HANDBOOK OF MICROEMULSION SCIENCE AND TECHNOLOGY

edited by

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Gillette Research Institute
Gaithersburg, Maryland

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Hopewell Junction, New York

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Applications of Microemulsions in Enhanced Oil Recovery

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I. INTRODUCTION

The recovery of oil from a reservoir can be divided into three stages. In the primary oil recovery process, oil is recovered due to the pressure of natural gases, which forces the oil out through production wells. When this pressure decreases to a point where it is no longer capable of expelling the oil, water is injected to repressurize the reservoir. This is generally called secondary oil recovery or water flooding. The average oil recovery during the primary and secondary stages is nearly 35% of oil-in-place. The purpose of the tertiary (enhanced) oil recovery process is to recover at least part of the remaining oil-in-place. Enhanced oil recovery (EOR) methods can be divided into two major groups: thermal processes and chemical flooding processes. In situ combustion, steam injection, and wet combustion methods fall into the first category, whereas caustic flooding, surfactant flooding, micellar polymer flooding, and CO_2 flooding fall into the second category of processes [1–5].

After water flooding, residual oil is believed to be in the form of discontinuous oil ganglia trapped in the pores of rocks in the reservoir. The two major forces acting on an oil ganglion are viscous forces and capillary forces, the ratio of which is represented by the capillary number. At the end of the secondary oil recovery stage, the capillary number is around 10^{-6}. To recover additional oil, the capillary number has to be increased to around $10^{-3}-10^{-2}$, which can be achieved by decreasing the interfacial tension at the oil/brine interface. Surfactants are used for this purpose.

II. SURFACTANTS IN OIL RECOVERY

A microemulsion is generally defined as a thermodynamically stable, isotropic dispersion of two relatively immiscible liquids, consisting of microdomains of one or both liquids stabilized by an interfacial film of surface-active molecules [1]. Microemulsions may be classified as water-in-oil (W/O) or oil-in-water (O/W) depending on the dispersed and con-

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† Deceased.

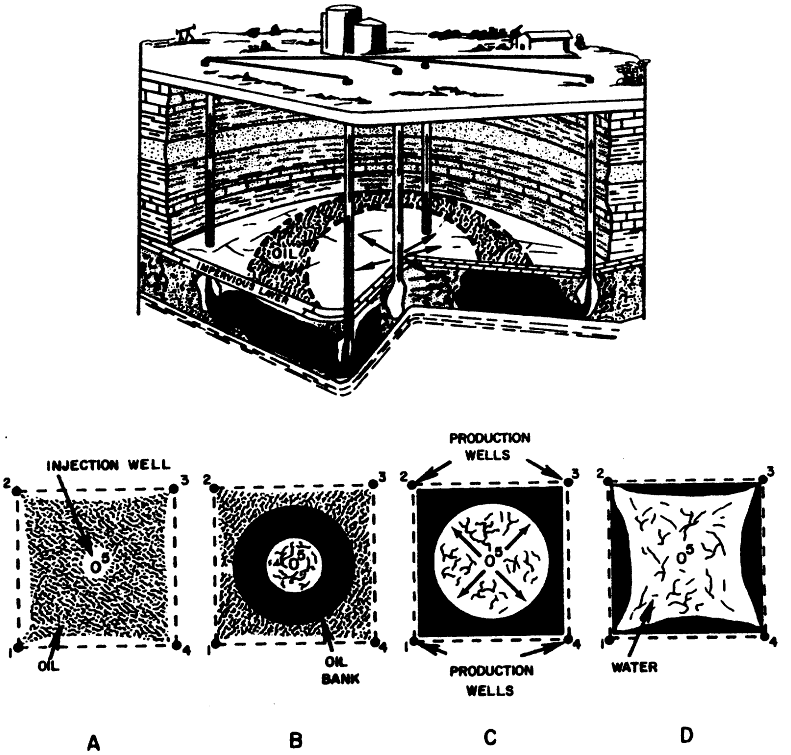

Figure 1 Three-dimensional view of a petroleum reservoir and the displacement of oil by water or surfactant solutions. Prior to EOR, oil in the reservoir is trapped within the rock in the form of oil ganglia (A). Injection of a surfactant solution mobilizes the oil ganglia (B) and forms an oil bank. The oil bank approaches (C) and subsequently reaches (D) the production wells.

tinuous phases present. In both cases, the dispersed phase consists of monodispersed droplets containing comparable amounts of oil and water. Some of these systems may show a bicontinuous, or even a cubic, structure [3,4,6].

