

Effect of Salinity and Alcohol Partitioning on Phase Behavior and Oil Displacement Efficiency in Surfactant-Polymer Flooding¹

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The equivalent alkane carbon number (EACN) of a crude oil, namely Ankleshwar crude, is successfully modeled by a mixture of pure alkanes. The EACN of the crude oil is found to be 9.3, and an appropriate mixture of nonane and decane exhibited phase behavior similar to that of the crude oil. A surfactant system for a water flooded reservoir at 80 C and having a salinity in the range of 2% to 3% NaCl is formulated by blending a phosphated ester with a petroleum sulfonate in the weight ratio of 2/5. The addition of phosphate ester not only increases the salt tolerance of the petroleum sulfonate system, it also broadens the IFT minimum. The oil displacement tests at 80 C in sandpacks and Berea cores showed that the surfactant formulation containing tertiary amyl alcohol (TAA) displaced 92% oil in sandpacks and 79% crude oil in Berea cores. The oil recovery efficiency was poor when formulations contained other alcohols. From the effluent surfactant concentration, it is shown that there is a correlation between the tertiary oil recovery, surfactant breakthrough and surfactant retention in porous media. It is proposed that, because alcohols such as isopropyl alcohol (IPA), isobutyl alcohol (IBA) and secondary butyl alcohol (SBA) partition significantly in the equilibrated excess brine phase, the alcohol-depleted surfactant slug forms stable emulsions resulting in faster breakthrough of surfactant in the effluent and lower oil displacement efficiency. In the case of TAA-containing formulation, there is a partitioning of TAA in the oil phase. Therefore, there is a mass transfer of alcohol from surfactant slug to the oil ganglia in porous media. This produces a transient ultralow IFT between residual oil and the surfactant solution which mobilizes oil, resulting in higher oil displacement efficiency.

A great deal of residual oil remains in the reservoir after primary and secondary methods. A number of tertiary methods presently are being investigated to recover this residual oil. These processes involve injection of a number of fluids which are designed to increase the portion of the reservoir being contacted and to do a better job of mobilizing oil than water flooding. The residual oil is trapped in the rock pores as blobs or ganglia. In order to mobilize a ganglion, the capillary forces holding it in the pore must be reduced. This task can be accomplished by lowering the interfacial tension (IFT) between the residual oil and the brine in the reservoir. Surfactant-polymer flooding is one of the tertiary methods, if designed properly, that can lower IFT and reduce oil saturation far below the values obtained with a water-flood. Polymer solutions are injected following the

surfactant slug to propagate the micellar system through the reservoir. The polymer solutions also provide mobility control in the reservoir. Considerable research has been directed toward developing the technology of surfactant flooding (1-8). Essentially, two different concepts have developed for using surfactants. One concept employs a large pore volume of a low-concentration surfactant solution which has given rise to the so-called low-tension flood processes. The other concept uses a small pore volume of a high-concentration surfactant dispersion. These dispersions are called micellar solutions, microemulsions, swollen micelles or soluble oils.

When a surfactant slug is injected into an oil reservoir, it undergoes complex changes as it traverses the reservoir. The surfactant slug is diluted as it mixes with reservoir oil and brine. This effect places stringent requirements on the design of the micellar flood. Initially, the micellar slug is miscible with the crude oil and brine. However, the flood can degenerate to an immiscible displacement due to dilution, surfactant adsorption to the rock, precipitation of surfactants by reservoir brine of high salinity and divalent cations or penetration of the slug by drive water or polymer solution due to adverse mobility (9). The retention of surfactant in the reservoir rock plays a major role in determining the effectiveness of micellar flooding (10,11). The main criteria for achieving high oil recovery besides surfactant retention are (i) ultralow IFT between chemical bank and residual oil and between chemical bank and drive fluid; (ii) brine compatibility and temperature stability; (iii) mobility control, and (iv) economy of the process (12,13). An understanding of the reservoir and fluid characteristics, such as the nature of oil and water content, relative permeability, mobility ratios, formation fractures and variation in permeability, is necessary in order to design a successful surfactant-polymer process (14,15).

Extensive work has been reported in literature (16) to formulate surfactant systems for different reservoir conditions, mainly reservoirs at low temperature and containing low salinity brine. In this paper, we report the design of surfactant formulation for a water flooded Ankleshwar oilfield which is located in western India with reservoir temperature of 80 C and brine salinity in the range of 2% to 3% NaCl. Toward this goal, the dead crude oil from the reservoir is characterized in terms of equivalent alkane carbon number (EACN). The effect of alcohol structure and salinity on oil displacement is discussed. The efficiency of oil displacement is explained in terms of partitioning of alcohol, the residence time and the integrity of surfactant slug and surfactant recovery in porous media.

EXPERIMENTAL

Materials. Petroleum sulfonates, TRS 10-80 and TRS 10-410 (Witco Chemical Co., New York, New York) were used as received. These surfactants have an average

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molecular weight of 418. KF AA-270 (BASF Wyandotte Company), a phosphated ester, was used as received. Alcohols and oils used in this study were purchased from Chemical Samples Company and were of 99% purity or greater. Sodium carbonate was obtained from Mallinckrodt Company and sodium tripolyphosphate was purchased from Fisher Chemical Company. Pusher-1000TM (Dow Chemical Company) was used to prepare polymer solutions. Deionized, distilled water was used to prepare the brine.

Methods. Interfacial tensions were measured by a spinning drop tensiometer after phase equilibration at 25 C. For the phase volume behavior studies, the petroleum sulfonate-cosurfactant blend was mixed with equal volumes of brine (of desired salinity) and oil. Surfactants and cosurfactants were added in oil while inorganic salts in brine (concentrations of these species will be mentioned in the text). The solutions were shaken vigorously and equilibrated at 80 C in sealed glass tubes until no further change in respective phase volumes was observed. The equilibration time for this study was about two weeks to a month. The alcohol concentrations in the equilibrated phases were measured using a Perkin-Elmer 900 gas chromatograph with SE30 column having 3% chromosorb support.

