Macro- and Microemulsions in Enhanced Oil Recovery

M. K. SHARMA and D. O. SHAH
Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, FL 32611

The physicochemical aspects of micro- and macroemulsions have been discussed in relation to enhanced oil recovery processes. The interfacial parameters (e.g., interfacial tension, interfacial viscosity, interfacial charge, contact angle, etc.) responsible for enhanced oil recovery by chemical flooding are described. In oil/brine/surfactant/alcohol systems, a middle phase microemulsion in equilibrium with excess oil and brine forms in a narrow salinity range. The salinity at which equal volumes of brine and oil are solubilized in the middle phase microemulsion is termed the optimal salinity. The optimal salinity of the system can be shifted to a desired value by varying the concentration and structure of alcohol. It was observed that the formulations consisting of ethoxylated sulfonates and petroleum sulfonates are relatively insensitive to divalent cations. The results show that a minimum in coalescence rate, interfacial tension, surfactant loss, apparent viscosity and a maximum in oil recovery are observed at the optimal salinity of the system. The flattening rate of an oil drop in a surfactant formulation increases strikingly in the presence of alcohol. It appears that the addition of alcohol promotes the mass transfer of surfactant from the aqueous phase to the interface. The addition of alcohol also promotes the coalescence of oil drops, presumably due to a decrease in the interfacial viscosity. Some novel concepts such as surfactant-polymer incompatibility, injection of an oil bank and demulsification to promote oil recovery have been discussed for surfactant flooding processes.

During the past two decades, much attention has been focused on enhanced oil recovery by chemical flooding processes in order to increase the world-wide energy supply. It is well recognized that the
macro- and microemulsion systems play an important role in the oil recovery processes. Recently, several major research findings in this area have been reported in the review articles and books [1-4]. Wagner and Leach [3], Taber [6] and Melrose and Brader [7] have suggested that capillary forces are responsible for entrapping a large amount of oil in the form of oil ganglia within the porous rocks of petroleum reservoirs. Foster [8] has also shown that interfacial tension at crude oil/brine interface, which plays a dominant role in controlling capillary forces, should be reduced by a factor 10,000 times (e.g. $10^{-3}$ to $10^{-4}$ dynes/cm) to achieve an efficient displacement of the crude oil. Such low interfacial tension can be achieved by appropriate surfactant formulations. The oil droplets can be deformed easily in the presence of low interfacial tension. Figure 1 schematically illustrates a two-dimensional view of the surfactant-polymer flooding process. After injecting a surfactant slug into the reservoir, a polymer slug is injected for mobility control. During this process, the displaced oil droplets coalesce and form an oil bank (Figure 2).

Once an oil bank is formed in the porous medium, it has to be propagated through the porous medium with minimum entrapment of oil at the trailing edge of the oil bank. The maintenance of ultralow interfacial tension at the oil bank/surfactant interface is necessary for minimizing the entrapment of the oil in the porous medium. The leading edge of the oil bank coalesces with additional oil ganglia. Moreover, besides interfacial tension and interfacial viscosity, another interfacial parameter which influences the oil recovery is the surface charge at the oil/brine and rock/brine interfaces [9, 10]. It has been shown that a high surface charge density leads to a lower interfacial tension, lower interfacial viscosity and higher oil recovery as shown in Figure 3.

In 1959, Wagner and Leach [11] suggested that increased oil recovery could be obtained by changing wettability of rock material from oil-wet to water-wet. Melrose and Brader [7] and Morrow [12] also suggested that for optimal recovery of residual oil by a low interfacial tension flood, the rock structure should be water-wet. Previous investigators [13, 14] have used sodium hydroxide to make the reservoir rock water-wet. Slattery and Oh [15] have shown that intermediate wettability may be less desirable than either oil-wet or water-wet rocks. Since, chemical floods satisfy many of these conditions, they have been considered promising for enhanced recovery of oil. The mechanism of oil displacement in porous media has been reviewed by Bansal and Shah [16] and more recently by Taber [17].