Microemulsions were first introduced by Schulman and his coworkers in 1943 [7]. They explained that microemulsions were spontaneously formed with the uptake of water or oil due to a negative transient interfacial tension, which allows the free energy to decrease as the total oil/water interfacial area increases [7,8]. At equilibrium, the oil/water interfacial tension becomes zero or a very small positive number on the order of 10^{-2}–10^{-3} mN/m.

Surfactant solutions for use in improved oil recovery can be of high (2.0–10.0%) or low (0.1–0.2%) surfactant concentration. In the low concentration systems, the ultralow interfacial tension occurs when the aqueous phase of the surfactant solution is at about the apparent critical micelle concentration (cmc).

In the high surfactant concentration systems, a middle-phase microemulsion forms that is in equilibrium with excess oil and brine. The basic components of this microemulsion are surfactant, water, oil, alcohol, and salt. High surfactant concentrations in the injected plug result in a relatively small pore volume (about 3–20%) compared to micellar solutions (15–60%). Figure 1 schematically shows a three-dimensional view of a petroleum reservoir. At the end of water flooding, the oil that remains in the reservoir is believed to be in the form of oil ganglia trapped in the pore structure of the rock as shown in Fig. 1A. These

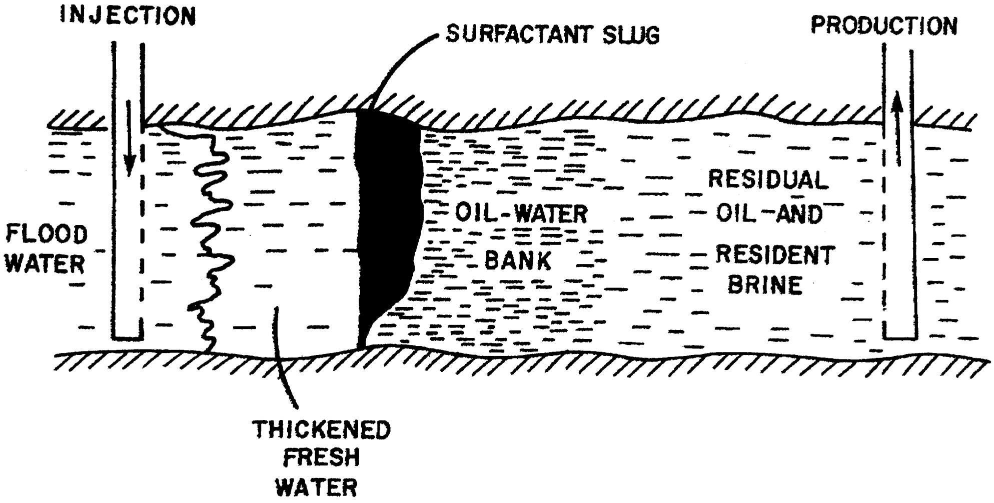

Figure 2 Two-dimensional view of the surfactant–polymer flooding process. Injection of a surfactant solution to coalesce the oil ganglia is followed by injection of a polymer slug to push the oil to production wells.

oil ganglia are entrapped because of capillary forces. However, if a surfactant solution is injected to lower the interfacial tension of the oil ganglia from its value of 20–30 mN/m to 10^{-3} mN/m, the oil ganglia can be mobilized and can move through narrow necks of the pores. Such mobilized oil ganglia form an oil bank as shown in Fig. 1B. Figures 1C and 1D diagrammatically illustrate the oil bank approaching the production well and the subsequent breakthrough of the drive water.

