A Study of Surfactant Flooding at High Salinity and Hardness

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ABSTRACT

The main purpose of this work was to evaluate surfactant systems in terms of viscosities and retention levels in Berea sandstone and in terms of their oil displacement efficiencies. Commercially available surfactants can act as effective cosurfactants to petroleum sulfonates in high salinity and high hardness environments. Such systems can achieve the ultralow interfacial tensions required for effective tertiary oil recovery. The two cosurfactants producing effective systems distribute between the phases in such a way that one is between the upper and middle phases, and the other is between the middle and lower phases. The cosurfactant material increases the excess phase uptake into the microemulsion-rich phase which is opposite to the behavior of alcohols used in low salinity formulations. Tertiary oil in Berea sandstone is recoverable by such surfactant systems in high salinity and high hardness environments. The chromatographic separation of surfactant species has been observed. Retention levels are quite high and must be reduced substantially before these systems can be commercialized.

INTRODUCTION

A large number of chemicals have been suggested for use as agents for enhanced oil recovery (EOR) by surfactant flooding. However, most field applications have been limited to using low-molecular-weight (MW) alcohols and petroleum sulfonates manufactured from feedstocks whose MW ranged from 350 to 500 g/mol. One of the greatest difficulties encountered in the application of these formulations has been their ineffectiveness in reservoir brines of higher salinity and high divalent ion content. Removal of these ions by displacement with softer brines is usually impractical due to complicated ion exchange phenomena between reservoir rock and injected fluids, or else impossible due to a lack of fresh water sources.

A variety of chemical compounds have been patented for use as cosurfactants with the goal of making petroleum sulfonates more compatible with reservoir fluids. Although most of the research in this area has dealt with fairly pure compounds (1), this work summarizes efforts being made at the Petroleum Recovery Institute using commercially available surfactant materials. Most chemicals reported in this paper are of commercial quality that have been supplied by chemical companies with the understanding that these compounds would be available in large quantities at reasonable cost.

Many factors must be incorporated into the design of an effective EOR microemulsion system. The more important ones reported in this work include the phase behavior and basic data studies followed by displacement tests in Berea sandstone that must be used to assess oil recovery potential.

MATERIALS

An earlier study examined the use of a large number of surfactant material (2), whereas this paper will describe the results obtained with two of the more promising formulations. The selected chemical components were: system A—Petrostep 465 (petroleum sulfonate)/Empilan NP9 (nonylphenol ethoxylate)/Klearfac 040 (phosphate ester); and system B—Petrostep 465/Richonol 7103 (alkyl ether sulfate)/Empilan KB3 (polyethanoxyalkyl ether). The suppliers were listed in the previous study (2). All components were provided free of charge by their manufacturers and were used as received.

Salts used in the synthetic brine were laboratory-grade $CaCl_2$, $MgCl_2$ and NaCl. The relative amounts of Na^+, Ca^{++}, and Mg^{++} in the brine were kept at the ratio of 20:2:1, with the total dissolved solids (TDS) content of 80,000 ppm, since this proportion is fairly typical for water in many Alberta reservoirs. Pure-grade octane was used as the hydrocarbon phase in all experiments.

Two of the chemicals were analyzed by high pressure liquid chromatographic (HPLC) techniques: (a) Petrostep 465—using water/methanol/acetonitrile/sodium dihydrophosphate solvents in the ion-exchange column; and (b) Empilan NP9—using water/acetonitrile solvent in C_{18}-Bondpak column. The Klearfac 040 was analyzed by a modified ASTM procedure for determination of phosphorus.

It is estimated that the Petrostep 465 analyses were the most accurate, with errors not exceeding 10%. The remaining surfactants were analyzed with errors estimated to be ca. 30%. These error estimates are based on assessing the material balances obtained during phase behavior studies.

Phase Behavior and Basic Data Measurements

The detailed methodology of surfactant and cosurfactant screening for the development of middle-phase microemulsions has been described previously (2). When oil, brine and surfactant components are combined, a surfactant-rich or microemulsion phase usually results. When there is excess oil and brine lying, respectively, above and below the single surfactant-rich phase, it is termed a middle-phase microemulsion. In general, one tries to combine surfactants and cosurfactants so that the largest possible amounts of brine and oil are solubilized in nearly equal volumes into the middle-phase microemulsion.