Sandpacks with a dimension of 30 cm length and 2.5 cm diameter were used as the porous media for the most part of the study. The sandpacks had a porosity of 38% and permeability of 3-4 Darcy. Rectangular Berea cores with a dimension of 30.5 by 2.5 cm by 2.5 cm also were used in the oil displacement test; they had a porosity of 22% and permeability of 0.415 Darcy. The porous medium was conditioned by saturating it with CO₂ to displace air and then flooded with brine which was filtered through 0.22 μ filter. The porous medium was then saturated with oil at a high flow rate to irreducible brine content and flooded with the resident brine to residual oil saturation. A 0.2 pore volume (PV) of surfactant slug was then injected; it was displaced by polymer solution (about 1.0 PV) and, subsequently, by drive water. The linear displacement velocity in the water flooding and the subsequent surfactant and polymer flooding was 1 ft/day. Oil displacement experiments were performed at 80 C under a back pressure of 30-40 psi to avoid development of gas saturation at 80 C. All phases in the effluent from the oil displacement tests were collected at less than 0.05 PV interval using a fraction collector. Surfactant concentration of the effluent was measured by two-phase, two-day titration method (17).

RESULTS AND DISCUSSION

EACN Determination. The EACN concept, which allows the substitution of a crude oil by an alkane or alkane mixture for phase volume or interfacial tension studies, has been generally accepted. This concept arises from the observation that the interfacial properties of any oil with a surfactant can be modeled by the behavior of alkanes. In addition, the EACN of a mixture of hydrocarbons follows the simple mixing rule

$$(EACN)_{mixture} = \sum x_i (EACN)_i$$

where x_i is the mole fraction of component i . It has been

reported (18) that the EACN of an oil (crude, pseudocrude or hydrocarbon) is independent of the surfactants and cosurfactants used in the formulation. Crude oil being dark in color and usually quite viscous can make equilibrium attainment very slow and phase observation difficult. Modeling a crude oil by the EACN concept facilitates screening of surfactant formulations.

Glinsman (19) defined the EACN of a crude oil by comparing its optimal salinity based on the equality of brine-microemulsion vs. microemulsion-oil interfacial tensions with those of a pure n-paraffin. Tham and Lorenz (20) used the same approach except that the optimal salinity was based on equal solubilization of brine and oil. Puerto and Reed (21) used a three-parameter representation to describe equivalent carbon number. The three parameters used were the optimal salinity, solubilization parameter and the oil molar volume. They concluded that this three-parameter representation provided a more nearly unique description of microemulsion phase behavior than had been available in the past.

In this study, the EACN of the Ankleshwar crude oil was determined by comparing optimal salinity based on equal brine and oil solubilization. The characteristics of Ankleshwar crude oil are listed in Table 1. The solubilization parameters of TRS 10-80/Isobutanol (IBA)/crude oil/brine formulation are shown in Figure 1. The parameters, V_o/V_s and V_w/V_s , indicate the solubilized volume of water and oil per unit volume of surfactant in the microemulsion phase. The intersections of these parameters as shown in Figure 1 provide the optimal salinity of the formulation. The surfactant concentration used in this section was 10% w/v, and the ratio of surfactant to alcohol was 1. The optimal salinities of the same formulation with pure alkanes nonane, decane, dodecane and tridecane also were determined and are reported elsewhere (22). The values of optimal salinity are plotted as functions of alkane carbon number (ACN) and shown in Figure 2. The optimal salinity increased linearly with ACN. This is in agreement with earlier studies carried out with petroleum sulfonate as well as with other formulations (23,24). It was observed that, as the alkane carbon number increased, the solubilization of brine and oil in the middle phase decreased. By comparing the optimal salinity of crude oil with pure hydrocarbons, the EACN of Ankleshwar crude oil was

TABLE 1
Characteristics of Ankleshwar Crude Oil

API gravity	43-51
Density (g/cc)—15 C	0.77- 0.81
Kinematic viscosity at 50 C	1.4 - 2.3 c.s.
Pour Point, °C	15-24
Sulfur (% wt)	0.01- 0.04
Wax (% wt)	6.8 -14.5
Asphaltenes (% wt)	0.08- 0.24
Resins (% wt)	0.57- 4.1
Gasoline (100-150 C), %	18.6 -42.2
Kerosene (150-200 C), %	22.9 -31.4
Gas oil (250-350 C), %	15.0 -26.1
Residue after 350 C, %	16.5 -28.0

found to be 9.3 as shown in Figure 2. The value of optimal salinity using TRS 10-80/IBA/crude oil was found to be around 0.73% NaCl (Fig. 1). This salinity is much lower than the salinity of Ankleshwar reservoir brine (2 to 3%). Therefore, it was necessary to design a formulation with high salt tolerance and capacity to solubilize more oil and brine in the microemulsion phase.

Salt tolerance of mixed surfactant systems. Petroleum sulfonates have been found to exhibit low salinity tolerance. A variety of chemical compounds have been patented for use as cosurfactants with the goal of making petroleum sulfonates more compatible with reservoir fluids (25). Nonionic surfactants tolerate higher levels of hardness and salinity, although they have lower surface activity (26) per unit weight and are more expensive than petroleum sulfonates. In this investigation, KF AA-270, a phosphated ester was used as a cosurfactant in different weight ratios to increase the salt tolerance of petroleum sulfonate. The total surfactant concentration used in this section was 0.2%, and the surfactant to alcohol (IBA) ratio was kept at 5/3. For interfacial tension measurements, octane was used as oil (WOR = 1.0). The equilibrated system was a two-phase system at various salt concentrations. Figure 3 shows the effect of salinity on IFT for the mixed surfactant systems. The first column of numbers in the legend represents TRS 10-410 concentration, and the second column represents KF AA-270 concentrations. When Klearfac was present in the formulation, the

salt tolerance of the formulation was only 2% NaCl; the minimum in IFT occurred at 1% NaCl. Increasing the salinity beyond 2% NaCl, the surfactant precipitated. As the concentration of KF AA-270 was increased, the salt tolerance of the formulation increased to as high as 15% NaCl. It is interesting to note that besides increasing the salt tolerance, the addition of KF AA-270 decreased the IFT and broadened the IFT minimum. However, KF AA-270 alone (without blending it with petroleum sulfonate) did not reduce the IFT. Similar results have been reported by Hayes et al. (27) for mixed surfactant system containing alkyl xylene sulfonates and KF AA-270.