Wagner and Leach [9], Taber [10], and Melrose and Brader [11] 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 [12] also showed that interfacial tension at the crude oil/brine interface, which plays a dominant role in controlling capillary forces, should be reduced by a factor of 10,000 to a value of 10^{-3}–10^{-4} mN/m to achieve efficient displacement of crude oil. Such low interfacial tensions can be achieved by appropriate surfactant formulations. Figure 2 schematically illustrates a two-dimensional view of the surfactant–polymer flooding process. A polymer slug, which is used for mobility control (i.e., to make the water more viscous), immediately follows after injection of the surfactant [13]. During this process, the displaced oil droplets coalesce and form an oil bank (see Fig. 3).

Once an oil bank is formed in the reservoir, 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 is necessary to minimize the entrapment of oil in the porous medium. The leading edge of the oil bank coalesces with additional oil ganglia. Besides interfacial tension and interfacial viscosity, another parameter that influences the oil recovery is the surface charge at the oil/brine and rock/brine interfaces [14,15]. It has been shown that a high surface charge density leads to lower interfacial tension, lower interfacial viscosity, and consequently higher recovery of oil as shown in Fig. 4.

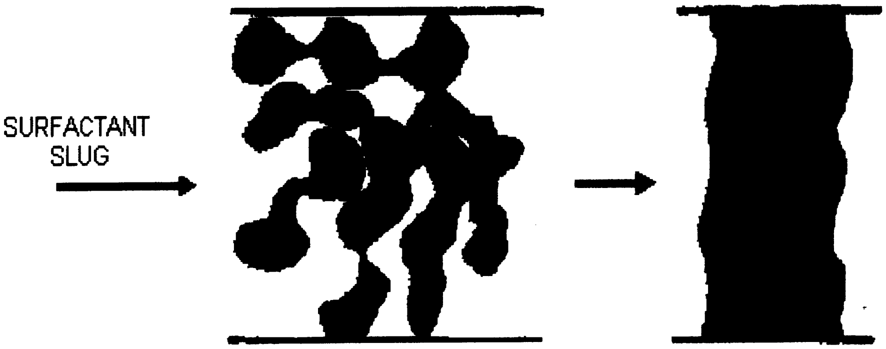

Figure 3 Schematic diagram of coalescence of oil ganglia due to low interfacial viscosity during the surfactant–polymer flooding process. Displaced oil ganglia must coalesce to form a continuous oil bank. For this, a very low interfacial viscosity is necessary.

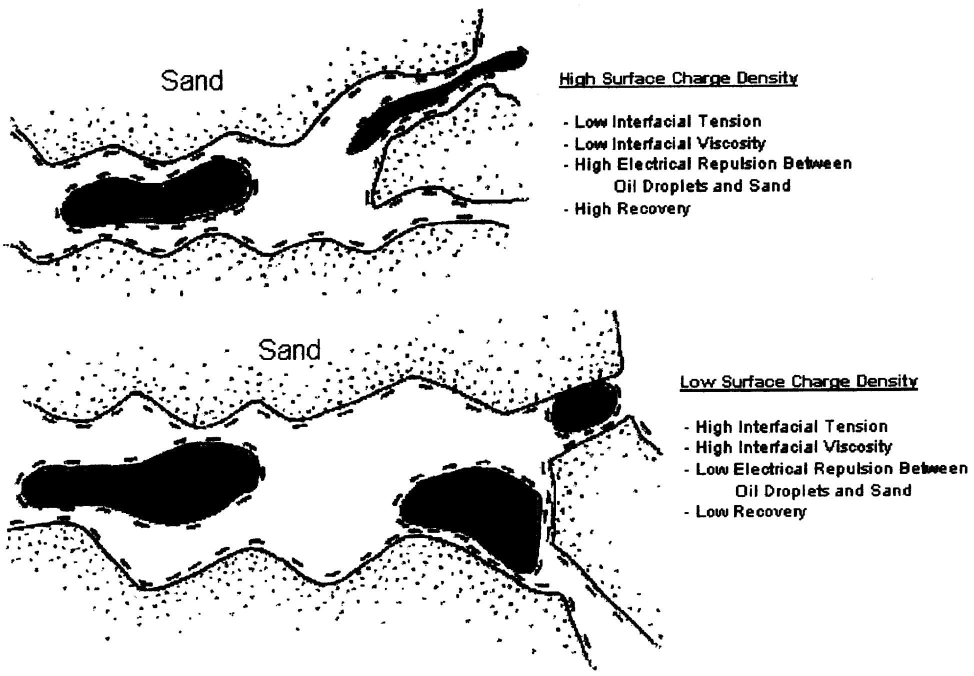

Figure 4 Schematic diagram of the role of surface charge in the oil displacement process. High surface charge density results in high oil recovery, while low surface charge density results in low oil yields.

