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THE EFFECT OF ALCOHOL ON SURFACTANT MASS TRANSFER ACROSS THE OIL/BRINE INTERFACE AND RELATED PHENOMENA

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ABSTRACT

The effect of alcohol on surfactant mass transfer from bulk solution to the oil/dilute micellar solution interface was studied. Various interfacial properties of the surfactant solutions and their ability for displacing oil were determined. For the surfactant-oil-brine systems studied, the interfacial tension (IFT) and surfactant partition coefficient did not change when isobutanol was added to the following systems: 0.1% TRS 10-410 in 1.5% NaCl vs n-dodecane and 0.05% TRS 10-80 in 1.0% NaCl vs n-octane. On the other hand, the interfacial viscosity, oil drop flattening time (i.e. the time required for an oil droplet to flatten out after being deposited on the underside of a polished quartz plate submerged in the micellar solution) and oil displacement efficiency were influenced markedly by the addition of alcohol.

In the presence of isobutanol, the oil/dilute micellar solution interface became more fluid and the flattening time decreased from 90 seconds to less than a second or 420 seconds to less than a second, and the final oil saturation decreased from 30% to 5.36% and 11.73% to 1.28% respectively for the two systems mentioned above. Furthermore, it was observed that after the arrival of the oil bank, the ΔP leveled off for the isobutanol containing systems, whereas it continuously increased for the systems without isobutanol. This observation is consistent with the proposed role of alcohol in lowering the interfacial viscosity and promoting coalescence of oil ganglia in porous media.

The flattening time was strikingly lower for the surfactant + alcohol system as compared to the flattening times in the presence of the surfactant or alcohol alone in the brine, suggesting that the rate of achieving ultra low IFT at the oil/micellar solution interface is strikingly enhanced by the presence of isobutanol resulting in greater oil recovery.

In order to delineate the effect of surfactant mass transfer on in situ behavior of oil ganglia, we carried out several oil displacement experiments using equilibrated and nonequilibrated oil/micellar solution systems. For equilibrated systems, the oil displacement efficiency showed an excellent correlation with IFT and capillary number. However, for unequilibrated systems, the oil displacement efficiency depended on salinity. Below optimal salinity, the oil displacement efficiency almost remained the same for both equilibrated and nonequilibrated systems, whereas at and above optimal salinity the oil displacement efficiency was higher for non-equilibrated systems as compared to equilibrated systems. This was attributed to mass transfer rate effects in these systems. Both sand packs and Berea cores gave similar results. The results of this study demonstrate the importance of transient phenomena at oil/dilute micellar solution interface for oil displacement process with emphasis on the effect of alcohol and salinity.

INTRODUCTION

Laboratory studies on oil displacement efficiency by surfactant-polymer flooding process have been reported by a number of investigators.[1-10] In general, the process is such that after being conditioned by field brine or preflush, a sandstone core or a sand pack is oil-saturated to the irreducible water content. It is then waterflooded to the residual oil level. Finally, a slug of surfactant solution followed by a mobility buffer is injected. The slug of surfactant solution can either be aqueous or oleic with a surfactant plus alcohol concentration of 5-15%.

Because of the cost and the time factors involved, oil displacement studies are always preceded by certain test tube screening procedures. Specifically, the interfacial tension (IFT) of less than 0.01 dyne/cm is recognized to be the necessary but not the sufficient criterion for selection of a surfactant system. Many investigators[10-15] have shown that ultralow IFT of less than 0.001 dyne/cm can be achieved with less than 0.1 wt.% surfactant solution. Since this low surfactant concentration system is several hundred times more dilute than the ones used in a typical surfactant-polymer flooding process, the economics dictates that the oil displacement by such low surfactant concentration solution should be explored. Moreover, it should be established that the IFT obtained in the oil/brine/sur-

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factant system after a rigorous equilibration procedure in a test tube can be indeed achieved in situ when the surfactant solution passes by the entrapped oil ganglia in porous media. In other words, is the rate of mass transfer of surfactant to and across the interface a major limiting factor in achieving ultra low IFT in porous media? The present paper attempts to answer some of these questions by comparing the behavior of equilibrated and non-equilibrated oil/surfactant solution systems in porous media.

In general, the surfactant formulations used for enhanced oil recovery contain a short chain alcohol. The addition of alcohol can influence the viscosity, IFT and birefringent structures of micellar solutions as well as coalescence rate of oil ganglia. The present paper reports the effect of addition of isobutanol to a dilute petroleum sulfonate (< 0.1% conc) solution on IFT, surface shear viscosity, surfactant partitioning, the rate of change of IFT (or flattening time) of oil drops in surfactant solutions and oil displacement efficiency. The two surfactant systems chosen for this study indeed exhibited ultra low IFT under appropriate conditions of salinity, surfactant concentration and oil chain length.[11,15,19]

MATERIALS AND METHODS

Surfactant Solutions:

Commercial petroleum sulfonate TRS 10-80 (80% active) or TRS 10-410 (61.2% active) obtained from Witco Co. and Fisher A.C.S. certified grade NaCl crystals (1% NaCl) were dissolved in distilled, deionized water to make the surfactant stock solutions by weight. Then, they were diluted by brine (1% NaCl) to the desired concentration just before the start of each run, so that the surfactant aging effect was minimized. The purity of n-octane or n-dodecane (Chemical Samples Co.) was > 99% and was used as the oil to equilibrate the surfactant solution at the volume ratio of 1:2 in a glass-stoppered 1-liter separatory funnel. After vigorous shaking, the surfactant and oil mixture was left standing for 10 days at room temperature until a clear mirror-like interface was reached. The equilibrated aqueous and oleic solutions were then drained into separate storage bottles. The effect of alcohol was studied by adding 99% pure isobutanol (IBA) (Chemical Samples Co.) to the surfactant solution at 1:1 weight ratio for the active component in TRS 10-80 or TRS 10-410.

Interfacial Tension Measurements:

Interfacial tension between various oleic and aqueous phases was measured using the Spinning Drop Tensiometer at 25°C. The spinning time and rate were kept constant so that comparative results could be obtained.

Interfacial Viscosity Measurements:

Interfacial viscosity (IFV) was measured using a viscous-traction interfacial viscometer constructed according to Wasan.[16] Teflon particles were used to measure the centerline velocity of oil/water interface.

Contact Angle in Quartz/Brine/Oil Systems:

The wettability of the quartz surface used to simulate the surface of sandstones, was studied by a contact-angle goniometer. Using a microsyringe, an oil drop was deposited on the underside of a smooth,

polished quartz surface submerged in the aqueous solution at 25°C. The angle through the oil phase was measured and Polaroid pictures of the oil drop were taken at different time intervals.