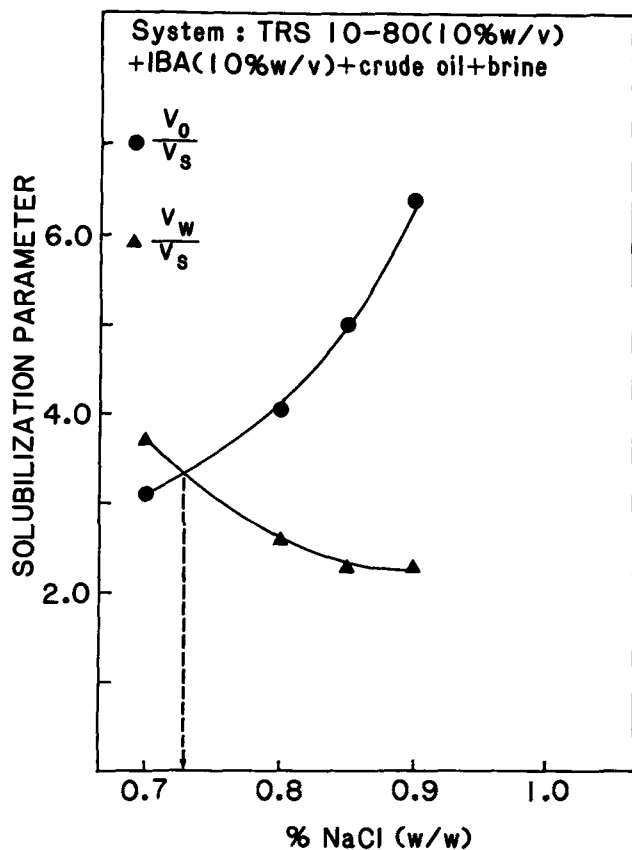


FIG. 1. Effect of salinity on solubilization parameters of TRS 10-80/IBA/crude oil/brine system.

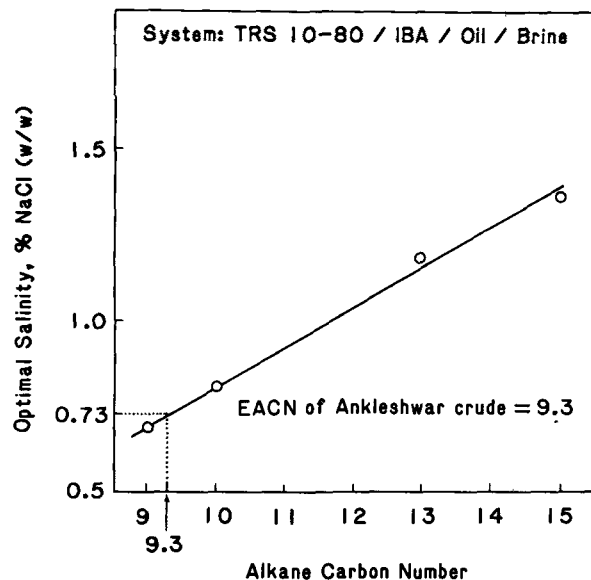


FIG. 2. Effect of alkane carbon number on optimal salinity of TRS 10-80/IBA/alkane/brine system.

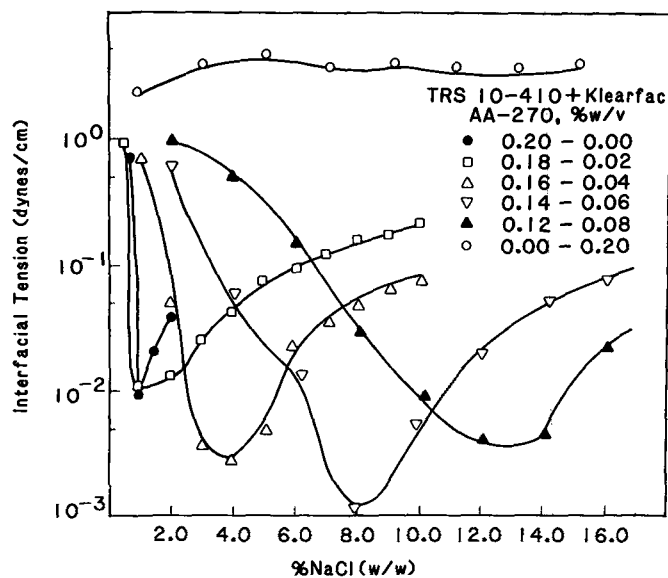


FIG. 3. Effect of addition of KF AA-270 on salt tolerance and broadening of IFT minimum of TRS 10-410/IBA/octane/brine system.

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Phase behavior studies. It has been shown in the literature (28-30) that the phase behavior of surfactant/oil/brine systems is a key factor in interpreting the performance of oil recovery by surfactant-polymer flooding. By systematically varying the salinity, higher solubilization of brine as well as oil in the middle phase and ultralow interfacial tension can be achieved in or near the salinity range giving three phases. Optimal salinity concept has been developed as a tool for designing microemulsions. The effect of salinity on the phase behavior in terms of the solubilization parameters and volume fraction of lower, middle and upper phases is shown in Figures 4 through 7. The formulation contained TRS 10-80 (5% w/v), KF AA-270 (2% w/v) and an alcohol (3% w/v). The alcohols used were isopropanol (IPA), isobutanol (IBA), secondary butanol (SBA) and tertiary amyl alcohol (TAA). The solid lines in these figures refer to the phase behavior with pure alkanes (EACN = 9.3), whereas the dotted lines refer to that with the Ankleshwar crude oil. Experiments also were conducted to determine the optimal salinity of this system in the absence of KF AA-270. Table 2 summarizes these results. In the absence of KF AA-270, the optimal salinity was found to be less than 1.3% for all the alcohols studied. However, when KF AA-270 was incorporated in the formulation, the optimal salinity increased significantly. The optimal salinity did not change significantly for different alcohols in each formulation. For reasons unknown, the optimal salinity of the TAA-containing formulation was slightly higher than either IBA- or SBA-containing formulations.