High levels of solubilization of both oil and brine are important for a number of reasons. First, as solubility of either oil or brine is increased, the interfacial tension between the microemulsion phase and the excess oil or brine phases is reduced (3). With high and equal solubilization, then, the interfacial tensions between both excess phases and the microemulsion phase are low and approximately equal. Thus, capillary forces responsible for trapping of oil, which are proportional to interfacial tensions, can be exceeded and residual oil can be mobilized by the microemulsion. Subsequently, due to low interfacial tension between the excess brine and the microemulsion, the microemulsion phase is not trapped and thus can itself be displaced by the chase water. Second, the capacity to solubilize and thus displace large quantities of oil with a brine-rich solution reduces the cost of the injected chemicals.

It is therefore important to develop formulations that have high levels of solubilization and which consequently reduce interfacial tensions to the range of a few μN/m. Additionally, it is advantageous that the ultralow levels of interfacial tensions be maintained over a fairly broad range of variables such as surfactant concentrations, surfactant/cosurfactant ratios, brine/oil ratios, salinities, divalent ion concentrations and possibly temperature. Previous work involved the evaluation of surfactant systems in terms of their volumetric phase behavior and interfacial tension measurements (2). The main purpose of this work was to extend this evaluation of these systems in terms of the viscosities of surfactant-containing phases and surfactant retention levels in Berea sandstone, and finally in terms of their oil displacement efficiencies.

The following combinations of surfactants produced middle-phase microemulsions which produced ultralow interfacial tensions between the microemulsion phase and the excess oil and brine phases. The volumetric phase behavior measured for the following formulations: system A—20 g/L Petrostep 465, 12 g/L Empilan NP9 and 8 g/L Klearfac 040; system B—36 g/L Petrostep 465, 36 g/L Richonol 7103 and 31.5 g/L Empilan KB3 when mixed with 8% TDS brine and *n*-octane, is presented in Figure 1. For system A, it can be seen that a middle-phase microemulsion formed with a 50:50 volumetric mixture of brine and oil. The amount of solubilization of aqueous and oleic phases into the microemulsion was nearly equal and was quite insensitive to changing the brine/oil ratio from 50:50 to 70:30. The formation of a middle-phase microemulsion in system B is shown to be quite sensitive to the brine/oil ratio as it passes from a lower phase microemulsion at a 50:50 ratio, through the optimal middle-phase behavior at 60:40, and finally into an upper phase situation at 70:30. Interfacial tensions at equal solubilization in system A are about 4 μN/m, whereas those at the optimal ratio are about 0.1 μN/m for system B. This interplay between phase stability and the level of interfacial tension is typical. Although system B would mobilize more of the trapped residual oil, system A would more likely be propagated in the middle-phase microemulsion form if the tensions are sufficiently low to prevent phase trapping.

Since the combined effects of dilution, dispersion, adsorption and phase partitioning of surfactant species on phase behavior may alter both the absolute and relative concentrations of individual species during a surfactant flood, the dependence of phase behavior on species concentrations is essential for a design of surfactant flooding experiments. The dependence of system A phase behavior on species concentration is shown, by comparing Figures 2 and 3, to be altered by brine/oil ratios. Although the addition of Petrostep 465 has relatively little effect in the 50:50 mixture, an alteration to 70:30 leads to increased oil solubilization in the microemulsion phase for the same change in Petrostep 465 content. It can also be seen that the addition of Empilan NP9 promotes brine solubilization whereas the addition of Klearfac 040 increases oil solubilization. In previous phase behavior work, it was shown that, by blending cosurfactant materials of such opposing tendencies with a hydrocarbon and brine that might be appropriate to a reservoir application, it was possible to tailor surfactant/cosurfactant mixtures to have optimal (equal brine and oil solubilization) phase behavior.

For system B, shown in Figures 4 and 5, the Petrostep 465 and Empilan KB3 lead to upper phase behavior with increasing concentration. However, the role of Richonol 7103 is somewhat less obvious in promoting an increase in lower phase solubilization with increasing concentration and may, in part, account for the restricted range of the middle-phase region pictured in Figure 1.