Surfactant Concentration Measurements:

The surfactant concentration in the effluent stream was measured by the two-phase titration method according to Reid et al.[17]

Oil Displacement in Porous Media:

Horizontally mounted sand packs and Berea cores encased in an air-circulating constant temperature box were used for oil displacement efficiency tests. The sand packs, 1.06" diameter by 7.0" long, had an average porosity of 38% and permeability of 3.0 darcy. The Berea cores were 1" square by 12" long cast in epoxy resin within 1.5" diameter by 14" long PVC pipes. They had an average porosity of 18% and permeability of 220 millidarcy.

Having been dry-filled with sands under vibration and tapping, the pack was flushed vertically with carbon dioxide to displace interstitial air. Deionized water was then pumped through and the pore volume (PV) was measured. Since carbon dioxide easily dissolves in water, trapped gas in the pack can be greatly reduced or eliminated. New sand packs and fresh Berea cores were used for each run. The brine salinity in porous media was the same as the salt concentration of surfactant solution. The injected oil and aqueous solutions were either pre-equilibrated or nonequilibrated. Constant fluid velocity of 10 ft/day was maintained during the oil saturation and 2.3 ft/day was maintained during aqueous solution or brine flooding. Because the viscosity of n-octane was 0.5 cp, a favorable mobility was assumed for aqueous surfactant solution flooding. Therefore, no polymer was added in the dilute surfactant solution.

Displacement tests were conducted for equilibrated and non-equilibrated systems. For the effect of surfactant concentration on oil recovery, the total amount of surfactant injected was the same, i.e., the slug size times the concentration was equal (70% PV x 0.5% = 35) for each run.

RESULTS AND DISCUSSION

Effect of Isobutanol on Oil Displacement Efficiency:

The following systems, 0.1% TRS 10-410 with/without 0.06% IBA in 1.5% NaCl vs n-dodecane and 0.05% TRS 10-80 with/without 0.04% IBA in 1.0% NaCl vs. n-octane were examined.

Figure 1 is the cumulative oil recovery profile of the systems studied. It shows that with the addition of 0.06% IBA into the TRS 10-410/n-dodecane system, the oil recovery by direct surfactant solution flooding (i.e. without waterflooding) is improved from 84.37% to 98.32% after 3.5 PV surfactant solution injection. The TRS 10-80/n-octane system showed an increase in oil recovery from 60% to 91% by the addition of isobutanol (Figure 1). It should be noted that the increase in oil recovery occurs only after the major oil bank comes out (i.e. after 1 PV of produced fluid). We propose that the presence of isobutanol promotes the coalescence of oil droplets in porous media leading to a better oil recovery efficiency. A much more drastic difference is seen in the TRS 10-80/n-octane system,

where the tertiary oil recovery increased from 0% without IBA to 76.84% with IBA (See Table 1) after 2.7 PV surfactant solution injection. Thus, for both secondary and tertiary oil recovery processes (i.e. with or without brine flooding stage) carried out in these laboratory scale experiments, the addition of isobutanol enhances the oil recovery efficiency presumably by promoting the coalescence in porous media.

Table 1 shows the effect of the addition of isobutanol on various properties of oil/brine/surfactant systems for TRS 10-410 and TRS 10-80. Because the same IFT values were obtained for the systems with and without IBA (Table 1), the observed differences in oil recovery cannot be explained in terms of any change in IFT. The presence of alcohol did not significantly influence the partition coefficient of surfactant in n-dodecane or n-octane. It is important to emphasize that the partition coefficient changes sharply near the ultra low IFT region.[19] Thus, the partition coefficient does not appear to correlate with the oil displacement efficiency. However, the presence of isobutanol decreases the interfacial viscosity and markedly influences the flattening time of the oil droplets. It has been suggested[18] that a rigid potassium oleate film at the oil/water interface can be liquefied by the penetration of the hexanol molecules in order to produce spherical microemulsion droplets. It has been shown[14] also that for a commercial petroleum sulfonate-crude oil system, the oil droplets with the alcohol coalesce much faster than the ones without alcohol. For the systems studied here, IBA is believed to have penetrated the petroleum sulfonate film as seen by the decrease in IFV. The decrease in interfacial viscosity would presumably promote the coalescence in porous media.

Since the shape of an oil droplet is an indication of IFT as measured in sessile drop method, the oil droplet flattening time reflects the rate of change in IFT. The results clearly show that the presence of alcohol increases the rate of achieving the final value of interfacial tension. This implies that the surfactant is coming to the interface much faster in the presence of alcohol. Zana[20] has shown that the kinetics of micellization is much rapid in the presence of alcohol. This is presumably due to loose packing of mixed micelles containing surfactant and alcohol. Thus, it appears that the kinetics of micellization could influence the rate at which molecules saturate the surface by the breakdown of micelles to provide monomers for adsorption.

We have shown[19] that the interfacial concentration of surfactant depends on the partition coefficient of the surfactant. When the partition coefficient is near unity, a maximum surface concentration of the surfactant is achieved. In flow through porous media, it is expected that achieving the equilibrium condition may take much longer time. Therefore, we investigated the equilibrated and non equilibrated systems in porous media to elucidate their effect on the oil recovery efficiency.

A Comparison of Equilibrated and Nonequilibrated Systems for Oil Displacement Efficiency:

Figure 2 shows the IFT and the percent oil recovery as a function of initial TRS 10-80 concentration in 1% NaCl for equilibrated and nonequilibrated systems. It was observed that for the pre-equilibrated system, 94% oil was recovered at 0.05% TRS 10-80

concentration corresponding to minimum IFT at this concentration. However, for nonequilibriated systems, the maximum oil recovery shifted from 0.05% to 0.1% TRS 10-80 concentration. The maximum oil recovery for nonequilibrated systems was much lower than that observed for equilibrated systems (Figure 2). Since the amount of surfactant injected was the same for each run (0.125 gm), the maximum oil recovery was interpreted as a result of the capillary number vs final oil saturation correlation.[21]

However, this correlation does not seem to hold under the typical (i.e., nonequilibrated) tertiary oil recovery conditions (Case A in Table 2). In order to find the amount of tertiary oil that can be recovered, the sand packs were saturated with fresh (i.e., nonequilibrated) n-octane and were brine-flooded to the residual oil level. A fresh surfactant slug of 0.05% TRS 10-80 in 1% NaCl was then pumped through the sand packs. It was interesting to note that in this case even after an injection of 10 PV surfactant slug, no or very little oil was recovered (Case A in Table 2). Because the effluent surfactant concentration approached that of the injected surfactant concentration, the poor oil recovery cannot be explained by the adsorption of the surfactant on sand particles. The observed excellent oil recovery for the equilibrated system is then believed to be due to the effective surfactant partitioning during equilibration procedure. Thus, for equilibrated systems, the ultra low IFT is achieved quickly in porous media which results in an excellent correlation of oil displacement efficiency with IFT (Figure 2). In general, the oil recovery is better for equilibrated systems as compared to nonequilibrated systems except at 0.5% TRS 10-80 concentration (Figure 2). For this nonequilibrated system, due to slow mass transfer process the interfacial concentration might be similar to equilibrated low surfactant concentration systems. This will cause lower IFT and hence better oil recovery (Figure 2).