The effect of Na_2CO_3 and sodium tripolyphosphate on

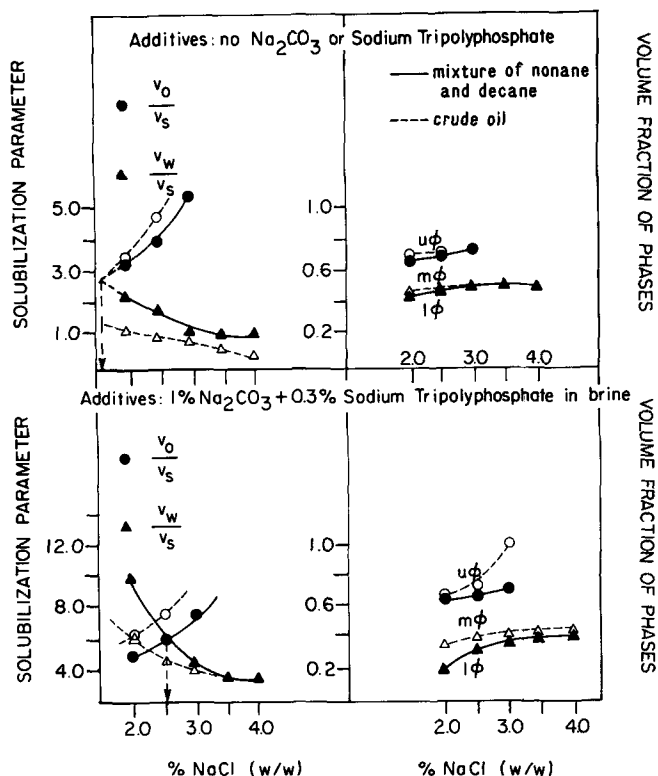


FIG. 5. Phase behavior of TRS 10-80 (5%) + KF AA-270 (2%) + IBA (3%) + oil at 80 C.

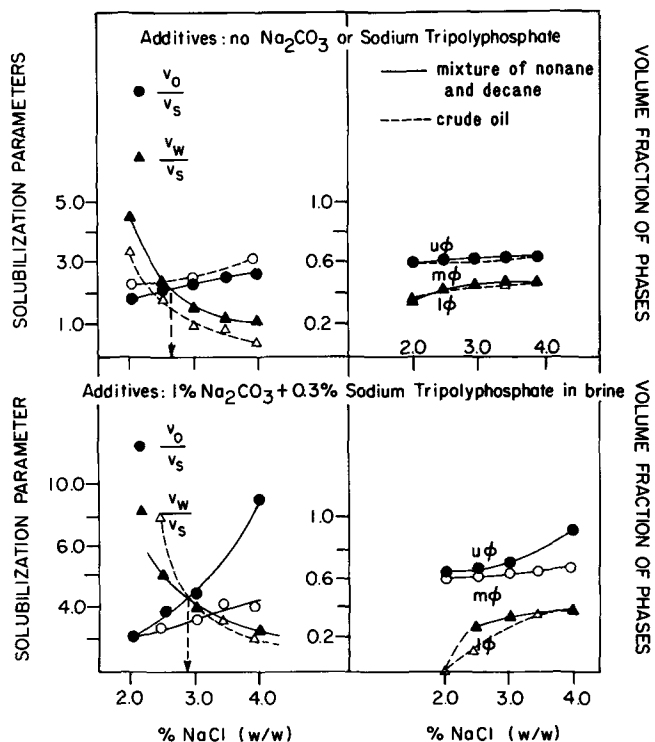


FIG. 4. Phase behavior of TRS 10-80 (5%) + KF AA-270 (2%) + IPA (3%) + oil at 80 C.

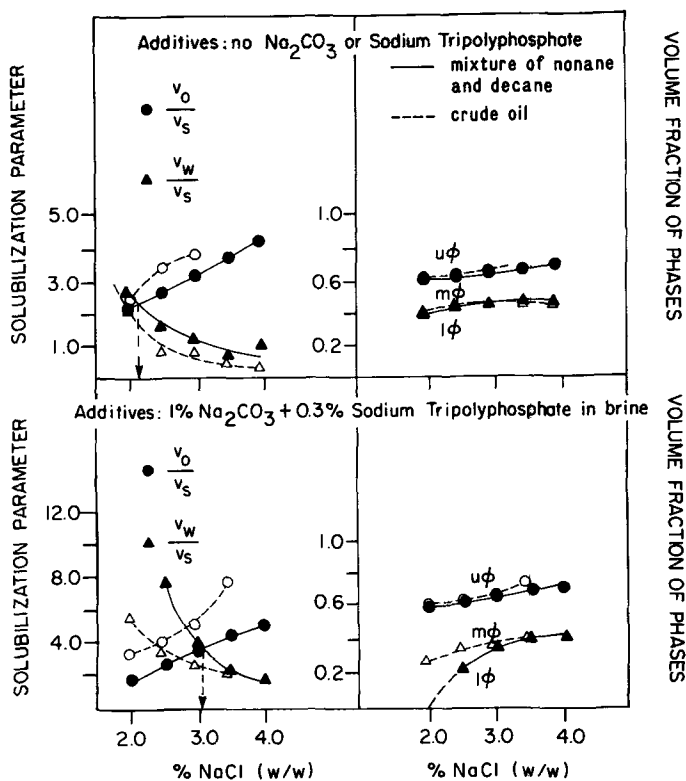


FIG. 6. Phase behavior of TRS 10-80 (5%) + KF AA-270 (2%) + SBA (3%) + oil at 80 C.

optimal salinity and solubilization parameter also was investigated. Sodium tripolyphosphate, a common detergent builder, is known (31) to minimize adsorption loss of anionic surfactant to the rock. When 1% Na_2CO_3 was added in brine for phase behavior, the optimal salinity increased [case (C) in Table 2] to a value in the range of 2.5 to 3.5% for all the alcohols. Moreover, the solubilization parameter almost doubled. The addition of 0.3% tripolyphosphate decreased the optimal salinity slightly. The optimal salinity of crude oil system was

somewhat lower than that of pure alkanes with EACN 9.3 in the presence of the additives.

The increase in the optimal salinity upon the addition of KF AA-270 does not seem to be due to the lowering of pH of the aqueous phase. The phase behavior of TRS 10-80/IPA/oil was investigated at the pH of the 2,7 and 11. The pH was adjusted by adding the appropriate amounts of aqueous phase of H_2SO_4 or Na_2CO_3 . The results are shown in Figure 8. The optimal salinity as well as the solubilization parameter did not change considerably at pH = 2 or pH = 11. Similar results were obtained at pH = 7.