Further illustration of the more stable phase behavior properties of system A is given in Figure 6 which shows the dilution effect of adding a 70:30 brine/oil mixture on the middle-phase microemulsion phase volume. The microemulsion volume remains fairly constant, and the volumes of oil and brine solubilized (proportional to the microemulsion phase thicknesses above and below the dotted lines in

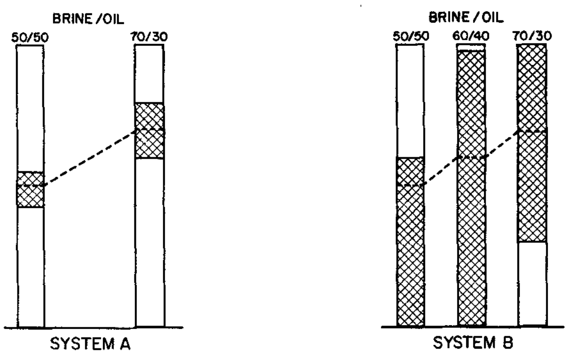

FIG. 1. Volumetric phase behavior of systems A and B.

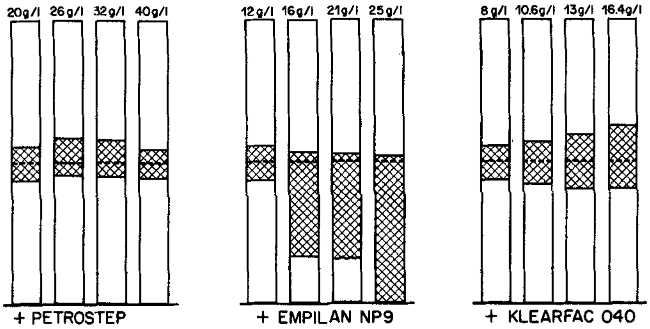

FIG. 2. Dependence of system A phase behavior on surfactant/cosurfactant concentrations (50:50 brine/oil ratio).

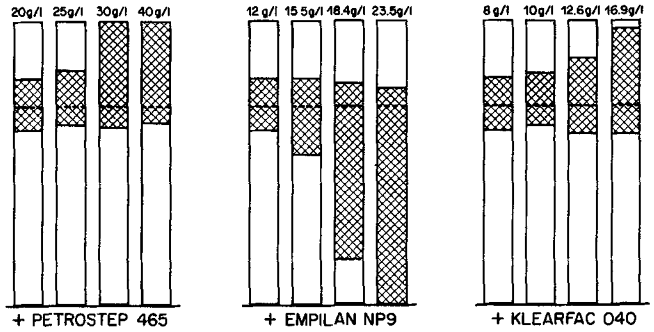

FIG. 3. Dependence of system A phase behavior on surfactant/cosurfactant concentrations (70:30 brine/oil ratio).

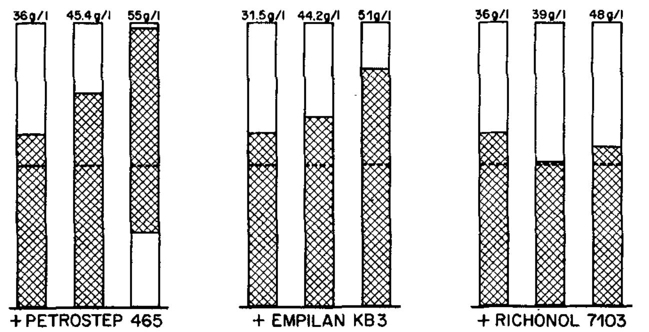

FIG. 4. Dependence of system B phase behavior on surfactant/cosurfactant concentrations (50:50 brine/oil ratio).

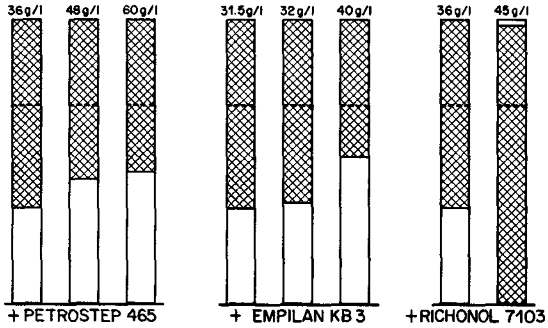

FIG. 5. Dependence of system B phase behavior on surfactant/cosurfactant concentrations (70:30 brine/oil ratio).

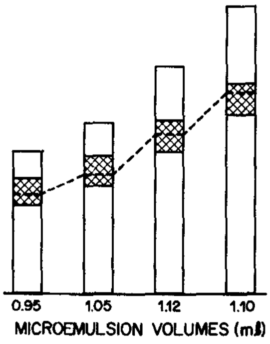

FIG. 6. Effect of dilution on phase behavior of system A.