Systematic and comprehensive studies on oil displacement by various fluids were made and the results are listed in Table 2 and Figure 3. It is clear that oil recovery in all cases was nearly complete at the end of the fresh PV injection of the surfactant solution (Figure 3). Case A corresponds to the typical tertiary oil recovery process while Case F shows 94% recovery of the equilibrated system (Table 2). A fair comparison of the equilibrated with nonequilibrated systems is Case F vs. Case C, the direct oil displacement by surfactant solution without brine-flooding. The equilibrated system (Case F) is better by 22% (94% vs 72%). This is a clear indication of the importance of surfactant partitioning during oil displacement.

As fresh n-octane in Case B and equilibrated n-octane in Case E were being displaced by both brine and equilibrated surfactant solutions, an oil recovery of 60% and 83% respectively, was observed. Again, the recovery of the equilibrated oil is better by 23%, the equilibrated of the same magnitude as the equilibrated system in Case F being compared with the nonequilibrated system in Case C. Thus, the equilibration of oil appears to be important for the observed oil recovery differences between the equilibrated and nonequilibrated systems. Comparing the equilibrated and nonequilibrated surfactant solutions (Cases A and B or Cases C and D) it is observed that there is either no difference in oil recovery or the equilibrated performs worse than the non-equilibrated. In order to

interpret the results shown in Table 2, let us consider the mechanism shown in Figure 4.

The commercial petroleum sulfonate such as TRS 10-80 is known to be a mixture of various low and high equivalent weight sulfonates. The higher equivalent weight species tend to be more oil-soluble or more hydrophobic, while the lower equivalent weight species tend to be more water-soluble or more hydrophilic. Schematically, it is depicted by the diagram on the right hand side of Figure 4. When such a surfactant is added to an oil/water mixture, each species partitions in the oil and brine according to its hydrophilic-lipophilic balance. The stipled region is proportional to the fraction partitioning in the oil, whereas, the clear region below is proportional to the fraction of water-soluble species.

Initially, the surfactant is dissolved in the aqueous solution. However, as this aqueous solution is equilibrated with an oil, the oil-soluble species partitions into the oil phase. From IFT data shown in Table 3 and the later discussion, it is evident that the oil/brine IFT, similar to that reported by Gale and Sandvik.[7]

The molecular species at the interface are in equilibrium with those in the aqueous and oil phases. If we consider the addition of a fresh oil drop in a micellar solution (Figure 4), the surfactant monomers should move to the interface first and then to the inside of the oil drop. As monomers get depleted in the vicinity of the interface due to adsorption, the micelles break down and produce additional monomers. From the interface, the oil soluble species preferentially migrate towards the inside of the oil droplet.

We propose that the interface is occupied with both water-soluble and oil-soluble species. For equilibrated systems, the surfactant species come from both sides of the interface and saturate the interface with surfactant molecules more quickly as compared to the non-equilibrated systems in which all surfactant species come only from one side (the aqueous phase) of the interface, containing more stable mixed micelles of water and oil soluble surfactant species. Moreover, for the non-equilibrated surfactant slug, the water soluble species may form a film at the oil/brine interface deterring the mass transfer from the aqueous phase to the oleic phase of the oil soluble species.

A comparison of cases B and D in Table 2 suggests that predominantly water soluble species of the equilibrated aqueous phase of the surfactant solution worsen the oil displacement process as compared to brine flooding presumably due to the formation of stable emulsions or a decrease in coalescence rate in porous media. It is hypothesized that a rigid surfactant film forms on the oil droplet when displaced by the equilibrated aqueous phase of the surfactant solution. This film prevents the coalescence of oil droplet in the narrow channels of the sand pack. It was observed that the differential pressure (ΔP) across the sand pack increases continuously beyond the water break through peak when flooded by the equilibrated surfactant solution, but ΔP decreases or levels off after the water break through when flooded by 1% NaCl. Hence, the apparent paradox in capillary number-oil recovery correlation (systems I and II in Table 3) can be resolved if the interfacial viscosity[16] is considered in addition to the IFT. Indeed, as alcohol

was incorporated into the system, IFV decreased and oil recovery increased (Table 1).

The results of cases B, C, and D suggest the beneficial effect of the presence of oil soluble species in improving oil recovery in Case C. The reason that equilibrated surfactant solution displaces less oil than the fresh surfactant solution as in Cases D and C in Table 2, is partially due to the fact that there is less surfactant in the equilibrated solution as compared to the fresh solution. During the equilibration process, some of the surfactant species must have migrated from the aqueous phase to the oleic phase resulting in a reduction in surfactant concentration in brine. This is substantiated by the measurement of surfactant concentration of 0.01% for the original 0.05% surfactant solution after equilibration.

Also, the results of Cases A and C as well as Cases E and F indicate that a lower final oil saturation, S_{of}, was obtained, if the sand pack was flooded directly by the surfactant solution without a secondary flooding by brine.

To explain the effect of equilibration on oil recovery, the liquid-liquid and liquid-rock interfaces (i.e., the IFTs and contact angles) were studied for these systems and the results are listed in Table 3. Except for the system of fresh oil/1% NaCl, the contact angle measurements followed the pattern shown in Figures 5 and 6. The oil drop formed a nearly sphere on the quartz surface initially. It then flattened out and finally, in some cases, disintegrated or emulsified into many small droplets. The time between the formation of the initial spherical droplet and the final emulsification is defined as the oil droplet flattening time. Except system III, there is a good correlation between the flattening time, the IFT value and the oil displacement efficiency.

Among systems I through V (Table 3), the lowest IFT existed for the interface between equilibrated oil and equilibrated surfactant solution. A drastic increase in IFT occurred as either equilibrated oil or equilibrated surfactant solution was replaced by fresh oil or fresh surfactant solution. However, examining systems II and IV, it is evident that the equilibrated oil rather than the equilibrated surfactant solution is responsible for the lowering of IFT. This suggests that the oil-soluble species are the low tension producing sulfonates in this system.

These hydrophobic species are mainly responsible for the oil droplet flattening phenomenon. The flattening time of a single oil drop has a direct bearing on the oil displacement efficiency. Because there are large numbers of oil droplets within the porous media, the amount of oil recovered depends on how easily each of them can be mobilized. The faster they are flattened, the easier it would be to mobilize, interconnect and displace them. Cash et al[12] demonstrated that oil displacement by the spontaneously emulsifying systems is better than the systems lacking spontaneous emulsification.