III. ENHANCED OIL RECOVERY BY MICROEMULSION FLOODING

The success of microemulsion flooding for improving oil recovery depends on the proper selection of chemicals in formulating the surfactant slug. During the past 30 years, it has been reported that many surfactant formulations for enhanced oil recovery generally form multiphase microemulsions [16–19]. From these studies, it is evident that a variety of phases can exist in equilibrium with each other. Figure 5 shows the effect of salinity on the phase behavior of oil–brine–surfactant–alcohol systems. The microemulsion slug partitions into three phases: a surfactant-rich middle phase and surfactant-lean brine and oil phases [20–22] in the intermediate salinity range. The surfactant-rich phase is the middle-phase microemulsion [22]. The middle-phase microemulsion consists of solubilized oil, brine, surfactant, and alcohol. The lower to middle to upper phase ($l \rightarrow m \rightarrow u$) transition of the microemulsion phase can be obtained by varying any of the eight variables listed in Fig. 5.

A. Interfacial Tension

It is well established that ultralow interfacial tension plays an important role in oil displacement processes [16,18]. The magnitude of interfacial tension can be affected by the surface concentration of surfactant, surface charge density, and solubilization of oil or brine. Experimentally, Shah et al. [23] demonstrated a direct correlation between interfacial tension and interfacial charge in various oil–water systems. Interfacial charge density is an important factor in lowering the interfacial tension. Figure 6 shows the interfacial tension and partition coefficient of surfactant as functions of 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 observed by Baviere [24] for the paraffin oil–sodium alkylbenzene sulfonate–isopropyl alcohol–brine system.

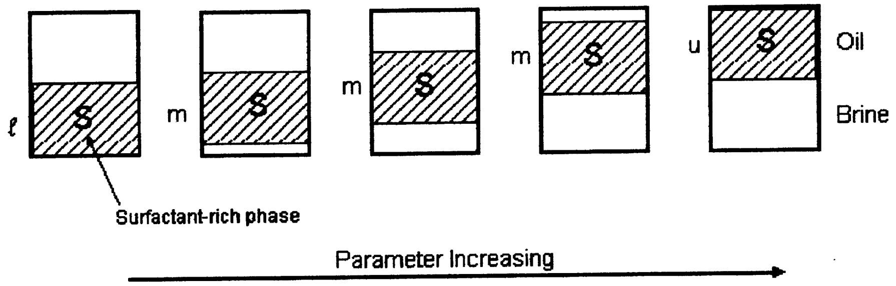

Figure 5 Illustration of the factors influencing the transition of a microemulsion from lower to middle to upper phase. The transition from lower to middle to upper phase ($l \rightarrow m \rightarrow u$) occurs by (1) increasing salinity, (2) decreasing oil chain length, (3) increasing alcohol concentration (C_4, C_5, C_6), (4) decreasing temperature, (5) increasing total surfactant concentration, (6) increasing brine/oil ratio, (7) increasing surfactant solution/oil ratio, and (8) increasing molecular weight of surfactant.