From this section, it can be concluded that the blending of petroleum sulfonate with phosphate ester exhibited a significantly higher optimal salinity than the formulations containing petroleum sulfonate alone. The addition of Na_2CO_3 increased the solubilization param-

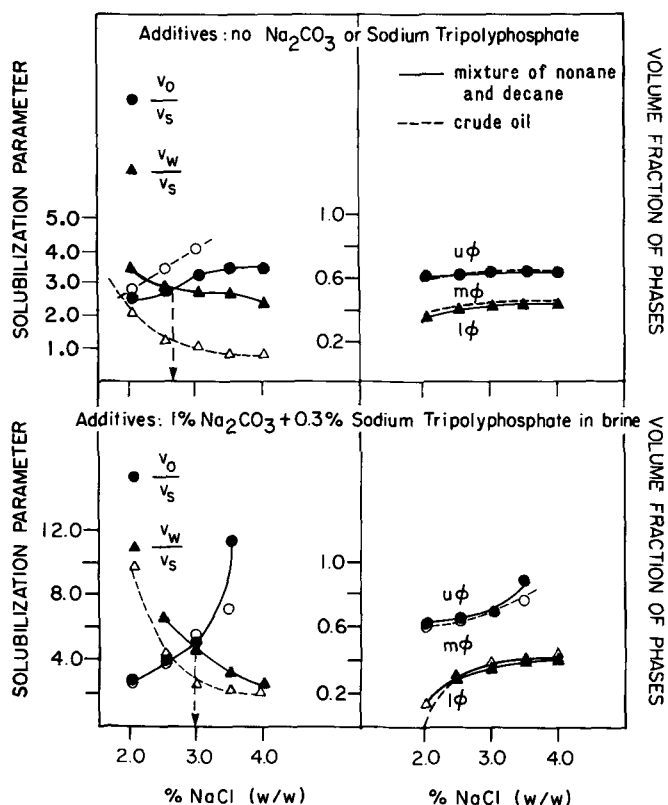


FIG. 7. Phase behavior of TRS 10-80 (5%) + KF AA-270 (2%) + TAA (3%) + oil at 80 C.

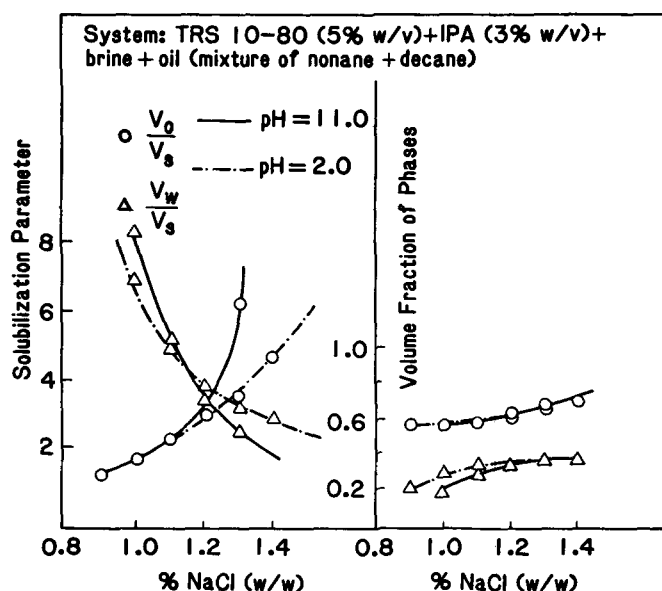


FIG. 8. Effect of pH on phase behavior of petroleum sulfonate system.

TABLE 2

Optimal Salinity and Solubilization Parameter at Optimal Salinity of Various Formulations

		Alcohol			
		IPA	IBA	SBA	TAA
(A) Without klearfac AA 270 and without Na_2CO_3 or Sodium Tripolyphosphate	o.s. ^a	1.3%	0.7%	< 1.0%	< 1.0%
	s.p. ^b	4.0	3.8	4.0	4.0
(B) Without Sodium Tripolyphosphate or Na_2CO_3	o.s.	2.6%	1.8%	2.1%	2.5%
	s.p.	2.2	2.7	2.3	2.5
(C) With 1% Na_2CO_3 but no Sodium Tripolyphosphate	s.p.	3.0%	2.8%	3.3%	3.4%
	s.p.	4.4	4.4	4.0	4.4
(D) With 1% Na_2CO_3 + 0.3% Sodium Tripolyphosphate	o.s.	2.8%	2.5%	3.1%	3.0%
	s.p.	4.2	4.0	3.6	4.5

^ao.s., Optimal salinity.

^bs.p., Solubilization parameter at optimal salinity. [$V_o/V_s = V_w/V_s$].

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eters. These observations are true for all four alcohols employed in this study.

Effect of alcohol structure on oil displacement. From phase behavior studies, it was shown that with an appropriate choice of cosurfactants, it is feasible to formulate a surfactant system which has an optimal salinity of desired value. The optimal salinities obtained with formulations containing different alcohols were not significantly different. Therefore, the effect of alcohol structure was not apparent from phase behavior. In this section, results of oil displacement tests are discussed wherein aqueous surfactant formulations were injected into sandpacks to displace a mixture of alkanes with EACN = 9.3 and into Berea cores to displace Ankleshwar crude oil. In all the oil displacement tests, 20% PV of aqueous surfactant solutions containing 5% TRS 10-80, 2% KF AA-270, 3% alcohols and electrolytes were used. These surfactant solutions also contained 1% Na₂CO₃ and 0.3% sodium tripolyphosphate. The oil displacement studies were carried out at 80 C. To delineate the effect of structure of alcohol on oil displacement, four alcohols (IPA, IBA, SBA and TAA) were employed. The surfactant solutions were prepared in the respective optimal salinity brines.

All phases in the produced effluent samples from the oil displacement tests were collected at less than 0.05 PV intervals and were analyzed for petroleum sulfonate using a two-phase titration technique (17). Figure 9 shows the surfactant concentration as a function of PV injected. The area under the curve provides the amount of surfactant recovered in the effluent. Table 3 summarizes oil recovery and the PV at which a maximum in surfactant concentration occurred for these flooding experiments. The highest tertiary oil recovery efficiency in sandpack was 92% in displacing pure alkanes with EACN = 9.3 and 79% in displacing crude

oil in Berea cores. The surfactant formulation responsible for such high oil recovery contained TAA. The oil recovery was poor (less than 31%) with the other three alcohols. The extent of surfactant retention in porous media was found to be the least (Table 3) for TAA containing surfactant formulation which gave highest oil recovery efficiency. However, a significant amount of surfactant also was recovered for the other floods. This suggests that better performing slugs are accompanied by lower surfactant retention, even though less retention does not necessarily mean higher oil recovery