In Table 3, the longest flattening time corresponds to the system that has the least amount of oil-soluble species present and the worst oil recovery. The only exception is system III, although the oil drops flattened faster than system IV, it gave poorer recovery than system IV. The following explanation is suggested. While flattening time is being measured, the oil soluble species from the fresh surfactant so-

lution quickly adsorb onto the quartz surface, which facilitates the flattening of the oil drop. However, the IFT is much higher in case III as compared to that in case IV. In agreement with the capillary number concept, we observed a better oil recovery in case IV than in case III.

To sum up, the following mechanism is proposed to account for the observed effects in IFT and oil droplet flattening phenomenon. As shown in Figure 4, mixed micelles in equilibrium with surfactant monomers are formed by the water soluble and oil-soluble species in the bulk aqueous solutions. During equilibration, the surfactant monomers transfer to the water/oil interface and then to the interior of the oil drop resulting in a reduction of IFT. The concentration of oil-soluble species in the surfactant solution dictates the absolute value of IFT and the rate of surfactant mass transfer, which in turn, determines the flattening time of the oil drop.

Because different batches of TRS 10-80 were used in making the sets of surfactant solutions in Figure 2 and Table 3, small variation in values of IFT for the equilibrated oil and equilibrated 0.05% TRS 10-80 in 1% NaCl was observed. Nevertheless, the trend of high and low IFT within each set remained the same. Therefore, the interpretation of IFT based on these values is believed to be valid.

Effect of Salinity on Oil Displacement Efficiency of Equilibrated and Nonequilibrated Systems

Figure 7 shows the effect of salinity on the oil recovery and IFT of 0.1% TRS 10-410 + 0.06% IBA vs. n-dodecane. It shows that at 0.5% and 1.0% NaCl concentrations, the oil recovery is the same for equilibrated systems. Only at and above the optimal salinity (i.e., 1.5% and 2.0% NaCl), the nonequilibrated systems produces better oil recovery than the equilibrated system. A possible explanation of this effect is as follows. It has been shown that for salt concentrations higher than the optimal salinity, the tendency for the surfactant to migrate from the aqueous phase to the oil phase increases. Therefore, when one takes a nonequilibrated system at or above optimal salinity, there is a significant driving force for the surfactant to migrate from the aqueous to oil phase. Moreover, the presence of alcohol in such solutions enhances the mass transfer of surfactant across the interface. Therefore, as the nonequilibrated surfactant solution contacts the oil ganglia, presumably a rapid mass transfer occurs resulting in ultralow interfacial tension. The oil ganglia thereby flatten out or spontaneously disintegrate. A successful flattening and subsequent coalescence of the oil ganglia in the initial stages presumably lead to the formation of an oil-water bank which then successfully sweeps additional oil ganglia along the porous media by coalescence process. By maintaining the ultralow IFT at the oil bank/surfactant solution interface decreases entrapment of the oil from the oil-water bank. Therefore, the improved performance of nonequilibrated systems at and above optimal salinity is related to the effective mass transfer of surfactant from the aqueous phase to the oil phase and the concomitant generation of ultralow IFT and presumably low IFV and associated spontaneous flattening of oil ganglia. This explanation is consistent with the results of oil displacement in Berea cores by the same surfactant system as shown in Figure 8. It shows the effect of salinity on the amount of oil recovery as a percent of oil-in-

place and a percent of final oil saturation. It indicates that more oil was displaced at and above optimal salinity and that close to 90% oil recovery was obtained.

Figure 9 is a production history of a typical run. The cumulative oil recovery, pressure difference (ΔP) across the porous bed, normalized effluent surfactant concentration and percent of oil cut have been plotted. The cumulative oil recovery curve and the ΔP curve rise sharply initially then change their slopes at 0.4% PV. The oil recovery curve further increases at a constant rate while ΔP decreases, then both change slopes again at 5 PV and, finally, the oil recovery graph reaches a constant value and ΔP keeps on rising continuously. Throughout the flooding process, the effluent surfactant concentration increases very slowly from 0% initially to 15% of the injected surfactant concentration at 6.5% PV. It jumps to 37% at 7PV and eventually reaches 42% at the end of the run. The oil cut drops drastically from the 100% at the beginning to 7% at 0.5% PV, then it maintains a 4% recovery for 4.5PV fluid production.

The initial fast rise of the oil recovery curve and the ΔP curve correspond to the 100% oil recovery in the effluent stream for the fully oil saturated Berea core. This is evident from the oil cut curve. The slopes change when water breaks through at the exit. In the next stage, oil is then produced in the form of oil-water bank, which is composed of the coalesced oil droplets mobilized by the surfactant solution. As oil is recovered at a constant rate, ΔP decreased gradually.

Toward the end of this constant rate of oil production, oil comes out as the tailing end of the oil-water bank. At the same time, enough surfactant has been accumulated in the sandstone core to form emulsions with the oil droplets _in situ_. Consequently, ΔP increased due to the blockage of the small pores and narrow channels by these oil-swollen surfactant-rich emulsions. As the process progresses, the surfactant-rich emulsion breaks through as a white opaque solution and manifests itself as a step increase on the C/C_o curve at 7 PV. Finally, as the end of the flooding process is approached, oil recovery diminishes, ΔP keeps on increasing as before, and C/C_o levels off.

It is interesting to note that the shape of the cumulative oil recovery curves in the unconsolidated sand pack is similar to that in the consolidated Berea core (Figures 1 and 9), except that oil is produced at a much faster rate for the sand packs. Therefore, the oil displacement mechanism is presumably the same in these two porous media for the continuous dilute surfactant solution flooding process. Chou and Shah[22] have shown that 1 or 4 ft sandpacks give identical results for oil recovery and the fluid production profile when plotted as a function of PV injected. Therefore, we believe that the use of small sandpacks is still meaningful for showing the phenomena in porous media.

It should be emphasized that the entire study reported in this paper relates to the low surfactant concentration systems (<0.5%) and does not involve the formation of middle phase microemulsions[23] etc in this oil displacement process. At all times, the oil/brine/surfactant systems were composed of only two phases, oil and brine, with surfactant distributed in both phases. Also, this study is carried out at low salini-

ty (< 2% NaCl) although we have reported elsewhere on high salinity formulations[24-26] which can produce ultralow IFT in millidynes/cm range at salt concentrations as high as 32%.

CONCLUSIONS

(1)   The study revealed that the addition of iso-butanol to dilute TRS 10-80 or TRS 10-410 petroleum sulfonate solutions did not influence significantly IFT, or surfactant partitioning but decreased interfacial viscosity and markedly reduced flattening time of oil drops and increased oil displacement efficiency, presumably by promoting coalescence of oil ganglia in porous media.