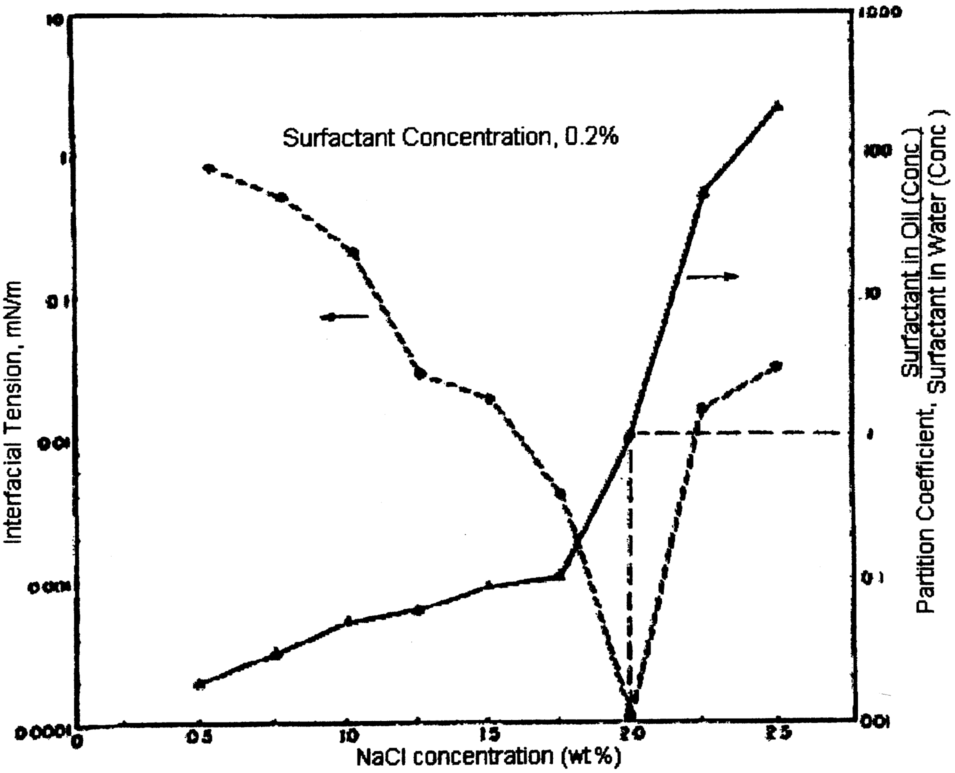

Figure 6 Effect of salinity on interfacial tension and surfactant partitioning in 0.2% TRS 10-80–brine–octane system.

Chan and Shah [25] 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 salinity, oil chain length, and surfactant concentration, a minimum in interfacial tension was found to occur when the equilibrated aqueous phase was at the 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 occurred when the concentration of the surfactant monomers in the aqueous phase was at a maximum.

B. Formation and Structure of Middle-Phase Microemulsion

The $l \rightarrow m \rightarrow u$ transitions of the microemulsion phase as a function of various parameters are shown in Fig. 5. Chan and Shah [26] compared the phenomenon of the formation of middle-phase microemulsions with that of the coacervation of micelles from the aqueous phase. They concluded that the repulsive forces between the micelles decreased due to the neutralization of the surface charge of micelles by counterions. The reduction in repulsive forces enhanced the aggregation of micelles, as the attractive forces between the micelles became predominant. This theory was verified by measuring the surface charge density of the equilibrated oil droplets in the middle phase [14].

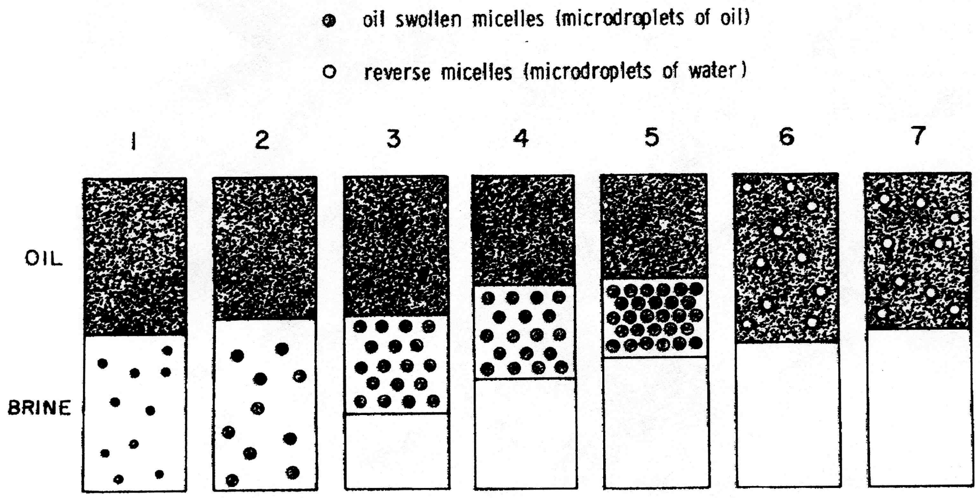

Figure 7 Schematic illustration of middle-phase microemulsion formation in surfactant–brine–oil systems. (●) Oil-swollen micelles (microdroplets of oil); (○) reverse micelles (microdroplets of water).

