

EOR With Penn State Surfactants

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Summary. Petroleum sulfonate surfactants were synthesized from C₁₉, C₂₂, and C₂₆ feedstocks and evaluated in core tests for their ability to enhance oil recovery. All three feedstocks are composed predominantly of saturated paraffinic and naphthenic hydrocarbons. The C₁₉ feedstock includes about 12% aromatics. The hydrocarbons were vapor-phase oxidized at low temperatures to provide cyclic ethers, which subsequently were sulfonated to form a product mixture of mono-, di-, and trisulfonates.

Corefloods were conducted with both sulfonates developed at Pennsylvania State U. and commercial sulfonates in Berea sandstone cores. Production performances have been related to recovery and interfacial activity of the sulfonates. The core tests show that the optimum use of Penn State sulfonates for oil recovery is in the form of dilute slugs. High oil recovery efficiencies are realized when the Penn State sulfonates are used without cosurfactants to form dilute chemical slugs. Specifically, the enhanced oil recoveries obtained with C₂₂ sulfonates are significantly larger than those obtained with the C₁₉ and C₂₆ sulfonates. This is consistent with the oil/water interfacial tension (IFT) and phase behavior of the three types of sulfonates. Furthermore, EOR results and core-effluent analysis studies indicate that sodium carbonate (Na₂CO₃) in low concentrations is an effective sacrificial agent for Penn State sulfonates.

Introduction

Conventional petroleum sulfonates are produced from aromatic crude oil fractions of suitable boiling-point range. These have been the most frequently considered surfactants for EOR by chemical flooding. Because they are also in demand as lubricant additives and for other uses, their supply is not adequate for large-scale EOR projects. Consequently, paraffinic and naphthenic crude oil fractions that normally cannot be sulfonated have been sulfonated at Penn State by use of a novel two-step process. In the first step, reactive sites are introduced by carefully controlled low-temperature vapor-phase oxidation. The main products are cyclic ethers, predominantly tetrahydrofurans,¹ which are sulfonated in the second step to form surfactants suitable for EOR.^{2,3} One of the possible reaction paths is shown in Fig. 1.

Unlike sulfonation of aromatics, the sulfonation reaction of oxidized paraffinic and naphthenic hydrocarbons is not limited to a specific site. The cyclic ether initially forms a sulfate zwitterion, which undergoes elimination to form a diene. Sulfonation of this diolefin is assumed to follow the same scheme as alkene sulfonation. The diene sulfonates to form a mixture of dienesulfonic acids, hydroxyolefin sulfonic acids, and sultones.⁴ Relative yields of these products may vary with reaction conditions. Further reaction to form polysulfonate occurs readily; therefore, reactions must be carefully controlled.^{2,3}

Numerous methods have been presented for formulating surfactant systems from petroleum sulfonates, cosurfactants, and electrolytes, usually by optimizing IFT or

phase behavior with the oil to be displaced. The average equivalent weight (EW) of the surfactants and the type and concentration of cosurfactants and electrolytes are varied to minimize IFT or to maximize the amounts of oil and water solubilized in a middle-phase microemulsion.⁵ In this study, a procedure based on these methods has been applied to nonaromatic Penn State sulfonates and conventional aromatic sulfonates. The connection between the molecular structures of the Penn State sulfonates, their interfacial activity, and their ability to displace oil in corefloods is explored.

Surfactant Synthesis

Three feedstocks were chosen for vapor-phase oxidation and sulfonation: a C₁₉ narrow boiling fraction, a C₂₂ white oil, and a C₂₆ oil. Table 1 lists some properties of the oils. The oxidation and sulfonation have been described in a previous paper,⁶ and hence only a brief description will be given.

Oxidation. The oxidation reaction was carried out in a single-pass tubular reactor 4.25 ft [1.3 m] long by 0.17 ft [0.05 m] in diameter with some 10 oxygen and 3 steam inlets along the reactor. The schematic of the reactor is shown in Fig. 2. The feed is diluted with sufficient steam and/or N₂ to keep all the hydrocarbons in the vapor phase and to moderate the heat of reaction. Low-temperature oxidation (570 to 750°F [300 to 400°C]) favors the production of oxygenated compounds, while high-temperature oxidation (930°F [500°C] and above) favors the production of olefins. The hydrocarbon-feed conversion

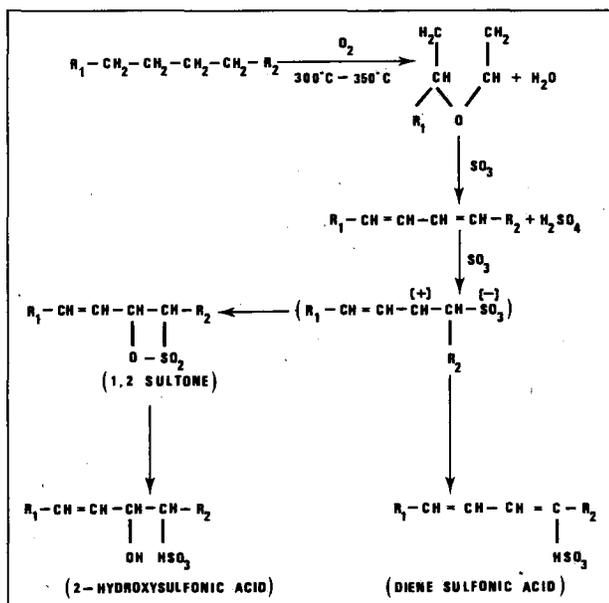


Fig. 1—Proposed reaction path for sulfonation.