(2)   The equilibrated and nonequilibrated oil/brine/surfactant systems differed in their oil displacement efficiency. The equilibrated oil rather than the equilibrated aqueous phase of the surfactant solution is responsible for the high oil displacement efficiency of dilute surfactant systems containing no alcohol. The oil soluble fraction of petroleum sulfonate is more effective in lowering the interfacial tension and in promoting the flattening of oil drops. Almost 98% oil recovery was achieved in sand packs by a low concentration (~ 0.1%) surfactant plus alcohol formulation when used in place of brine flooding.

(3)   The lower values of final oil saturation were obtained for the systems flooded directly by the surfactant formulation without first being brine-flooded.

(4)   For equilibrated systems, there is an excellent correlation between the capillary number and oil recovery efficiency. However, in calculating capillary number for nonequilibrated systems, care should be exercised because the IFT measured in vitro may not be achieved in situ and, in certain cases, the interfacial viscosity and not interfacial tension, may be a predominant factor influencing the oil displacement efficiency.

(5)   The effect of salinity on oil displacement efficiency revealed that for the alcohol containing formulations, the nonequilibrated system was more efficient for oil recovery as compared to the equilibrated system at and above, optimal salinity. It is proposed that not only the equilibrium values of the parameters such as interfacial tension and interfacial viscosity are important but the dynamic process of surfactant partitioning is also important in mobilization of oil ganglia. The conditions that promote the efficient mass transfer from the aqueous phase to the interface promote the deformation and mobilization of oil ganglia. This would facilitate an early formation of oil bank and displacement of oil from porous media.

ACKNOWLEDGEMENTS

REFERENCES

1. Holm, L.W., J. Pet. Tech. (Dec. 1971) 1475-1483.

2. Taber, J.J., Soc. Pet. Eng. J. (March 1969) 3-12.

3. Healey, R.N. and Reed, R.L., "Improved Oil Recovery by Surfactant and Polymer Flooding" Vol. II, eds. Shah, D.O. and Schechter, R.S., Academic Press, N.Y., 383-437, 1977.

4. Cash, R.L. Jr., Cayias, J.L., Hayes, M., MacAllister, D.J., Schares, T., Schechter, R.S., and Wade, W.H., SPE 5562 presented at Fall SPE Meeting, Dallas, Texas, Sept. 28-Oct. 1, 1975.

5. Trushenski, S.O., Dauben, D.L. and Parrish, D.R., Soc. Pet. Eng. J., (Dec. 1974) 633-645.

6. Stegemier, G.L., "Improved Oil Recovery by Surfactant and Polymer Flooding", Vol. I, eds. Shah, D.O. and Schechter, R.S., Academic Press, N.Y., 1977.

7. Gale, W.W. and Sandvik, E.I., Soc. Pet. Eng. J. (Aug. 1973) 191-199.

8. Gogarty, W.B. and Tosch, W.C., J. Pet. Tech. (Dec. 1968) 1407-1414.

9. Jones, S.C. and Dreher, K.D., SPE 5566 presented at Fall SPE Meeting, Dallas, Texas, Sept. 28-Oct. 1, 1975.

10. Foster, W.R., J. Pet. Tech. (Feb. 1973) 205-210.

11. Hsieh, W.C. and Shah, D.O., SPE 6594 presented at SPE International Symposium on Oilfield and Geothermal Chemistry, LaJolla, CA, June 27-28, 1977.

12. Cash, R.L., Cayias, J.L., Fournier, R.G., Jacobson, J.K., Schares, T., Schechter, R.S. and Wade, W.H., SPE 5813 presented at SPE Improved Oil Recovery Symposium, Tulsa, OK March 22-24, 1976.

13. Anderson, D.R., Binder, M.S., Davis, H.T., Manning, C.D. and Scriven, L.E., SPE 5811, presented at SPE Improved Oil Recovery Symposium, Tulsa, OK, March 22-24, 1976.

14. Wasan, D.T. and Mohan, V., "Improved Oil Recovery by Surfactant and Polymer Flooding" Vol. I, eds. Shah, D.O. and Schechter, R.S., Academic Press, N.Y. 161-203, 1977.

15. Chan, K.S., Ph.D. Dissertation, University of Florida, Gainesville, FL 1978.

16. Wasan, D.T. et al.: "Interfacial Shear Viscosity at Fluid-Fluid Interfaces," AIChE J. 17 (June, 1977) 1287-1295.

17. Reid, V.W. et al.: "Determination of Anionic-Active Detergents by Two Phase Titration," Tenside 4 292-304 (1967).

18. Shah, D.O., Tamjeedi, A., Falco, J.W. and Walker, R.D., AIChE J Vol. 18, No. 6 (Nov. 1972), 1116-1120.

19. Chan, K. S. and Shah, D.O., J. Disp. Sci. & Tech., 1(1), 55-95, 1980.

20. Zana, R., In Surface Phenomena In Enhanced Oil Recovery, ed. D.O. Shah, Proc. Stockholm Symposium, August 1979, Plenum Press, N.Y. (in press).

21. Melrose, J.C. and Brandner, C.F., J. Canadian Petr. Tech. (Oct. - Dec. 1974), 58.

22. Chou, S.I. and Shah, D.O., In Surface Phenomena In Enhanced Oil Recovery, Ed. D.O. Shah, Proc. Stockholm Symposium, August 1979, Plenum Press, N.Y. (in press).

23. Chan, K.S. and Shah, D.O., SPE 7896 presented at SPE International Symposium on Oilfield and Geothermal Chemistry, Houston, TX, Jan. 22-24, 1979.

24. Bansal, V.K. and Shah, D.O., J. Colloid Interface Sci. 65, 451, 1978.

25. Bansal, V.K. and Shah, D.O., Soc. Pet. Eng. J. (June 1978), 167-172.

26. Bansal, V.K. and Shah, D.O. J. Am. Oil Chem. Society 55, No. 3, 367-370, 1978.

Table 1

The Effect of IBA on Flattening Time,
IFT, IFV, Partition Coefficient, and Oil
Displacement Efficiency

SYSTEM	0.1% TRS 10-410 in 1.5% NaCl vs. n-Dodecane	0.1% TRS 10-410 + 0.06% IBA in 1.5% NaCl vs. n-Dodecane	0.05% TRS 10-80 in 1% NaCl vs. n-Octane	0.05% TRS 10-80 + 0.04% IBA in 1% NaCl vs. n-Octane
Run	S100-48	S100-43	S100-02	S100-44
Flattening Time	90 sec	< 1 sec	420 sec	< 1 sec
IFT (dynes/cm)	0.086	0.088	0.025	0.024
Interfacial Viscosity (s.p.)	0.096	0.086	0.023	0.018
Partition Coefficient	0.010	0.009	0.3	1.36
Secondary Recovery				
By Brine Flooding	–	–	61.2%	60.08%
By Surfactant Soln Flooding	84.37%	98.32%	60%	91%
Tertiary Recovery	–	–	0	76.84%
Final Oil Saturation	11.73%	1.28%	30%	5.36%

*All displacement experiments are carried out with nonequilibrated systems in sand packs at 25°C; Dimensions and flow rates same as given in Table 2.