It was observed that the surface charge density increased to a maximum at the salinity at which the middle phase began to form. Beyond this salinity, the surface charge density decreased in the three-phase region. Based on several observations of different surfactant–brine–oil systems, Chan and Shah [26] proposed the mechanism of middle-phase microemulsion formation shown in Fig. 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 the optimal salinity for the surfactant–oil–brine systems under given physicochemical conditions [20,22]. Some investigators [21,27] showed that 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 [26] proposed that the middle-phase microemulsion in three-phase systems at or 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 microscopy revealed the structure to be a water-external microemulsion [26]. The droplet size in the middle-phase microemulsion decreases with increasing salinity. A freeze-fracture electron micrograph of a middle-phase microemulsion is shown in Fig. 8. It clearly indicates that the discrete spherical structure of the oil droplets in a continuous aqueous phase is consistent with the mechanism proposed in Fig. 7. This system was extensively studied by Reed and coworkers [20–22].

C. 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% recovery of oil should be possible.

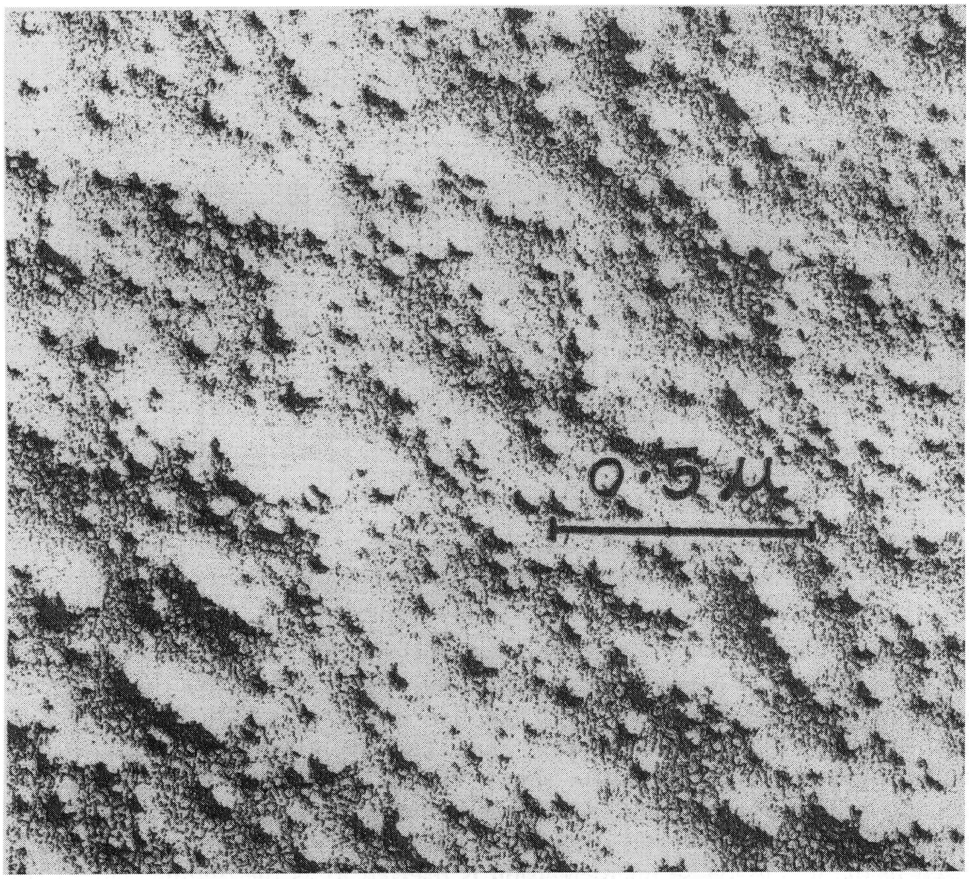

Figure 8 Freeze-fracture scanning electron micrograph of a middle-phase microemulsion. The spherical shapes are oil droplets suspended within the continuous aqueous phase. (The black bar represents 0.5 μm.)