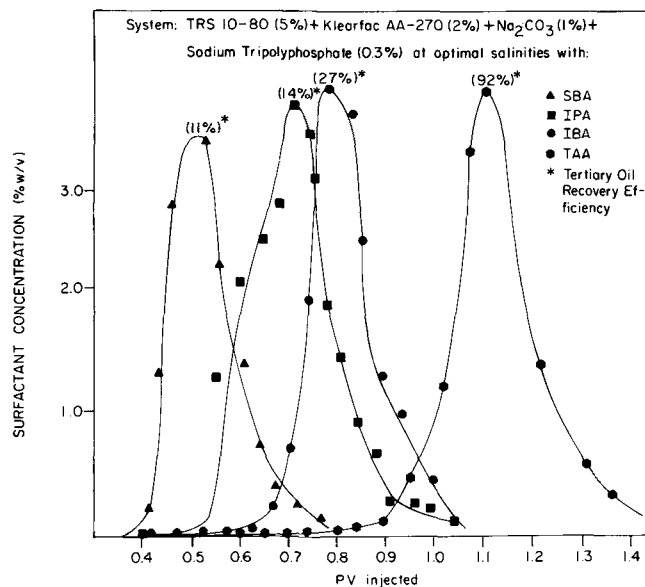


FIG. 9. Effect of alcohol on surfactant concentration in the produced fluids at optimal salinity of various formulations.

TABLE 3

Summary of Flooding Results: Effect of Alcohol*

Alcohol used	Residual oil after water flooding (% PV)	Tertiary oil recovery efficiency (%)	Surfactant recovery (%)	PV at which surfactant concentration reached a maximum
SBA ^a	22	11	57.6	0.50
IPA ^a	22	14	63.8	0.71
IBA ^a	15	27	61.3	0.77
TAA ^a	10	92	78.5	1.10
TAA ^b	43	79	—	—

^aA mixture of nonane and decane with EACN = 9.3 was displaced in sandpacks.

^bAnkleshwar crude oil was displaced in Berea core.

*0.2 PV of surfactant slug containing 5% (w/v) TRS 10-80, 2% KF AA-270, 3% alcohol in optimal salinity brine with 1% sodium carbonate and 0.3% sodium tripolyphosphate was injected in porous media (sandpack dimensions: 2.5 cm diameter, 30.0 cm length, permeability of 2-3 darcy; Berea core dimensions: 30.5 cm by 2.5 cm by 2.5 cm, permeability of 0.415 Darcy). Back pressure of 40 psi was applied. Flow rate of the injected fluids was 1 ft/day and the temperature was kept at 80 C. When displacing the pure alkanes, 1500 ppm Dow Pusher in optimal salinity brine was used after the surfactant slug. When displacing the crude oil, 2000 ppm Dow Pusher in optimal salinity brine was used after the surfactant slug.

(10,11,32). The mechanisms which are viewed as responsible for the mobilization of residual oil during surfactant flooding have been discussed (33-35). The principal mechanism is the solubilization of oil droplets in a water-external, stable homogeneous middle-phase microemulsion, whose volume depends on the surfactant concentration. A further mechanism which can contribute to the mobilization of residual oil is the inclusion of water into originally immobile residual oil phase, resulting from the transfer of surfactant to the oil phase. The volume increase of the oil phase, which is designated as swelling, gives rise to an increase of relative permeability to oil and thus mobilization of residual oil (36).

The drastic difference in oil recovery efficiency when the formulations contained different alcohols cannot be accounted for by the small changes in the viscosity of the middle-phase microemulsions containing different alcohols at their respective optimal salinities (37). The highest oil recovery efficiency by TAA-containing surfactant formulation suggests that the choice of alcohol is an important parameter for designing formulations for moderate temperature and salinity conditions. As shown in Figure 9, the surfactant breakthrough occurred at different pore volumes for different alcohols. When the surfactant formulations contained IPA, IBA or SBA, the surfactant breakthrough in porous media was much earlier than TAA-containing formulation. Therefore, the surfactant slug rushed through the porous media much faster in all systems except TAA-containing formulations. Moreover, the PV at which the surfactant concentration

peaked was highest for TAA formulation. The residence time available for contacting the residual oil was highest for the TAA-containing system. Hence, this formulation could displace the highest amount of oil in the porous media.

To delineate the behavior of surfactant slugs containing different alcohols, experiments were carried out to determine the alcohol partitioning in equilibrated phases. The alcohol concentration in the equilibrated phases (excess brine, middle and excess oil phase), at 80 C in the three phase region is plotted as a function of salinity in Figures 10 through 12 for the system TRS 10-80 (5%)/KF AA-270 (3%)/alcohol (2%)/alkanes (EACN = 9.3). Isopropanol partitioned mainly in the excess brine phase, as shown in Figure 10, and in the middle phase (Fig. 11), whereas TAA partitioned in the excess oil phase and in the middle phase, as shown in Figures 12 and 11, respectively. The alcohol concentration did not change appreciably as the salinity was increased except for TAA, which decreased slightly at a higher salinity. The partitioning of alcohols in excess oil phase increased as the salinity was increased for all alcohols except for IPA, which remained unchanged. In the middle phase, however, significant amounts of each alcohol partitioned in the entire three-phase region. TAA and IPA again showed opposite effects in terms of their partitioning dependence of salinity. TAA concentration increased while IPA concentration decreased in the middle phase upon increasing the salinity. This is expected because as the salinity was increased, brine solubilization in the middle phase decreased and oil solubilization increased. Now because IPA partitioned

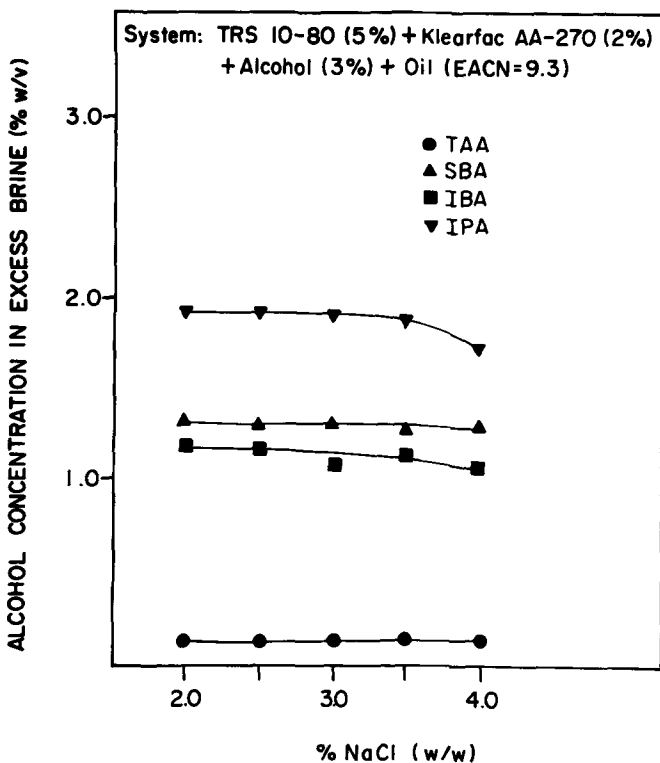


FIG. 10. Effect of salinity on alcohol partitioning in equilibrated excess brine phase in three-phase region for different alcohols.