Secondary and tertiary oil recovery values are percent of oil-in-place, whereas final oil saturation is percent of total pore volume.

Table 2

0.05% TRSIO-80 IN 1% NaCl DISPLACING n-OCTANE IN SAND PACKS AT 25°C

SEQUENCE OF FLUID INJECTION	Run	Secondary Recovery	Tertiary Recovery	Final Oil Saturation
A. FRESH Surfactant Soln. | BRINE | FRESH OIL | BRINE	S100-02 S100-03	61.2% 63.7%	0% 7.14%	30.86% 24.59%
B. Equilibrated Surfactant Soln. | BRINE | FRESH OIL | BRINE	S100-09	60.36%	0%	30%
C. FRESH Surfactant Soln. | FRESH OIL | BRINE	S100-06 S100-07 S100-08	71.4% 71.99% 75.16%	—— —— ——	23.02% 20.48% 20.81%
D. Equilibrated Surfactant Soln. | FRESH OIL | BRINE	S100-10 S100-11	51.88% 44.29%	—— ——	36.91% 43.3%
E. Equilibrated Surfactant Soln. | BRINE | EQU. OIL | BRINE	S100-04	83.04%	0%	15.58%
F. Equilibrated Surfactant Soln. | EQU. OIL | BRINE	S100-05	93.78%	——	6.13%

SAND PACK DIMENSION: 1.06" DIA. X 7" LONG ; PERMEABILITY: 3 DARCY ; FLOW RATE: 2.3 FT./DAY

BRINE: 1% NaCl

Table 3

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

SYSTEM		IFT (mN/m)	FLATTENING TIME* (seconds)	OIL RECOVERY[+] (% OIP)
I.	Fresh Oil/1% NaCl	≈50.8**	∞	61–63
II.	Fresh Oil/Equilibrated Surfactant Solution	0.731	6600	44–52
III.	Fresh Oil/Fresh Surfactant Solution	0.627	480	75–77
IV.	Equilibrated Oil/1% NaCl	0.121	900	83
V.	Equilibrated Oil/Equilibrated Surfactant Solution	0.0267	240	94
VI.	Equilibrated Oil/Fresh Surfactant Solution	0.00209	15	—

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

**Octane/H_2O, 20°C, IFT = 50.8 mN/m, "Interfacial Phenomena", Davies and Rideal, Chapter 1, p. 17 Table1, Academic Press, N.Y. 1963.

[+]Porous media dimensions, sequence and rate of fluid injection are given in Table 2.
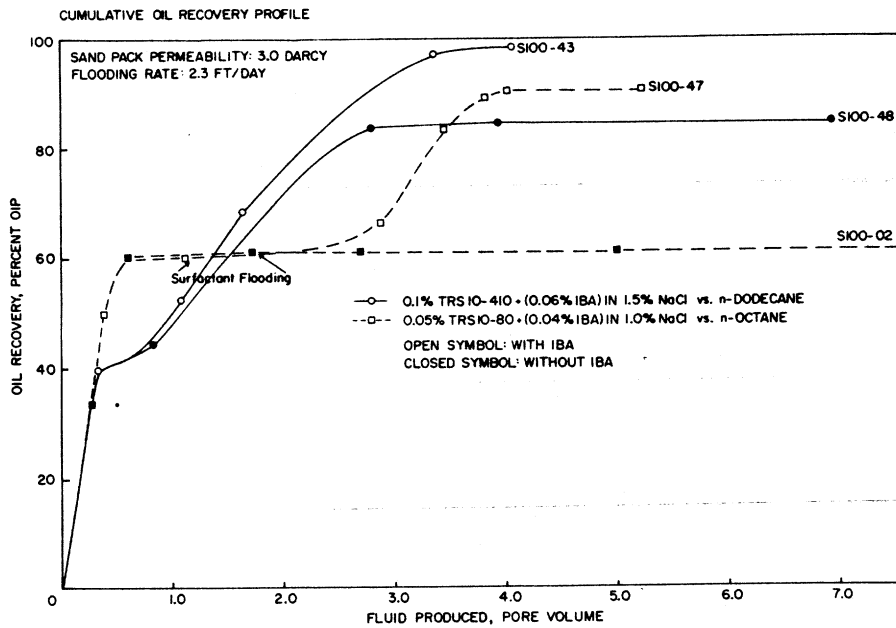
CUMULATIVE OIL RECOVERY PROFILE

Fig. 1 - Effect of addition of Isobutanol to surfac-
tant solutions on oil recovery for octane and dodecane
in sand packs by continuous injection of surfactant
solutions, 25°C.