The effect of hydrated radii, valence, and concentration of counterions on oil-external and middle-phase microemulsions was investigated by Chou and Shah [28]. It was observed that 1 mol of $CaCl_2$ was equivalent to 16–19 mol of NaCl for solubilization in middle-phase microemulsions, whereas for solubilization in oil-external microemulsions, 1 mol of $CaCl_2$ was equivalent to only 4 mol of NaCl. For monovalent electrolytes, the values for optimal salinity of solubilization in oil-external and middle-phase microemulsions are in the order $LiCl > NaCl > KCl > NH_4Cl$, 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 miroemulsions. Based on these findings, it was concluded that the middle-phase microemulsion behaved like a water-continuous system with respect to the effect of counterions [28].

The effect of alcohol concentration on the solubilization of brine was studied by Hsieh and Shah [29]. They observed that there was an optimal alcohol concentration that could solubilize a maximum amount of brine and 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 was studied by Zana [30].

D. 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 splits into two phases, and the aqueous phase consists of micelles or oil-in-water microemulsions, depending on the amount of oil solubilized. If most of the surfactant remains in the oil phase, a two-phase system is formed with reverse micelles or the water-in-oil microemulsions 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 concentration surfactant systems, the surfactant concentration in the oil phase changes considerably near the phase inversion point.

In summary, several phenomena occurring at optimal salinity in relation to enhanced oil recovery by microemulsion flooding are shown in Fig. 9. It is evident that the maximum in oil recovery efficiency correlates well with various transient and equilibrium properties of microemulsion systems. We have observed that surfactant loss in porous media is minimum at optimal salinity, presumably due to reduction in the entrapment process for the surfactant phase. Therefore, the maximum oil recovery may be due to the combined effect of all these processes occurring at optimal salinity.

IV. CURRENT PROGRESS

Until about 1980, the use of surfactants in enhanced oil recovery was mainly in the area of microemulsion flooding. Current low oil prices, however, have not provided adequate financial incentives for continued use of such methods [31], and the oil industry has turned to "gas" flooding, especially with carbon dioxide, as the main enhanced oil recovery tool. With the cheaper production of many of the commonly used surfactants, polymers, and alkalies, enhanced oil recovery with surfactants can once again become an affordable method of industrial oil production [32]. Additional advances in technology and equipment are making possible studies of interfacial systems at high temperatures and pressures [33]. The results of these studies will greatly expand the viability of oil recovery by microemulsion flooding techniques.

One recent attempt to decrease the costs associated with surfactant flooding has been to inject surfactant-producing bacteria into oil reservoirs. This technique involves the injection of selected microorganisms into the reservoir and the subsequent stimulation and transportation of their growth products in order to recover more of the oil-in-place [34]. Some of the mechanisms proposed by which these microbes can stimulate oil production include reservoir repressurization, modification of reservoir rock, degradation and alteration of oil, decrease of viscosity, and increase in emulsification [35].