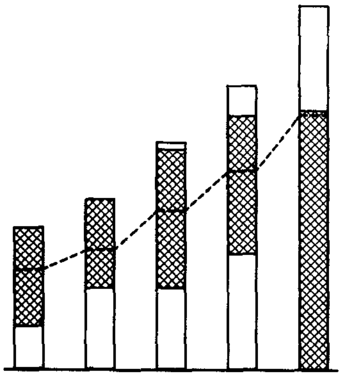

FIG. 7. Effect of dilution on phase behavior of system B.

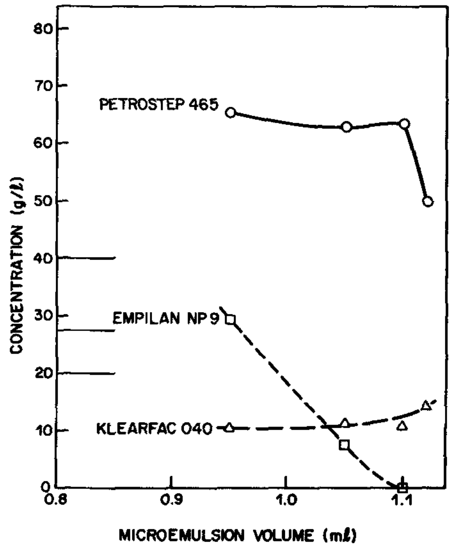

FIG. 8. Dependence of surfactant/cosurfactant concentrations in microemulsion phase on dilution (see Fig. 6).

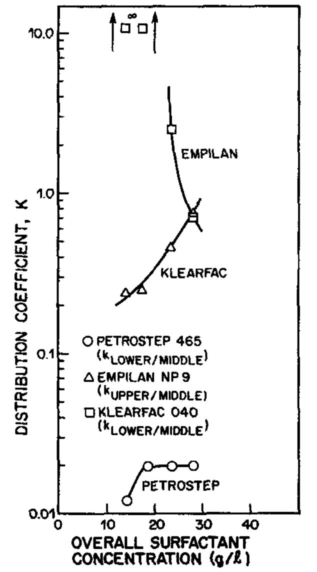

FIG. 9. Dependence of surfactant/cosurfactant phase distribution coefficients on dilution (see Fig. 6).

Fig. 6) change only by small amounts. In system B, pictured in Figure 7, the system appears to move from upper- (or middle-) phase to lower-phase behavior with a much more limited range displaying middle-phase microemulsion behavior.

It is evident that phase behavior changes can be quite abrupt and that such changes are likely to occur during a complex displacement process such as surfactant flooding. Specific changes depend on adsorption levels and the amounts of mixing at the microemulsion/oil/brine displacement front and at the chase water/microemulsion drive front. In order to anticipate and understand the possible phase behavior possibilities, it is necessary to quantify the distribution of surfactant components. Experimentally, this is a difficult problem compounded by the need to analyze minute amounts in both complex aqueous and crude oil environments. To date, only the analytical procedures for system A have been developed and tested.

For the dilution sequence pictured in Figure 6, the surfactant concentration in the microemulsion phase and the partitioning of surfactant materials in the excess phases have been determined and are presented in Figures 8 and 9, respectively. As the microemulsion volume increases, there are reductions in its Petrostep 465 and Empilan NP9 concentrations and a slight increase in its Klearfac 040 concentration (Fig. 8). In Figure 9, it can be seen that virtually all of the sulfonate, Petrostep 465, is in the microemulsion phase with about 2% existing in the aqueous phase. This behavior is consistent with the numerous reports on low-salinity systems reported elsewhere (4). Most interesting is the fact that Empilan NP9 partitions into the oleic phase whereas Klearfac 040 partitions into the brine phase.

Based on the limited data, the following observations can be made: (a) as the amount of brine taken into the microemulsion phase increases, there is increased partitioning of Klearfac 040 from the excess brine into the microemulsion phase; and (b) as the amount of oil in the microemulsion phase is reduced, the amount of Empilan NP9 in the middle phase drops to zero. Thus, it can be concluded that increased uptake of each excess phase must be accompanied by its own surfactant material which would appear to enhance its solubility. This aspect of the work is in a formative stage and more data need to be gathered. Then, as various surfactant structures are tested, optimal cosurfactant materials can be deduced.