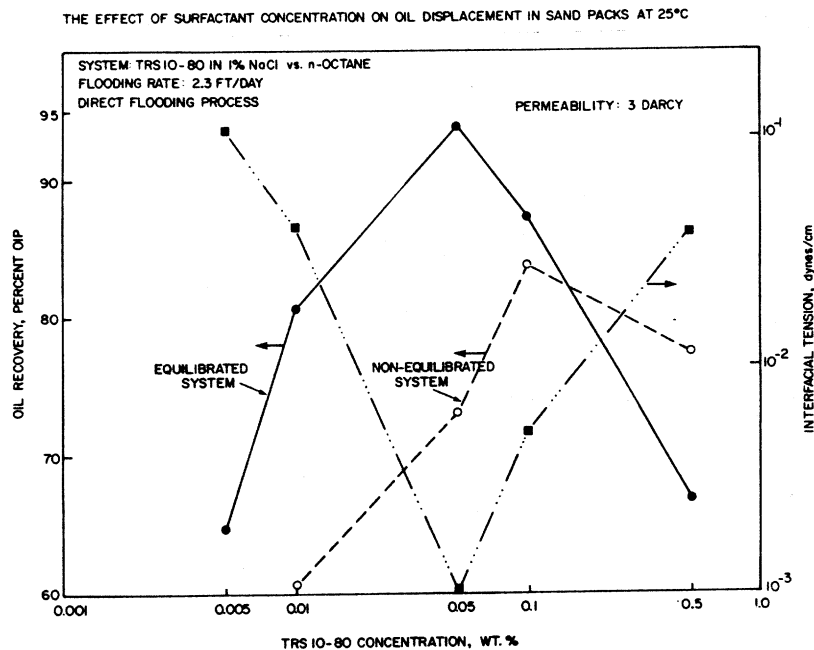THE EFFECT OF SURFACTANT CONCENTRATION ON OIL DISPLACEMENT IN SAND PACKS AT 25°C

Fig. 2 - A correlation of IFT with oil recovery for
equilibrated oil/brine/surfactant systems. The oil
recovery is strikingly different for nonequilibrated
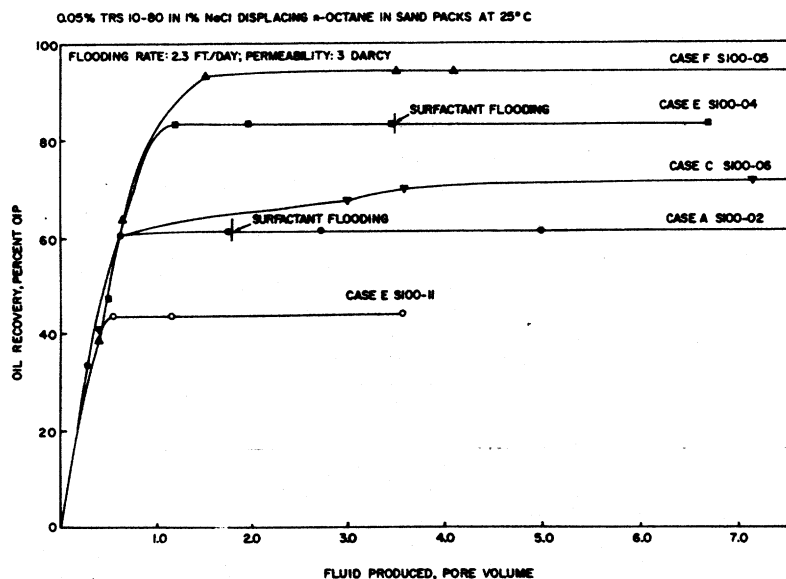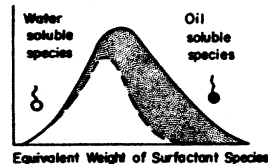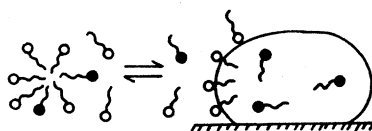systems (sand packs, dimensions are given in Table 2).

Fig. 3 - 0.05% TRS 10-80 in 1% NaCl displacing n-octane in sand packs at 25°C (Details in Table 2).

MASS TRANSFER PROCESS FOR SURFACTANT MONOMERS:

SURFACTANT SOLUTION——▶INTERFACE——▶INTERIOR OF OIL DROP

— INTERFACIAL TENSION DECREASE DUE TO SURFACTANT MASS TRANSFER

— RATE OF MASS TRANSFER DEPENDS UPON THE CONCENTRATION OF OIL
   SOLUBLE SPECIES IN THE SURFACTANT SOLUTION

Fig. 4 - Schematic representation of and various steps involved in mass transfer of petroleum sulfonate from aqueous solution to the interface and then to the oil phase. The right hand side of the diagram illustrates the role of preferentially water soluble and oil soluble surfactant species in partitioning of the petroleum sulfonate.

T = 2 SECONDS

T = 0.5 MINUTES

T = 5 SECONDS

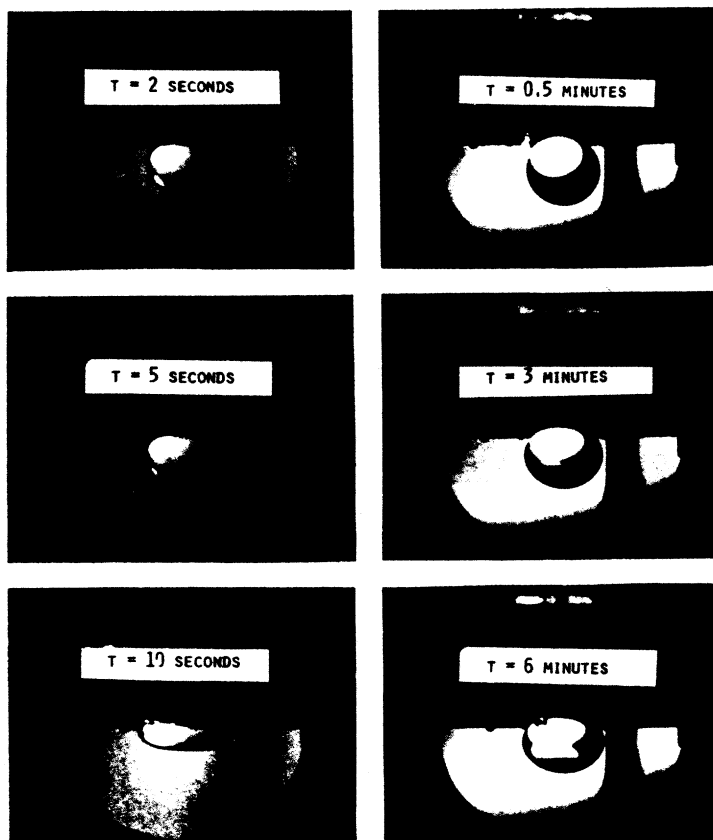T = 3 MINUTES

T = 10 SECONDS

T = 6 MINUTES

Fig. 5 – The left hand side column illustrates the spreading of a drop of equilibrated n-octane on a quartz surface submerged in fresh 0.05% TRS 10-80 in 1% NaCl solution (Case VI in Table 3). The right hand side column illustrates the spreading of equilibrated n-octane drop on quartz in 1% NaCl solution (Case IV in Table 3).
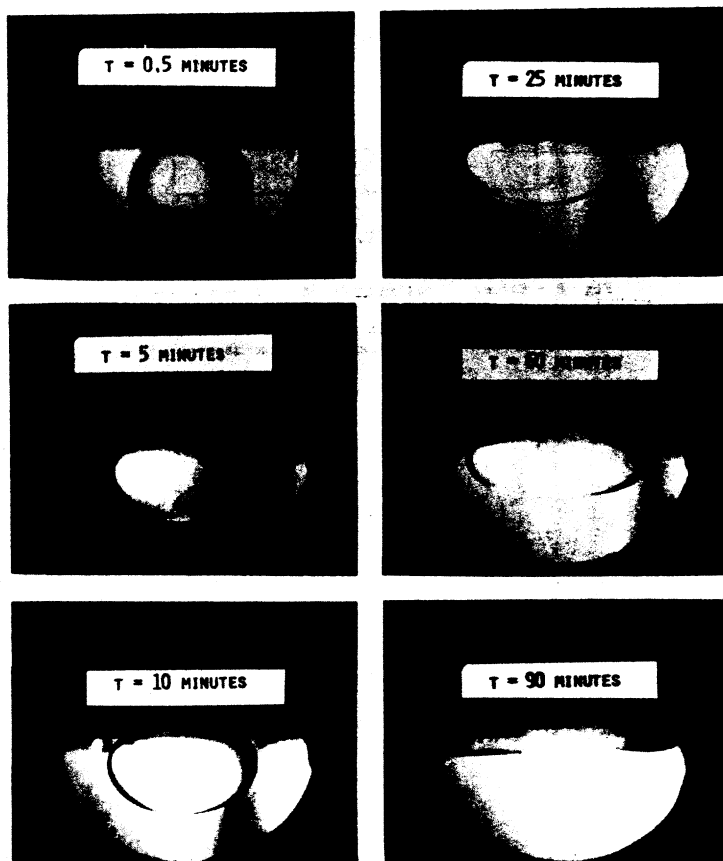
n-OCTANE vs. EQUILIBRATED 0.05% TRS 10-80 IN 1% NaCl

T = 0.5 MINUTES

T = 25 MINUTES

T = 5 MINUTES

T = 50 MINUTES

T = 10 MINUTES

T = 90 MINUTES

Fig. 6 – The spreading of a drop of n-octane on quartz surface submerged in the equilibrated aqueous phase of 0.05% TRS 10-80 in 1% NaCl solution (Case II in Table 3).