Enhanced Oil Recovery By Microemulsion Flooding

In this section, several important aspects of microemulsions in relation to enhanced oil recovery will be discussed. It is well recognized that the success of the microemulsion flooding process for improving oil recovery depends on the proper selection of chemicals in formulating the surfactant slug. During the past decade, it has been reported that many surfactant formulations for enhanced oil recovery generally form multiphase microemulsions [18-20]. From these studies, it is evident
that a variety of phases can exist in equilibrium with each other. Figure 4 shows the effect of salinity on the phase behavior of oil/brine/surfactant/alcohol systems. The microemulsion slug partitions into three phases (Figure 4), namely, a surfactant-rich middle phase and a surfactant-lean brine and oil phase (21-23) in the intermediate salinity range. This surfactant-rich phase was termed the middle phase microemulsion (23). The middle phase microemulsion consists of solubilized oil, brine, surfactant and alcohol. The 1+m+u transition of the microemulsion phase can be obtained by varying any of the eight variables listed in Figure 4.

Interfacial Tension. It is well established that ultralow interfacial tension plays an important role in oil displacement process (18,20). Figure 5 schematically illustrates the factors affecting the magnitude of the interfacial tension. Using this conceptual approach, one can broaden the surface interfacial tension as well as increase the salt tolerance limit of the surfactant formulation. Experimentally, Shah et al. (24) demonstrated a direct correlation between interfacial tension and interfacial charge in various oil-water systems. It was established that the interfacial charge density plays a dominant role in lowering the interfacial tension. Figure 5 shows the interfacial tension and partition coefficient of surfactant as a function of the salinity. The minimum interfacial tension occurs at the same salinity where the partition coefficient is near unity. The same correlation between interfacial tension and partition coefficient was also observed by Baviere (25) for paraffin oil/sodium alkylbenzene sulfonate (average MW 350)/isopropyl alcohol/brine system.

Chan and Shah (26) proposed a unified theory to explain the ultralow interfacial tension minimum observed in dilute petroleum sulfonate solution/oil systems encountered in tertiary oil recovery processes. For several variables such as the salinity, the oil chain length and the surfactant concentration, the minimum in interfacial tension was found to occur when the equilibrated aqueous phase was at CMC. This interfacial minimum also corresponded to the partition coefficient near unity for surfactant distribution in oil and brine. It was observed that the minimum in ultralow interfacial tension occurs when the concentration of the surfactant monomers in aqueous phase is maximum.

Formation and Structure of Middle Phase Microemulsion. The 1+m+u transitions of the microemulsion phase as a function of various parameters are shown in Figure 4. Chan and Shah (31) compared the phenomenon of the formation of middle phase microemulsion with that of the coacervation of micelles from the aqueous phase. They concluded that the repulsive forces between the micelles decreases due to the neutralization of surface charge of micelles by counterions. The reduction in repulsive forces enhances the aggregation of micelles as the attractive forces between the micelles become dominant. This theory was verified by measuring the surface charge density of the equilibrated oil droplets in the middle phase (9). It was observed that the surface charge density increases to a maximum at the salinity at which the middle phase begins to form. Beyond this salinity, the surface charge density decreases in the
three-phase region. Based on several observations of different surfactant/brine/oil systems, Chan and Shah (31) proposed the mechanism of middle phase microemulsion formation as shown in Figure 7. In general, the higher the solubilization of brine or oil in the middle phase microemulsion, the lower the interfacial tension with the excess phases. The salinity at which equal volumes of brine and oil are solubilized in the middle phase microemulsion is referred to as optimal salinity for the surfactant/oil/brine systems under given physicochemical conditions (21, 22). Previous investigators (22, 29, 30) have shown that the oil recovery is maximum near the optimal salinity of the system. Therefore, one can conclude that the middle phase microemulsion plays a major role in enhanced oil recovery processes.