A final aspect that strongly impacts on the displacement behavior of microemulsions is its viscometric behavior. Ideally, a flood is designed so that the mobility of the microemulsion matches that of the oil and brine being displaced, and the mobility of the drive water is less than that of the microemulsion it is displacing. If the mobilities are not reasonably matched, displacement instabilities that can lead to a deterioration of the microemulsion slug and a collapse of the process may result. Figure 10 shows microemulsion viscosities for system A that resulted by scanning salinity. The viscosities are low for brine-continuous microemulsions at low salinity and for oil-continuous microemulsions at high salinity. The maxima that occur correspond to the boundaries of three-phase behavior, and a local minimum occurs near the point of equal solubilization of brine and oil. It should be noted here that viscosities were measured with a capillary viscometer and thus may not completely reflect porous media behavior. Figure 11 shows similar behavior with system A for a scan of Klearfac 040 concentration. Consequently, the aspect of the depletion of surfactant components away from the surfactant-rich phase must be considered for a field application.

Also shown in Figure 11 is the effect of adding a simple alcohol, 2-butanol. The solubilization of oil and brine is much lower than that for system A without alcohol. Cosurfactants in systems A and B increase the middle phase volume at optimal solubilization; the alcohol acts in reverse and reduces microemulsion volume. The alcohol promotes increased phase stability but also causes higher interfacial tensions. The addition of alcohol also tempers the viscosity behavior so that the mobility design could be made easier.

Displacement Experiments

Ultimately, the ability of a surfactant formulation to recover oil and to propagate within porous rock must be examined using displacement tests in cores. The most common type of experiment is that which is performed in linear cores. The displacement results reported here were performed with 2.5 cm x 2.5 cm square, and 30 cm long Berea sandstone cores at low displacement pressures and 25 C. The apparatus used is pictured in Figure 12.

Examples of tertiary flooding results for systems A and B are described next. The surfactant materials to be injected were dispersed in a brine in such concentrations that, when mixed with an equal volume of oil, would lead to middle-phase microemulsion behavior. For system A, the interfacial tension between the middle phase and the excess oil was determined to be 4 μN/m. The brine slug was injected at residual oil saturation within the core and was followed by surfactant-free brine until oil production from the core ceased. A measure of the amount of surfactant, Q, in the slug is given by Q = C x V, where C is the concentration in g/L, and V is the slug volume in terms of percentage pore volume of the core.

Recovery results using system A and a value of Q = 2500 are presented in Figure 13. Ultimate recovery of oil amounted to only 9% of the residual oil in place (ROIP). In order to determine if the recovery was limited by the amount of surfactant injected, the slug size was doubled to Q = 5000 with the result (pictured in Fig. 14) that oil recovery increased substantially to 52% ROIP. Summaries of results are tabulated in Table I.

System B gave slightly better results (Figs. 15 and 16, Table I), with a recovery of 27% ROIP for Q = 2500 and 56% ROIP for Q = 5000. It would seem reasonable to relate the slightly better oil recovery for system B to higher levels of solubilization of brine and oil, and hence, lower

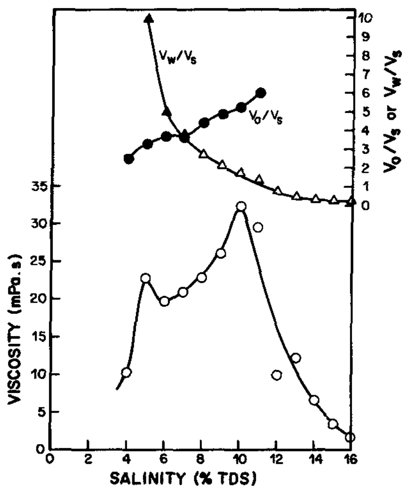

FIG. 10. Dependence of viscosity of surfactant-rich phase on brine salinity (system A).

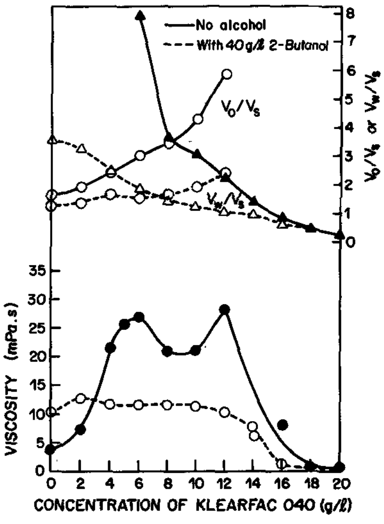

FIG. 11. Dependence of viscosity of surfactant-rich phase on cosurfactant concentration (system A).

