.
Fig. 32. This summary of the relations among $C_y$, $\gamma(C_y)$, temperature and $N$ is useful to find the value of $N$ most suitable to a given reservoir environment.

Fig. 33. Effect of cosolvent on the system 3% 63/37 MEAC12OXS/cosolvent, 48.5% 90/10 I/H, 48.5% X% NaCl. Note the symmetry of the TBA data.
These data, together with physical reasoning, provide the rationale for fitting solubilization parameter correlations with curves rather than straight lines.

Increasing alcohol molecular weight at constant salinity causes $\gamma_{mo}$ and $V_W/V_S$ to decrease, $\gamma_{mw}$ and $V_O/V_S$ to increase, and $l \to m \to u$.

4. Other Variables

Interfacial tension and solubilization parameter were measured as functions of salinity to ascertain effects of several other variables (3), all with respect to 3% 63/37 MEAC12OX/TSAA, and WOR = 1.
Increasing aromatic content of the oil from 0% (100% Isopar M) to 10% (90/10 I/H) decreased both optimal salinity and tension. Increasing aromaticity at constant salinity resulted in \( l \rightarrow m \rightarrow u \).

Neither optimal tension nor salinity were significantly affected by presence of 750 ppm of XC biopolymer in the aqueous phase. This is in marked contrast to the detrimental effect this polymer has on extent of the miscible region (see IV E).

Addition of \( \text{Ca}^{++} \) to the aqueous phase in the ratio 10/1 \( \text{NaCl}/\text{CaCl}_2\cdot2\text{H}_2\text{O} \) decreased optimal salinity from 1.4% \( \text{NaCl} \) to 1.1% total dissolved solids, but the effect on optimal tension was very small. This agrees with a previous finding that \( \text{Ca}^{++} \) caused a decrease in \( C_m \), but extent of the multiphase region was not significantly affected.

Finally, addition of both 750 ppm XC biopolymer and \( \text{Ca}^{++} \) to the brine produces interfacial tensions that are very nearly the same as those found for \( \text{NaCl} \) brine.

G. Summary

For the systems studied, Table II shows trends in \( y \) and phase behavior that result from increasing a given variable of interest, providing the overall composition is constant.

<table>
<thead>
<tr>
<th>Increasing Variable</th>
<th>Phase Behavior</th>
<th>( \gamma_m )</th>
<th>( \frac{V_o}{V_s} )</th>
<th>( \gamma_{mw} )</th>
<th>( \frac{V_w}{V_s} )</th>
<th>( C_y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity</td>
<td>( l \rightarrow m \rightarrow u )</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Alkyl Chain Carbon No. (N), Molecular wt. of alcohol cosolvent, oil aromaticity ( \text{Ca}^{++}/\text{NaCl} ) Ratio</td>
<td>( l \rightarrow m \rightarrow u )</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Temperature</td>
<td>( u \rightarrow m \rightarrow l )</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>XC Biopolymer Conc.</td>
<td>Insignificant Changes</td>
<td>(-) indicates a decrease</td>
<td>( + ) indicates an increase</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE II**

**SUMMARY OF INFLUENCE OF SOME VARIABLES ON PHASE BEHAVIOR, INTERFACIAL TENSION AND SOLUBILIZATION PARAMETER**
Tabulated results show that whenever phase behavior changes in the direction \( l \rightarrow m \rightarrow u \), associated trends are that \( \gamma_{mo} \) and \( V_w/V_S \) decrease, while \( \gamma_{mw} \) and \( V_o/V_S \) increase. When the direction of phase behavior change is opposite \((u \rightarrow m \rightarrow l)\), opposite trends are observed. It is conjectured these results will hold for all surfactant systems.

H. Immiscible-Microemulsion Floods

It will be recalled that an immiscible microemulsion flood has an injection composition on or close to the multi-phase boundary (see IIIG and Figure 6, Type I). Now that considerable detail of the multiphase region has been accumulated, it affords an opportunity to study this type of flood and determine the extent to which concepts we have introduced bear a relation to oil recovery. For this purpose it is necessary to further introduce controlling interfacial tension, \( \gamma_c \), as the larger of \( \gamma_{mo} \) and \( \gamma_{mw} \) i.e., \( \gamma_c = \max(\gamma_{mo},\gamma_{mw}) \). Thus \( \gamma_c = \gamma_{mo} \) for lower-phase microemulsions; \( \gamma_c = \gamma_{mw} \) for upper-phase microemulsions; and for middle-phase microemulsions, \( \gamma_c \) may be either \( \gamma_{mw} \) or \( \gamma_{mo} \) depending on which is greater. \( \gamma_c \) is minimized when \( \gamma_{mo} = \gamma_{mw} \).