Using various physicochemical techniques such as high resolution NMR, viscosity and electrical resistivity measurements, Chan and Shah (31) have proposed that the middle phase microemulsion in three-phase systems at and near optimal salinity is a water-external microemulsion of spherical droplets of oil. Extended studies to characterize the middle phase microemulsions by several techniques including freeze-fracture electron micrographs revealed the structure as a water-external microemulsion (31). The droplet size in the middle phase microemulsion decreases with increasing salinity. The freeze-fracture electron microscopy of a middle phase microemulsion is shown in Figure 8. This system was extensively studied by Reed and Healy (21–23). It clearly indicates that the discrete spherical structure of the droplets in a continuous aqueous phase is consistent with the mechanism proposed in Figure 7. It should be pointed out that several investigators (32–39) have proposed the possibility of bicontinuous structure or coexistence of water-external and oil-external microemulsions in the middle phase. For very high surfactant concentration (30–40%) systems, the existence of anomalous structures which are neither conventional oil-external nor water-external microemulsions, have been proposed to explain some unusual behavior of these systems (32–36).

Solubilization. The effectiveness of surfactant formulations for enhanced oil recovery depends on the magnitude of solubilization. By injecting a chemical slug of complete miscibility with both oil and brine present in the reservoir, 100% oil recovery can be achieved.

The effect of hydrated radii, valency and concentration of counterions on oil-external and middle phase microemulsions was investigated by Chou and Shah (40). It was observed that 1 mole of CaCl₂ was equivalent to 16–19 moles of NaCl for solubilization in middle phase microemulsion, whereas for solubilization in oil-external microemulsions, 1 mole of CaCl₂ was equivalent to only 4 moles of NaCl. For monovalent electrolytes, the values for optimal salinity for solubilization in oil-external and middle phase microemulsions are in the order: LiCl > NaCl > KCl > NH₄Cl, which correlates with the Stokes radii of hydrated counterions. The optimal salinity for middle phase microemulsions and critical electrolyte concentration varied in a similar fashion with Stokes radii of counterions, which was distinctly different for the solubilization in oil-external microemulsions. Based on these findings, it was
concluded that the middle phase microemulsion behaves like a water continuous system with respect to the effect of counterions (40).

The effect of alcohol concentration on the solubilization of brine has been studied in this laboratory (41). It was observed that there is an optimal alcohol concentration which can solubilize the maximum amount of brine and can also produce ultralow interfacial tension. The optimal alcohol concentration depends on the brine concentration of the system. The effect of different alcohols on the equilibrium properties and dynamics of micellar solutions has been studied by Zana (42).

Phase Behavior. The surfactant formulations for enhanced oil recovery consist of surfactant, alcohol and brine with or without added oil. As the alcohol and surfactant are added to equal volumes of oil and brine, the surfactant partitioning between oil and brine phases depends on the relative solubilities of the surfactant in each phase. If most of the surfactant remains in the brine phase, the system becomes two phases, and the aqueous phase consists of micelles or oil-in-water microemulsions depending upon the amount of oil solubilized. If most of the surfactant remains in the oil phase, a two-phase system is formed with reversed micelles or the water-in-oil microemulsion in equilibrium with an aqueous phase.

The phase behavior of surfactant formulations for enhanced oil recovery is also affected by the oil solubilization capacity of the mixed micelles of surfactant and alcohol. For low-surfactant systems, the surfactant concentration in oil phase changes considerably near the phase inversion point. The experimental value of partition coefficient is near unity at the phase inversion point (28). The phase inversion also occurs at the partition coefficient near unity in the high-surfactant concentration systems (31). Similar results were also reported by previous investigators (43) for pure alkyl benzene sulfonate systems.

Figure 9 shows the effect of surfactant concentration on the volume of the middle phase microemulsion. It is interesting that the plot goes through the origin indicating that even at very low surfactant concentrations, a microscopic amount of the middle phase microemulsion must exist at the interface between oil and brine.

Salinity Tolerance. As the petroleum reservoir salinity can be very high, the surfactant formulations should be designed for high salt tolerance. The widely used petroleum sulfonates for enhanced oil recovery exhibit relatively low salt tolerance in the range 2–2.5% NaCl concentration, and even smaller for the optimal salinity. The presence of divalent cations in the brine decreases the optimal salinity of surfactant formulations (44).