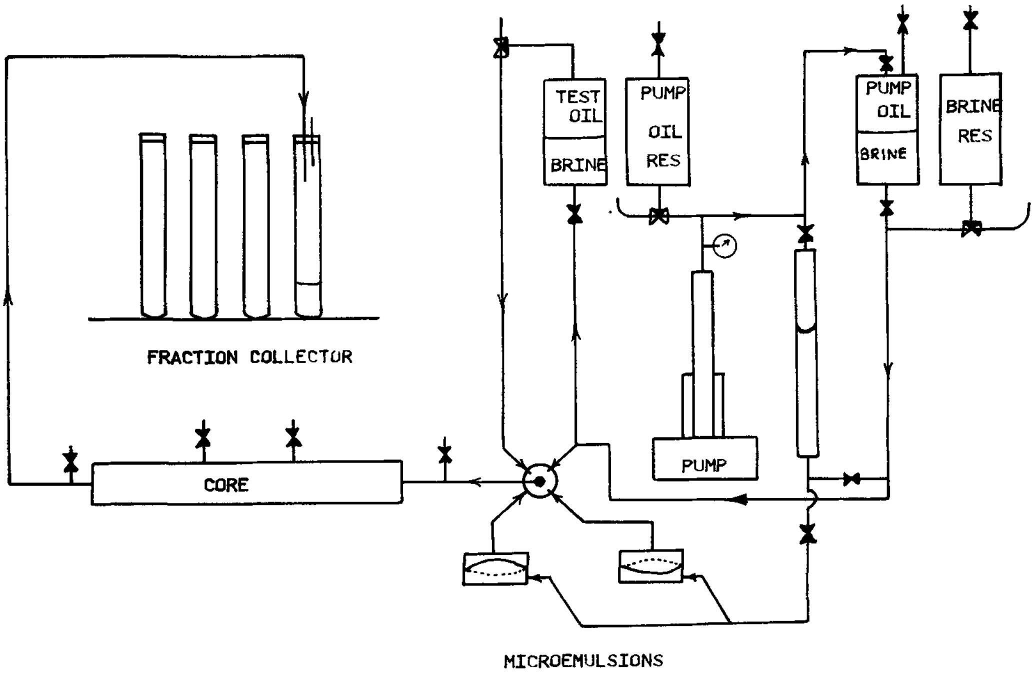

FIG. 12. Schematic of displacement apparatus.

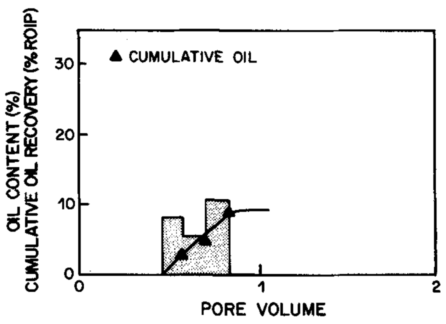

FIG. 13. Oil recovery by system A (Q = 2,500).

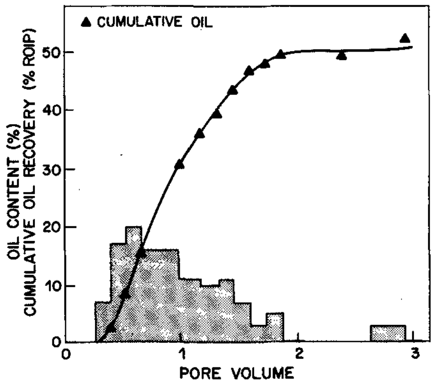

FIG. 14. Oil recovery by system A (Q = 5,000).

TABLE I

Summary of Flooding Experiments

Type of experiment	Q = C[g/L] X PV[%]	Residual oil after water-flood (%)	Residual oil after surfactant flood (%)	Oil recovery (% ROIP)	Highest Fractional flow of oil (%)
System A	2,500	32	29.2	9	11
System A	5,000	36	17.4	52	20
System A— after lignosulfonate preflush	2,500	35	30.5	13	24
System B	2,500	32	23.0	27	26
System B	5,000	33	14.3	56	30
Modified system A	5,000	34	22.6	34	31

levels of interfacial tensions.