1. Continuous Injection

Lower-, middle-, or upper-phase microemulsions having \( N = 9 \) or \( 12 \) were employed in core flooding experiments wherein microemulsion was continuously injected. The floods were conducted at constant rate in the range 0.5-2.3 ft/day, and fractional flows of oil, \( f_o \), and water, \( f_w \), during production of the stabilized oil bank were measured. (See Reference 4 for details.)

For \( N = 9 \) or \( 12 \), Figure 35 shows fractional flow data correlated with \( N_c(\gamma_{mo}) \) or \( N_c(\gamma_{mw}) \). Since \( f_o \) is independent of \( \gamma_{mw} \), it suggests nearly all resident water was displaced; and \( f_o \) is determined, in part, by the influence of \( \gamma_{mo} \) on oil saturation left behind the microemulsion front. A similar interpretation applies to \( f_w(\gamma_{mw}) \).

2. Bank Injection

Banks of lower-, middle-, and upper-phase microemulsions were injected at constant rates in the range 0.5-1.3 ft/day and final oil saturation determined from

\[
S_{of} = \frac{V_{o,\text{inj}} + V_{o,\text{initial}} - V_{o,\text{prod}}}{PV_{\text{core}}}
\]

Figure 36 shows that \( S_{of} \) broadly decreases with \( N_c \), but the correlation depends on which tension is controlling. The scatter was anticipated in view of changing injection composition, mobility ratio and surfactant retention.
Fig. 35. Fractional oil flow for floods where microemulsion is continuously injected correlates with capillary number based on the controlling interfacial tension.

Fig. 36. Final oil saturation after floods using immiscible microemulsion banks broadly correlates with capillary number based on the controlling interfacial tension.
Other considerations are that the correlating group of Figure 36 does not contain $\cos \theta$ as suggested in Section III B; and, as remarked earlier (III C), displacement of residual oil is not the problem once an oil bank is formed; rather it is to maintain oil filament continuity to as low a saturation as possible, so that perhaps other dimensionless groups come into play. (See, however, Reference 12.) Although the correlation is expected, to depend on properties of the specific system of interest, it is conjectured that $S_{of}$ decreases with $N_c$ for all systems having favorable mobility, provided surfactant retention does not dominate oil recovery behavior.

A possible physical interpretation of results from these slug floods is that $\gamma_{mo}$ determines the effectiveness of the displacement of oil by microemulsion at the slug front; while displacement of microemulsion by drive water at the slug rear is controlled by $\gamma_{mw}$. The least effective of these displacements determines the outcome.

3. Oil Recovery in Relation to Several Variables

By this time the reader should be aware that the concepts of optimal salinity, temperature, etc., were introduced in expectation that the best oil recoveries would be obtained at these conditions. By way of verification, some effects on oil recovery of salinity, surfactant and cosolvent molecular structures, temperature, and composition, were determined using immiscible microemulsion slugs. Details are given in Reference 4.

An example of the kind of result obtained is shown in Figure 37 where both interfacial tension and final oil saturation are graphed as functions of salinity. If $C^*$ is defined as the optimal salinity for oil recovery, then it can be seen that $C^* = 1.5\%$ and $C_r = 1.4\%$ NaCl. Figure 38 shows $C^*$ is in good agreement with $C_\phi \approx C_r$ for all variables studied. This means, the salinity that determines the best oil recovery can be estimated from solubilization parameter data alone; i.e., all that is required to find the best salinity for a given surfactant system is to make a few volume measurements on equilibrated multiphase systems as a function of salinity (see Figure 23). This procedure can be used for variables other than salinity, and this is discussed in the following section.

I. Screening

Microemulsion flooding may be unique in that so many different variables are available and all functionally related. Consequently, any procedure that can systematically point to variable combinations that give good oil recovery is useful.
Let a variable $X$ represent, for example, temperature, salinity, oil composition, or surfactant and cosolvent structural parameters. The screening method assumes $X^{*} = X_{\phi}$ and oil recovery correlates with $N_c(\gamma_c)$. Situations may arise wherein variables such as mobility control or surfactant retention influence oil recovery to an extent that these assumptions are invalid; nevertheless, we have found the approach applicable to a number of anionic surfactant systems.