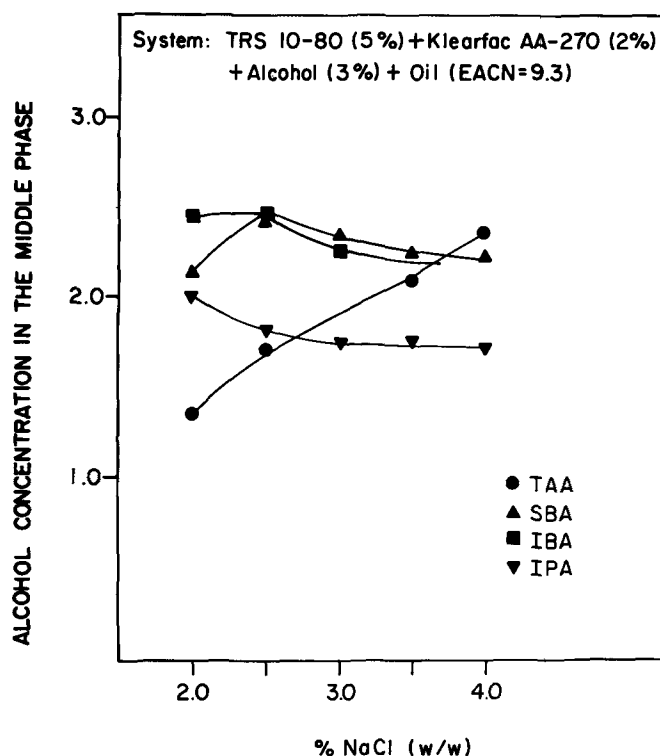


FIG. 11. Effect of salinity on alcohol partitioning in equilibrated middle phase for different alcohols.

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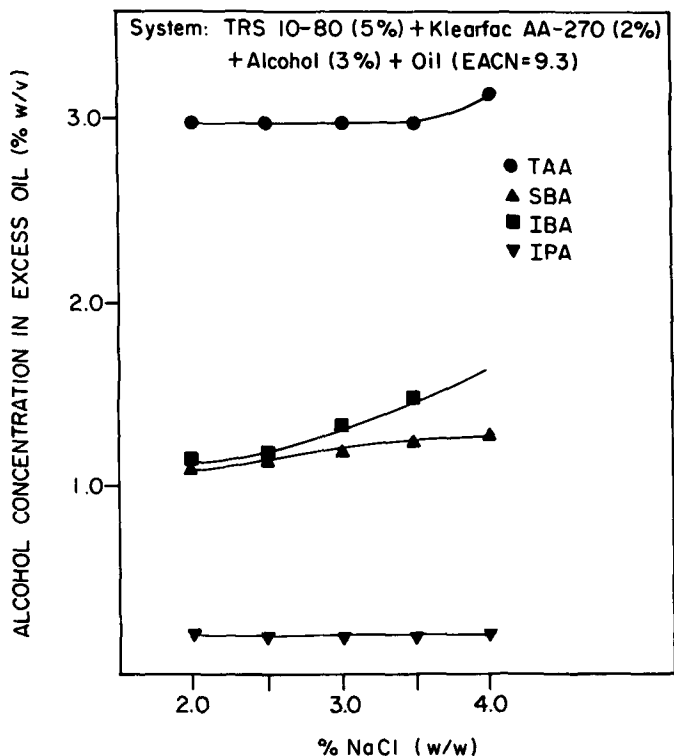


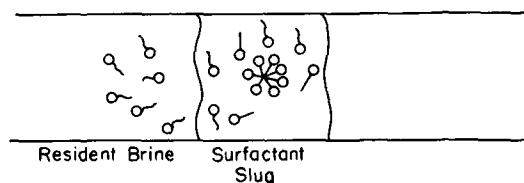
FIG. 12. Effect of salinity on alcohol partitioning in equilibrated excess oil phase in three-phase region for different alcohols.

mainly in the excess brine phase, its concentration in the middle phase decreased upon increasing the salinity. However, TAA partitioned mainly in the oil phase and hence its concentration in the middle phase increased upon increasing the salinity.

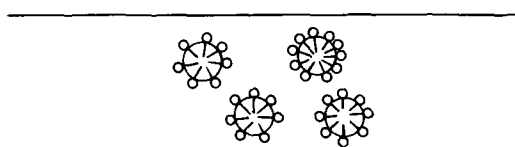
A proposed mechanism for the behavior of the surfactant slug containing IPA, IBA and SBA in porous media is shown in Figure 13. As discussed above, these alcohols partition significantly in the equilibrated aqueous phase (Fig. 10). This leads to the loss of such alcohols in resident brine in porous media; in other words, there is a chromatographic separation of alcohol and surfactant resulting in formation of stable emulsions by alcohol depleted surfactant slug. These emulsion droplets act as dead pores or block several pore throats, resulting in the early breakthrough of surfactant in the effluent. Therefore, the surfactant slug does not come in contact with a significant number of oil droplets and is unable to mobilize these droplets, resulting in poor oil recovery efficiency.

A proposed explanation for the behavior of the surfactant slug containing TAA in porous media is shown in Figure 14. As discussed above, TAA partitions significantly in the equilibrated oil phase (Fig. 12). This partitioning seems to be responsible for the mass transfer of alcohol from surfactant to oil ganglia. This produces ultra low interfacial tension at the oil/brine interface, promoting the mobilization and formation of an oil bank. Hence, a condition of plug flow exists for the surfactant slug in

Mass transfer of alcohol from surfactant slug to resident brine.