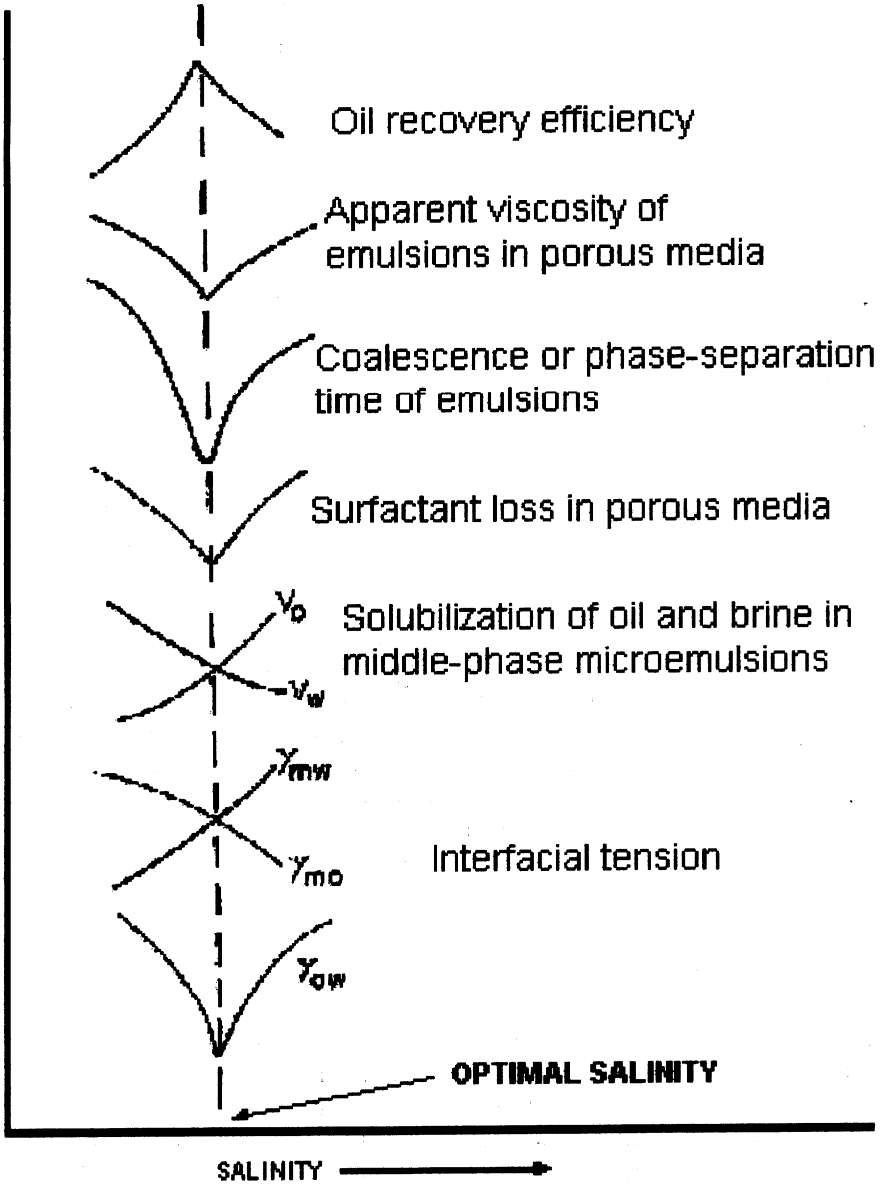

Figure 9 A summary of various phenomena occurring at optimal salinity in relation to enhanced oil recovery.

V. CONCLUSIONS

Microemulsions are clear, isotropic dispersions of water or oil droplets 10–100 nm in diameter dispersed in a continuous oil or water phase and stabilized by an interfacial film of surfactants. Due to these unique properties, microemulsions are relevant in a variety of technological processes, including enhanced oil recovery (EOR). Several concepts and processes involving EOR are described in a keynote paper presented by Shah at the First European Symposium on Enhanced Oil Recovery [36]. Although oil prices are currently too low to justify the use of surfactants in enhanced oil recovery, advances in technology and lower surfactant costs may one day make the use of surfactants a viable approach in industrial oil recovery.

ACKNOWLEDGMENTS

We thank the industrial consortium of the Alberta Research Council, American Cyanamid Co., Amoco Production Co., Atlantic-Richfield Co., BASF-Wyandotte Co., British Petroleum Co., Calgon Corp., Cities Service Oil Co., Continental Oil Co., Ethyl Corp., Exxon Production Research Co., Getty Oil Co., Gulf Research and Development Co., Marathon Oil Co., Mobil Research and Development Co., Nalco Chemical Co., Phillips Petroleum Co., Shell Development Co., Standard Oil of Ohio Co., Stepan Chemical Co., Sun Oil Chemical Co., Texaco Inc., Union Carbide Corp., Union Oil Co., Westvaco, Inc., and Witco Chemical Co. for supporting the University of Florida Enhanced Oil Recovery Research Program. We also gratefully acknowledge the support of the Department of Energy (grant DE-AC1979BC10075), Defense Advanced Research Project Agency (DARPA), National Science Foundation (grants CBT-8807321 and CTS-8922574), and Electric Power Research Institute (ERPI grant RP800922).

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