Samples are prepared where $X$ varies monotonically, other composition variables remaining fixed. A water-oil ratio of unity is preferred. Samples are thoroughly mixed and allowed to remain undisturbed at constant temperature until the initial opaque emulsion completely disappears, and distinct translucent phases remain. Graphs of $V_o/V_s$ and $V_w/V_s$ as functions of $X$ are then prepared, $X_{\phi}$ determined, and viscosity of each microemulsion phase measured. Values of $N_c = \frac{\nu \mu}{\gamma_c}$ for the various microemulsion phases are determined and used to provide estimates of oil recovery.

*Fig. 37. Interfacial tension and oil recovery data show that interfacial tension optimal salinity very nearly corresponds to the best oil recovery*
If $N_c$ is sufficiently large in the neighborhood of $X_\phi$, laboratory core floods are run to determine oil recovery as a function of $X$. A graph of $S_{oef}$ vs $X$ determines $X^*$ and the minimum value of $S_{oef}$. The value of $N_c$ that is "sufficiently large" depends on the specific system being investigated. For one system studied here, a value greater than $10^{-3}$ was necessary for good oil recovery.

A modification of the screening method can sometimes be applied to develop effective high water content microemulsions, which have an economic advantage. In this case, $X_\phi$ is determined as above; but the best oil recovery is established from core floods using microemulsions equilibrated at high WOR in the overall mixture. In one case, reported elsewhere (4), maximal oil recovery and $C^*$ were independent of WOR.

J. Connection Between Locally Miscible and Immiscible Microemulsion Flooding

The immediate vicinity of the multiphase boundary is the demarcation between injection compositions for miscible-type, high concentration, or soluble oil microemulsion floods, on the one hand, and immiscible microemulsion floods on the other.
It has been pointed out (III G) that minimizing height of the multiphase boundary prolongs locally miscible microemulsion displacement, whereas decreasing controlling interfacial tension enhances immiscible microemulsion displacement. A question arises as to whether these two considerations are related or quite independent. The following developments answer this question and make use of the result.

Along any line passing through $C_S = 1$, i.e., 100% surfactant, $V_W / V_O$ is a constant, say $\xi$. Since $C_o + C_w + C_s = 1$, $C_w / C_o = V_w / V_o$, $C_o / C_s = V_o / V_s$ and $C_w / C_s = V_w / V_s$. It follows from Equations 1 and 2 that

\[
\log \left( \frac{\gamma_{mo}}{\gamma_{mo}'} \right) = \frac{a}{\frac{m_o}{1 + \xi} \left[ \frac{1 - C_s}{C_s} \right]^x + 1} , \quad (3)
\]

\[
\log \left( \frac{\gamma_{mw}}{\gamma_{mw}'} \right) = \frac{b}{\frac{m_w}{1 + \xi} \left[ \frac{1 - C_s}{C_s} \right]^y + 1} . \quad (4)
\]

Equation (3) applies to a lower- or middle-phase microemulsion. Equation (4) applies to an upper- or middle-phase microemulsion. If a middle-phase occurs, then $C_s$ is the same in Equations (3) and (4) so that $\gamma_{mo}$ and $\gamma_{mw}$ are related through the expression

\[
\frac{m_w}{m_o} \frac{\xi}{-1 + b/\log \left( \frac{\gamma_{mw}}{\gamma_{mw}'} \right)} = \frac{-1 + a/\log \left( \frac{\gamma_{mo}}{\gamma_{mo}'} \right)}{-1 + b/\log \left( \frac{\gamma_{mw}}{\gamma_{mw}'} \right)}
\]

For a fixed water-oil ratio, $\xi$, Equations (3) and (4) relate height of the multiphase region $C_s(\xi)$ to $\gamma_{mo}$ and $\gamma_{mw}$. These equations are graphed for $\xi = 1$ in Figure 39, using parameters estimated from Section V C. Also shown in Figure 39 is the $\gamma - C_s$ path followed when a variable is changed monotonically so the microemulsion phase undergoes the transition $l \rightarrow m \rightarrow u$. Every point on the path ABCD corresponds to a different ternary diagram. Along AB, all microemulsions are lower-phase; and interfacial tension, $\gamma_{mo}$, decreases as height $C_s$ decreases. At B, the multiphase region having the least height at $\xi = 1$ is achieved, and a middle phase forms having the two tensions $\gamma_{mo}(B)$ and $\gamma_{mw}(C)$. Once past the optimum, $C_{s,\text{min}}$, microemulsions along CD are upper-phase; and interfacial tension, $\gamma_{mw}$, increases as height $C_s$ increases.