Since optimal salinity leads to a favorable condition for maximum oil recovery, one would like to design methods to adjust the optimal salinity of a given surfactant formulation (45,46). Figure 10 shows the optimal salinity of a mixed surfactant formulation consisting of a petroleum sulfonate and an ethoxylated sulfonate. It is evident that the optimal salinity of the formulation increases with increasing concentration of ethoxylated sulfonate, the optimal salinity increases from 1% to 24% NaCl brine. Moreover, it is interesting to note that these formulations, when equilibrated with
oil, produce middle phase microemulsion with very low interfacial tension (< \(10^{-3}\) dynes/cm). Similar results were also obtained using ethoxylated alcohols in surfactant formulations by previous investigators (42). It is interesting that the ethoxylated sulfonate alone (curve F in Figure 10) is unable to produce ultralow interfacial tension. However, when mixed with petroleum sulfonate, it produces very low interfacial tension. Therefore, the surfactant formulations consisting of mixed petroleum sulfonates and ethoxylated sulfonates or alcohols are promising for enhanced oil recovery from high salinity reservoirs.

**Macroemulsions in Enhanced Oil Recovery Processes**

As the surfactant slug is injected into the reservoir, the mixing of injected slug with reservoir components takes place. The mixing of surfactant with reservoir oil and brine often produces emulsions. Moreover, the reservoir parameters such as porosity, pressure, temperature, composition of connate water and crude oil as well as gas-oil ratio affect the formation of oil field emulsions.

Usually, the formation of stable macroemulsions in the oil fields is considered undesirable and can cause severe problems. Previous investigators (48-50) have reported poor oil recovery due to problems associated with stable emulsions. In addition, water-in-oil emulsions should be resolved before the oil refining process because presence of considerable amounts of emulsified water in crude oil increases the cost of oil transportation and leads to other maintenance problems. Because of corrosion problems, most pipelines do not accept crude oil with significant amount of emulsified water. On the other hand, McAuliffe (51) has shown a beneficial effect of macroemulsions in oil recovery as their injection into sandstone cores increased sweep efficiency. According to this concept, the emulsion droplet enters a pore constriction smaller than itself. For an emulsion to be most effective, the oil droplets in the emulsion must be larger than the pore-throat constrictions in the porous media. The injected emulsion enters the highly permeable zones, which in turn reduces the channeling of water. Therefore, water starts to flow into low permeable zones, resulting in a greater sweep efficiency. Based on this concept, a field test was conducted which showed an improvement in oil recovery by macroemulsion flooding process. In order to understand the effect of macroemulsions on the oil recovery process, the following parameters should be discussed.

**Electrophoretic Mobility.** The electrophoretic mobility of the crude oil droplets as a function of caustic concentration has been determined in relation to enhanced oil recovery (52). It was observed that a maximum in electrophoretic mobility corresponds to a minimum in interfacial tension at the crude oil/caustic interface (Figure 11). The maximum electrophoretic mobility at minimum interfacial tension can be attributed to the ionization of carboxyl groups present in the crude oil, which in turn determine the charge density at the crude oil/caustic interface, depending on NaOH concentration.

The experimental procedure used for the measurement of interfacial tension and the electrophoretic mobility to determine the
optimum caustic concentration is extremely time consuming and laborious. Therefore, optical transmission or absorbance measurements were made on diluted emulsions to overcome this problem. There was a very good correlation between the ultralow interfacial tension and absorbance measurements. It has been observed for several crude oils that the caustic concentration which yields the maximum absorbance also shows a maximum in electrophoretic mobility and a minimum in interfacial tension. These parameters play a prominent role in the oil recovery by caustic flooding process.

### Transient Processes.

There are several transient processes such as formation and coalescence of oil drops as well as their flow through porous media, that are likely to occur during the flooding process. Figure 12 shows the coalescence or phase separation time for hand-shaken and sonicated macroemulsions as a function of salinity. It is evident that a minimum in phase separation time or the fastest coalescence rate occurs at the optimal salinity ($S^*$). The rapid coalescence could contribute significantly to the formation of an oil bank from the mobilized oil ganglia. This also suggests that at the optimal salinity of the system, the interfacial viscosity must be very low to promote the rapid coalescence.