Oil Recovery in Sand Packs at 25°C
Continuous injection of 0.1% TRS 10-410+
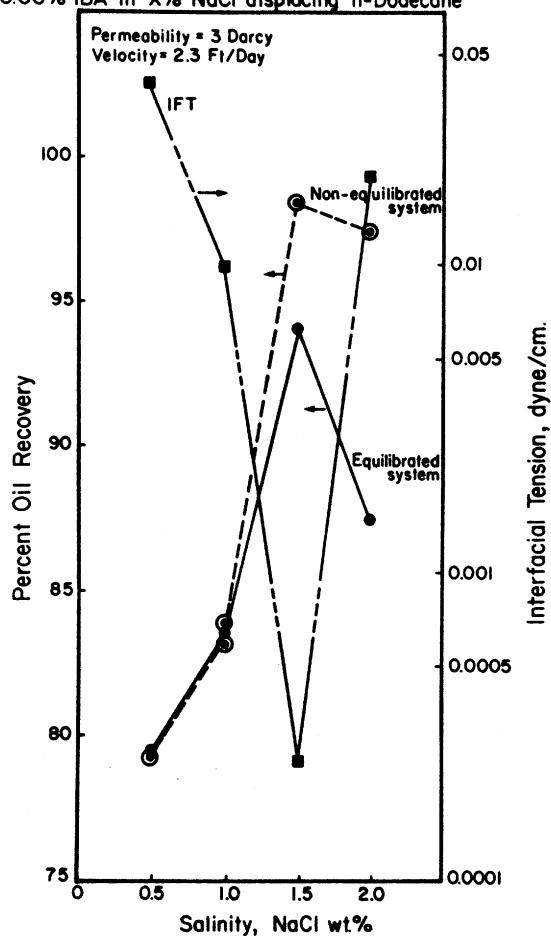0.06% IBA in X% NaCl displacing n-Dodecane

Fig. 7 - Effect of salinity on oil recovery by con-
tinuous injection of 0.1% TRS 10-410 + 0.06% IBA on
n-dodecane displacement in sand packs at 25°C
(Dimensions of sand packs are the same as given in
Table 2).

Oil Recovery in Berea Cores at 25°C
Continuous injection of 0.1% TRS 10-410+
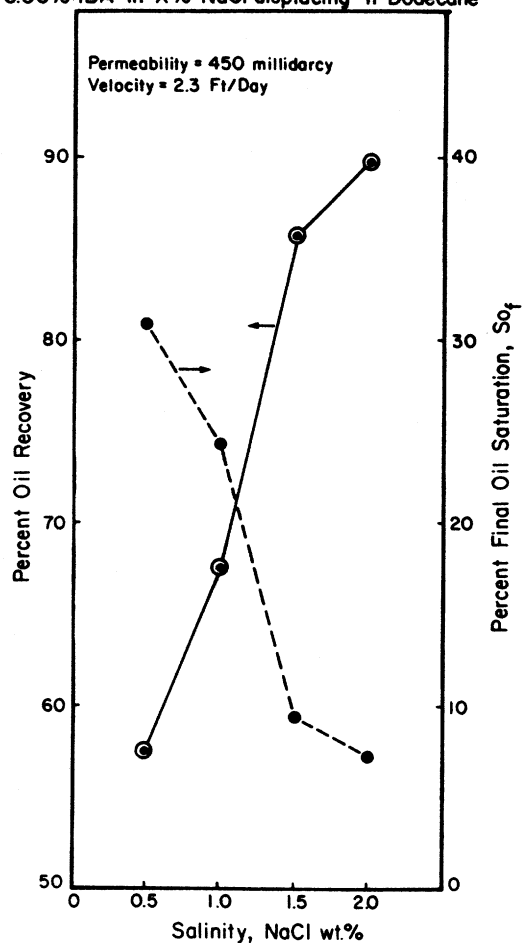0.06% IBA in X% NaCl displacing n-Dodecane

Fig. 8 - Effect of salinity on oil recovery by
continuous injection of 0.1% TRS 10-410 + 0.06% IBA
on n-dodecane displacement in Berea cores at 25°C
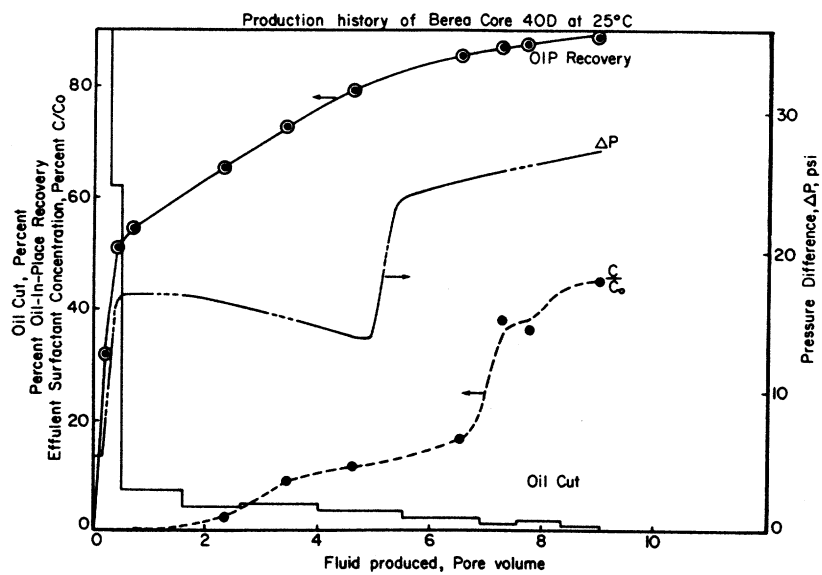(Details given in the text).

Fig. 9 - Oil displacement history of produced fluids
upon continuous injection of 0.1% TRS 10-410 + 0.06%
IBA in 2% NaCl brine to displace n-dodecane in Berea
cores, 25°C (Berea core details given in the text).