Formation of stable emulsions by alcohol depleted surfactant slug.



Leading to blockage of several pore throats, resulting in the early breakthrough of surfactant slug.

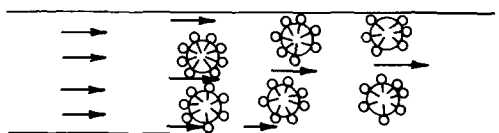
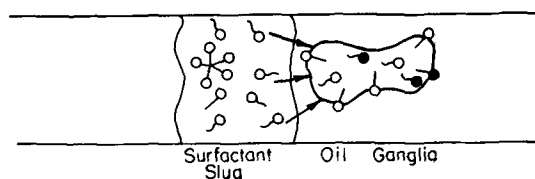
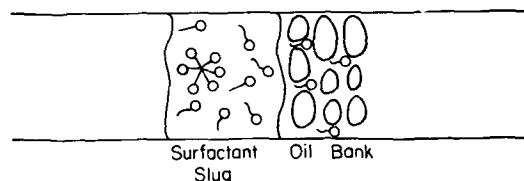


FIG. 13. A proposed mechanism for the behavior of surfactant slug containing IPA, IBA and SBA in porous media.

Mass transfer of alcohol from surfactant slug to oil ganglia.



Produces ultra-low IFT and hence promotes mobilization and formation of an oil bank.



Leading to plug flow condition of the surfactant slug and surfactant breakthrough around IPV of injected fluid.

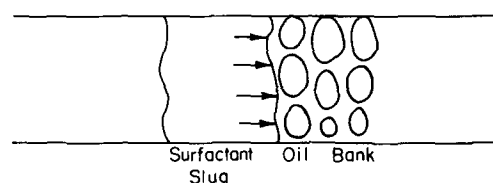


FIG. 14. A proposed mechanism for the surfactant slug containing TAA in porous media.

porous media. The TAA-containing surfactant slug then comes in contact with most of the residual oil. This is supported by the surfactant breakthrough around 1 PV and oil displacement efficiency of 92% when the residual oil was displaced by a surfactant system containing TAA (Table 3).

Effect of salinity on oil displacement. For the TAA-containing formulations, a series of displacement tests were conducted wherein the salinity of the system was varied around optimal salinity value thereby changing the phase environment and, hence, the phase characteristics of the microemulsion formed in situ. Table 4 summarizes the results of these flooding tests. The oil recovery efficiency was the highest at optimal salinity and lowest at salinity higher than the optimal value. The optimal salinity concept involves the formation of middle phase microemulsion that has ultralow IFT with both oil and brine and is capable of displacing the residual oil.

Figure 15 shows the surfactant concentration in effluent as a function of the pore volume of fluids injected at different salinities. The surfactant breakthrough was the earliest when the injected surfactant slug contained brine of higher than optimal salinity value. Moreover, at this salinity, the surfactant recovery which is given by the area under the curve was the lowest. This indicates a significant surfactant retention in porous media because of the precipitation of surfactant at higher salinities. This can decrease the stability or prevent the generation of microemulsion in situ and thus can cause an unstable, heterogeneous phase to occur. These changes frequently are associated

with extremely pronounced differences in the mobility of the phase flowing through the porous medium (33), which results in poor oil recovery.

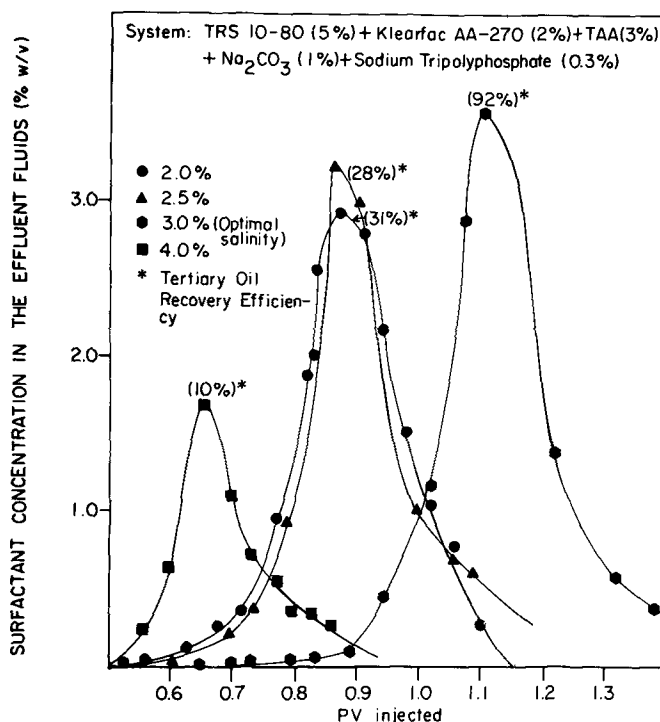


FIG. 15. Effect of salinity on surfactant concentration in the produced fluids.

TABLE 4

Summary of Flooding Results: Effect of Salinity*

Salinity of surfactant slug (% NaCl)	Residual oil after water flooding (% PV)	Tertiary oil recovery efficiency (%)	Surfactant recovery (%)	PV at which surfactant concentration reached a maximum
2.0 ^a	18	31	68.7	0.86
2.5 ^a	16	28	59.0	0.86
3.0 ^a (optimal salinity)	10	92	78.5	1.10
4.0 ^a	18	10	23.0	0.65
2.8 ^b (optimal salinity)	43	79	—	—

^aAmixture of nonane and decane with EACN = 9.3 was displaced in sandpacks.

^bAnkleshwar crude oil was displaced in Berea core.

*0.2 PV of surfactant slug containing 5% (w/v) TRS 10-80, 2% KF AA-270, 3% TAA in resident brine with 1% sodium carbonate and 0.3% sodium tripolyphosphate was injected in porous media (sandpack dimensions: 2.5 cm diameter, 30.0 cm length, permeability of 2-3 darcy; Berea core dimensions: 30.5 cm by 2.5 cm by 2.5 cm, permeability of 0.415 Darcy). Back pressure of 40 psi was applied. Flow rate of the injected fluids was 1 ft/day and the temperature was kept at 80 C. When displacing the pure alkanes, 1500 ppm Dow Pusher in resident salinity brine was used after the surfactant slug. When displacing the crude oil, 2000 ppm Dow Pusher in resident brine was used after the surfactant slug.

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