In summary, for surfactants studied here, interfacial tensions are decreasing functions of solubilization parameters.
When this is the case, at any fixed water-oil ratio, interfacial tension decreases as height of the multiphase region decreases. It follows that ternary diagrams favorable to immiscible microemulsion floods are also favorable to locally miscible microemulsion floods; and therefore the screening method developed here is applicable to both approaches to oil recovery.

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VII. NOMENCLATURE

a - constant, dimensionless
b - constant, dimensionless
C\(^*\) - optimal salinity for oil recovery, % TDS (total dissolved solids)
C\(_{\gamma}\) - optimal salinity for interfacial tension, % TDS
C\(_o\) - oil concentration in microemulsion, vol. %
C\(_{\phi}\) - optimal salinity for phase behavior, % TDS
C\(_m\) - optimal salinity for miscibility, % TDS
C\(_s\) - surfactant concentration in microemulsion, vol. %
C\(_{s,\text{min}}\) - surfactant concentration in microemulsion corresponding to minimum height of multiphase region, vol. %
C\(_w\) - water concentration in microemulsion, vol. %
E\(_{\text{hw}}\) - hydrophile-water interaction energy
E\(_{1o}\) - lipophile-oil interaction energy
f\(_o\) - fractional oil flow, dimensionless
f\(_w\) - fractional water flow, dimensionless
G - gel
K - effective permeability, darcys or md
l - lower-phase microemulsion
L - length, cm
m - middle-phase microemulsion
m\(_a\) - constant, dimensionless
m\(_w\) - constant, dimensionless
N - carbon number of alkyl side chain
N\(_c\) - capillary number, dimensionless
P - pressure, dyne/cm\(^2\) or psi
P\(_c\) - capillary pressure, dyne/cm\(^2\)
P\(_{\text{core}}\) - core pore volume, ml
r - pore radius, cm
R - cohesive energy ratio (E\(_{1o}/\) E\(_{\text{hw}}\)), dimensionless
S\(_1\) - spherical water-external micelles with oil cores
S\(_2\) - spherical oil-external micelles with water cores
S\(_o\) - oil saturation, dimensionless
S\(_{of}\) - final oil saturation, dimensionless
u - upper-phase microemulsion
v - velocity, cm/sec or ft/day
V\(_o\) - volume of oil in microemulsion, ml
V\(_{o,\text{initial}}\) - volume of oil initially contained in core, ml
V\(_{o,\text{inj}}\) - volume of oil injected, ml
V\(_{o,\text{prod}}\) - volume of oil produced, ml
V\(_o/\) V\(_s\) - solubilization parameter for oil in microemulsion, volume ratio of oil to surfactant in microemulsion phase
V\(_s\) - volume of surfactant in microemulsion, ml
V\(_w\) - volume of water in microemulsion, ml
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$V_{w}/V_{s}$ - solubilization parameter for water in micro-emulsion, volume ratio of water to surfactant in microemulsion phase

WOR - water-oil ratio, dimensionless

$X$ - a variable

$X^*$ - optimal $X$ for oil recovery

$X_{ph}$ - optimal $X$ for phase behavior

$\gamma$ - interfacial tension, dyne/cm

$\gamma_{c}$ - controlling interfacial tension, dyne/cm

$\gamma_{mo}$ - microemulsion-oil interfacial tension, dyne/cm

$\gamma'_{mo}$ - a constant, dyne/cm

$\gamma_{mw}$ - microemulsion-water interfacial tension, dyne/cm

$\gamma'_{mw}$ - a constant, dyne/cm

$\Delta P$ - pressure drop, dyne/cm$^2$ or psi

$\mu$ - viscosity, poise or cp

$\theta$ - contact angle, degrees

$\xi$ - water-oil ratio in microemulsion, dimensionless

VIII. LITERATURE CITED