The flow through porous media behavior of various macroemulsions was studied by measuring the pressure drop across a porous medium (Figure 13). It is obvious that a minimum in pressure drop occurs near the optimal salinity of the surfactant formulation. One can conclude that the interfacial tension is an important parameter which influences the pressure drop across porous media ($S^*$). Figure 14 shows a very interesting and an important correlation between the rate of coalescence in macroemulsions and the apparent viscosity in the flow through porous media. It was observed that a minimum in apparent viscosity for the flow of macroemulsions in porous media coincides with a minimum in phase separation time at the optimal salinity. This correlation between the phenomena occurring in the porous medium and outside the porous medium allows us to use coalescence measurements as a screening criterion for many oil recovery formulations for their possible behavior in porous media. It is very likely that a rapidly coalescing macroemulsion may give a lower apparent viscosity for the flow in porous media ($S^*$).

The variation in the shape of an oil drop (n-Octane) upon contacting a surfactant formulation consisting of 0.05% TRS 10–80 in 1% NaCl as a function of time is shown in Figure 15. It is evident that as surfactant molecules migrate from the aqueous phase to the interface and subsequently, to the oil phase, the interfacial tension decreases and the spherical drop gradually flattens out. This flattening time reflects the rate at which surfactant molecules accumulate at the oil-brine interface. As shown in Table 1, there is a good correlation between the flattening time, interfacial tension, and the oil recovery. The reduction in flattening time leads to favorable oil recovery efficiency ($S^*$). Table 2 shows the effect of alcohol concentration on various parameters and oil recovery in porous media. It is evident that the flattening time decreases strikingly in the presence of alcohol suggesting that the alcohol promotes the mass transfer to the interface and a rapid reduction in the magnitude of the interfacial tension.
Figure 12. Effect of salinity on the phase separation or coalescence rate of hand-shaken and sonicated macroemulsions.

Figure 13. Effect of salinity on the pressure drop-flow rate curves of sonicated macroemulsions.

Figure 14. A correlation between the apparent viscosity and coalescence rate of sonicated macroemulsions.
Figure 15. An illustration of the drop flattening process for an octane drop upon contacting 0.05% TRS 10-80 in 1% NaCl.

Table I. IFT, Flattening Time and Oil Recovery Efficiency of 0.05% TRS 10-80 in 1% NaCl vs. n-Octane at 25°C

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>IFT (mN/m)</th>
<th>FLATTENING TIME (Seconds)</th>
<th>OIL RECOVERY (X10P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Fresh Oil/1% NaCl</td>
<td><em>50.8</em>*</td>
<td>∞</td>
<td>61-63</td>
</tr>
<tr>
<td>II. Fresh Oil/Equilibrated Surfactant Solution</td>
<td>0.731</td>
<td>6600</td>
<td>44-52</td>
</tr>
<tr>
<td>III. Fresh Oil/Fresh Surfactant Solution</td>
<td>0.627</td>
<td>480</td>
<td>75-77</td>
</tr>
<tr>
<td>IV. Equilibrated Oil/2% NaCl</td>
<td>0.121</td>
<td>900</td>
<td>83</td>
</tr>
<tr>
<td>V. Equilibrated Oil/Equilibrated Surfactant Solution</td>
<td>0.0267</td>
<td>240</td>
<td>94</td>
</tr>
<tr>
<td>VI. Equilibrated Oil/Fresh Surfactant Solution</td>
<td>0.00209</td>
<td>15</td>
<td>-</td>
</tr>
</tbody>
</table>

*Flattening time is defined as the time required for the n-octane drop to gradually flatten out.

**Octane/H₂O, 20°C, IFT = 50.8 mN/m, "Interfacial Phenomena", Davies and Rideal, Chapter 1, p. 17 Table 1, Academic Press, N.Y. 1963.

+Sandpack dimensions: 1.06" dia. x 7" long; Permeability = 3 darcy; flow rate: 2.3 ft./day.
### Table II. The Effect of IBA on Flattening Time, IF, IVF, Partition Coefficient, and Oil Displacement Efficiency

<table>
<thead>
<tr>
<th>System</th>
<th>Oil or NaCl vs. n-octane</th>
<th>0.1% IBA vs. 0.02% TBS vs. 0.1% TBS vs. 0.1% NaCl</th>
<th>0.1% IBA vs. 0.02% TBS vs. 0.1% TBS vs. 0.1% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane</td>
<td>S100-02</td>
<td>420 sec</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>S100-04</td>
<td>&lt; 1 sec</td>
<td>0.024</td>
</tr>
<tr>
<td>Kelly Yeast Oil</td>
<td>S100-04</td>
<td>420 sec</td>
<td>0.025</td>
</tr>
<tr>
<td>S100-02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**All displacement experiments were carried out with non-equilibrated systems in sand packs at 21°C. Values and core data are given in Table I.**