In both systems, it can be seen that the recoveries at low volumes of surfactant injection were inferior to those in which large slug volumes were used, and the adsorption of surfactant would appear to be a major problem. One way of attempting to reduce adsorption is through the use of sacrificial adsorption agents. Lignosulfonates, which are a waste byproduct of the sulfite pulp-making process, have been suggested as possible candidates, and one core flood using lignosulfonate ERA 16 at 30 mg/L concentration and a value of Q = 750 was conducted with system A. The results for a surfactant slug size equivalent to Q = 2500 are presented in Figure 17. The oil recovery value of 13% ROIP, although an improvement over that without lignosulfonate (9% ROIP, Fig. 13), is not substantial. Applying a scarificial agent may have interfered with the phase behavior of the surfactant system and its application is a complex phenomenon that is currently under detailed study.

In order to obtain a better quantification of adsorption, an experiment was conducted with system A components. Their combination, however, was not optimal with the concentration of Petrostep 465 being two times and the two cosurfactants being 1.5 times that injected in the previous steps with system A. Figure 18 gives the oil recovery of 34% ROIP obtained for a value of Q = 5000 which was poorer than the 52% ROIP corresponding to the optimal combination in Figure 14. The production of surfactant/cosurfactant materials in the effluent is given in Figure 19. All of the surfactant materials arrived at the core exit near the end of the oil production, and the results include measurements of surfactant materials in all of the produced phases. The Petrostep 465 and Empilan NP9 were produced first, with the Empilan NP9 reaching 3% of the injected concentration at 0.75 pore volume. The Petrostep 465 peak occurred later at about 1 pore volume and its height was ca. 6% of the injected value. The other cosurfactant, Klearfac

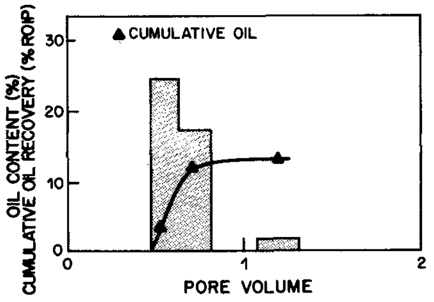

FIG. 17. Oil recovery by system A after lignosulfonate preflush (Q = 2,500).

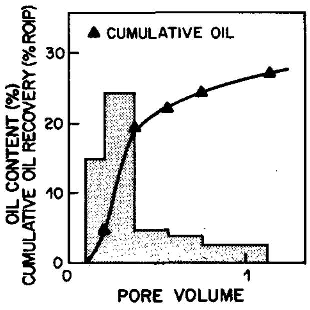

FIG. 15. Oil recovery by system B (Q = 2,500).

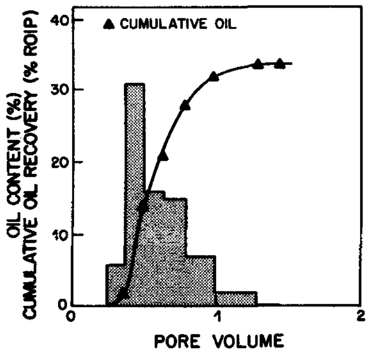

FIG. 18. Oil recovery by modified system A (Q = 5,000).

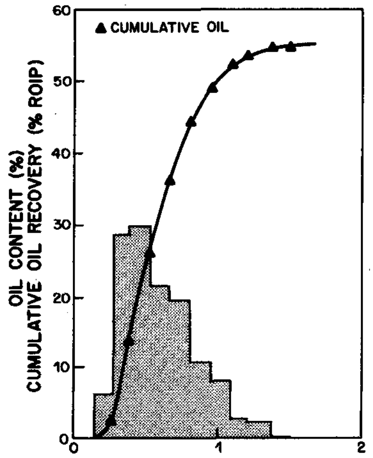

FIG. 16. Oil recovery by system B (Q = 5,000).

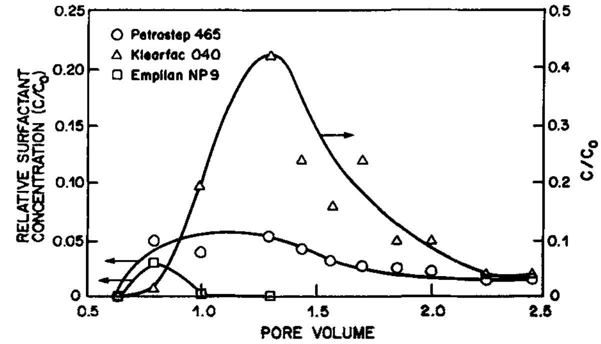

FIG. 19. Surfactant/cosurfactant effluent profiles (modified system A, Q = 5,000).