The mixing of surfactant and polymer in the porous medium occurs due to both dispersion and the excluded volume effect for the flow of polymer molecules in porous media, which in turn could lead to the phase separation. Figure 16 illustrates the schematic explanation of the surfactant-polymer incompatibility and concomitant phase separation. We propose that around each micelle there is a region of solvent that is excluded to polymer molecules. However, when these micelles approach each other, there is overlapping of this excluded region. Therefore, if all micelles separate out then the excluded region diminishes due to the overlap of the shell and more solvent becomes available for the polymer molecules. This effect is very similar to the polymer depletion stabilization (35). Therefore, this is similar to osmotic effect where the polymer molecule tends to maximize the solvent for all possible configurations.

In oil recovery processes, the formation of an oil bank is very important for an efficient oil displacement process in porous media. This was established from studies on the injection of an artificial oil bank followed by the surfactant formulation which can produce ultra-low interfacial tension with the injected oil. We observed that the oil recovery increased considerably and the residual oil saturation decreased with the injection of an oil bank as compared to the same studies carried out in the absence of an injected oil bank (56). Figure 17 schematically represents the oil bank formation and its propagation in porous media, which is analogous to the snowball effect. If an early oil bank is formed then it moves through the porous medium accumulating additional oil ganglia resulting in an excellent oil recovery, whereas a late oil bank formation will result in a poor oil recovery.

In summary, several phenomena occurring at the optimal salinity in relation to enhanced oil recovery by macro- and microemulsion flooding are schematically shown in Figure 18. It is evident that the maximum in oil recovery efficiency correlates well with various transient and equilibrium properties of macro- and microemulsion systems. We have observed that the surfactant loss in porous media is minimum at the optimal salinity presumably due to the reduction in the entrainment process for the surfactant phase. Therefore, the maximum in oil recovery may be due to a combined effect of all these processes occurring at the optimal salinity.

Demulsification. It is necessary to demulsify the macroemulsions formed due to surfactant flooding. The problem of separating two immiscible liquids when one is dispersed within the other is frequently encountered in petroleum technology. Demulsification by definition is agglomeration and coalescence of dispersed phase, eventually resulting in a breakdown of the macroemulsion into two separate phases. A wide variety of materials such as cotton, wool, glass fibers and Teflon have been used to promote the coalescence rate of macroemulsions. The addition of acids or bases apparently causes neutralization of the particle charge and subsequently, leads to coagulation of droplets.

Several patents have been granted for methods to demulsify the crude oil macroemulsions. In the electrical method, the imposition
Figure 16. Schematic illustration of surfactant-polymer incompatibility leading to phase separation in mixed surfactant-polymer systems.

Figure 17. Schematic illustration of the injection of an oil bank and the subsequent "snowball effect" in enhanced oil recovery.

Figure 18. A summary of various phenomena occurring at the optimal salinity in relation to enhanced oil recovery by surfactant-polymer flooding.
of high potentials on macroemulsions leads to coagulation of water droplets. In enhanced oil recovery methods by chemical flooding, the macroemulsions are stabilized by the surfactants. In order to break these macroemulsions, it is necessary to rupture the interfacial film. This can be achieved to some extent by heat treatment. A widely used method for the breaking of oil field macroemulsions is the use of elevated temperatures (27-28). By the action of heat, the surfactant becomes more soluble in either the aqueous phase or oil phase, which destabilizes the interfacial film, and the separation of two phases occurs.

Literature Cited

20. Wilson, P.M.; Murphy, C.L.; Foster, W.R.; SPE 5812 presented at SPE Improved Oil Recovery Symposium, Tulsa, OK, 1976.
32. Shinoda, K., J. Colloid Interface Sci., 1967, 26, 70.
REFERENCES


RECEIVED December 11, 1984