040, though it was slightly delayed at breakthrough, showed the highest peak at 20% of the injected concentration. In terms of surfactant retention in this particular experiment, the levels were: Petrostep 465, 2.7 mg/g rock; Empilan NP9, 1.3 mg/g rock; and Klearfac 040, 0.5 mg/g rock, for a total of 4.5 mg/g rock. These levels are fairly high when compared to the low salanity formulation retention levels of between 0.5 and 1 mg/g rock. Consequently, additional work with sacrificial agents and, perhaps, with less adsorptive materials will be required before commercialization can be realized.

Variations in the arrival time, and adsorption and retention of components clearly show the severity of chromatographic separations that can occur. Due to variations in the ratios of component quantities, many phase transitions of the surfactant would likely occur during the course of the displacement. This aspect is of major concern and can only be addressed by very complete phase behavior and adsorption studies combined with numerical simulation.

ACKNOWLEDGMENTS

L.A. Baxter, V. Masata and R. French performed most of the experimental work reported in this paper and B. Moore typed the manuscript.

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Enhanced Oil Recovery Chemical Needs

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ABSTRACT

A large fraction of known petroleum resources will not be recoverable by conventional methods. Enhanced oil recovery (EOR) is costly, but a significant amount of production is possible at current world oil prices, and additional production is possible at prices equivalent to synthetic alternates. Many opportunities exist for uses of chemicals in EOR. In particular, polymers and surfactants that are effective and stable at high temperatures and high salinities are needed for surfactant flooding to achieve its potential. Potential markets can be large in the 1990s and beyond. Many factors other than improved chemicals will impact on the future development of EOR. Risks to the chemical industry in new product development would appear to be reasonable, as long as oil producers continue a major effort to develop EOR processes.

INTRODUCTION

Enhanced oil recovery (EOR) offers many challenging opportunities for the chemical industry. However, if one does not have a background in petroleum production, the initial challenge is often to understand why chemicals can play such an important role in EOR. The objective of this paper is to provide a general background for those readers who are unfamiliar with EOR. It provides information on the following subjects: what is enhanced oil recovery? Why is so much oil left behind after conventional oil production ceases? What processes are being developed to recover this oil? What role can chemicals play? What chemical properties are needed? Why is the interrelationship between surfactants and polymers so important in surfactant EOR processes? Beyond chemical needs, what other constraints exist on EOR processes that use chemicals? It is hoped this information will suggest areas where the chemical industry can make major contributions to EOR.

BACKGROUND

Enhanced Oil Recovery Targets

In 1981, Welch (1) spoke on the "Status and Future of Enhanced Oil Recovery." In the U.S., as of Jan. 1980, ca. 120 billion barrels had been produced from known resources of almost 500 billion barrels (Fig. 1). Another 30 billion barrels is thought to be producible using conventional techniques. But, over 300 billion barrels, or about 70% of the total known resources, is expected to remain unrecoverable by conventional methods. In the U.S., most of the unrecoverable oil is light and medium oil. Heavy oil comprises only a relatively small fraction of the total U.S. resources.

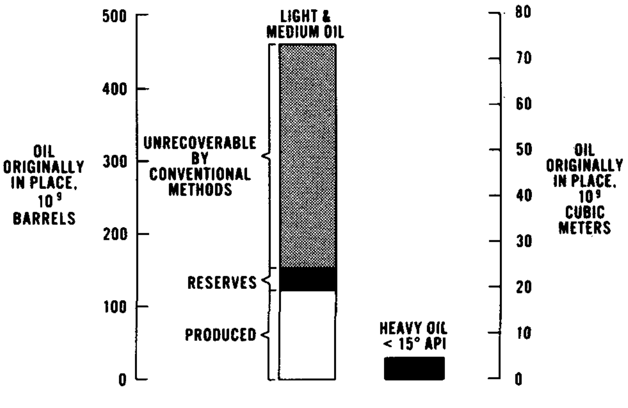

FIG. 1. Known U.S.A. petroleum resources as of Jan. 1, 1980.