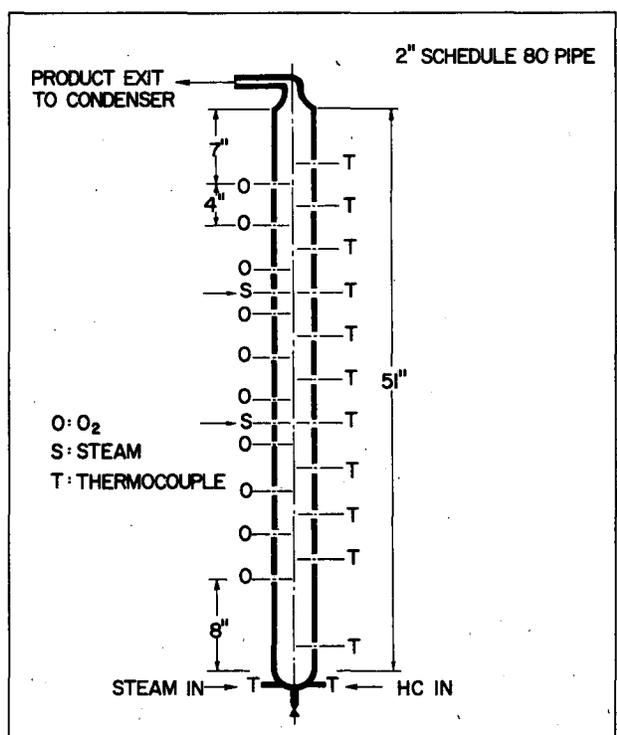


Fig. 2—Steam-moderated vapor-phase oxidation reactor.

depends on several process variables: oxygen-to-feed mole ratio, contact time, reaction temperature, and proportion of steam used. Excess oxygen, a long contact time, and high temperatures increase the feed conversion. They also increase the yields of carbon oxides, olefins, and low-boiling oxidized products, however, and thus decrease the yield of desirable high-boiling oxygenated liquid products. The typical reaction conditions for a successful conversion of the feedstock to the desired oxygenated liquid products are an oxygen-to-feed mole ratio of 1:3, an average reactor temperature of 580 to 660°F [305 to 350°C], N₂-and-steam-to-feed mole ratio of 19:25 (weight ratio of 1:1.3), and a contact time of about 5 to 10 seconds.

These conditions gave conversions of 44 to 70% with 98 to 83% of the product in the same boiling range as the feed. Liquid product yields near 100 wt% of the hydrocarbon feed show that combustion to CO₂ and water and cracking to light ends were minimal. Most molecules undergo only a single oxidation, converting mainly to cyclic ethers plus some olefinic hydrocarbon byproducts.

Sulfonation. Once the reactive groups are introduced into the hydrocarbon molecules through vapor-phase oxidation reaction, the second step, sulfonation, is carried out to produce sulfonates.^{2,3} The surfactants used in this study are sulfonates synthesized in a continuous-wiped-film reactor with SO₃ vapor diluted with N₂. Fig. 3 shows a schematic of the reactor. The reactor consists of a double-walled glass cylindrical tube (30×0.6-in. [75×1.5-cm] ID) fitted with a spinning band (polyethylene band) that continuously forces the viscous products from the reaction zone downward into a receiver. By constant removal of the product from the reaction zone in this manner, polysulfonation was reduced. The polyethylene band undergoes surface charring on initial use but has lasted more than 6 months without further significant deterioration. We used 1,1,2-trichloroethane as a solvent and diluent and found it superior to other chlorinated hydrocarbons in preventing viscous polysulfonic acids from building up in the reactor. Products from the continuous-sulfonation reactor are neutralized and isolated in batches. The method used for isolating and characteriz-

Hydrocarbon	Average Molecular Weight	Normal Boiling Point Range (°C)	Carbon in Aromatic Ring (wt%)	Carbon in Naphthenic Ring (wt%)	Carbon in Paraffinic Chain (wt%)	Carbon in Olefins (wt%)
MLO-7591 (C ₂₆)	366	390 to 460	2.8	30.2	67.0	0.0
Carnation white oil (C ₂₂)	335	220 to 420	0.97	31.9	67.1	0.0
Kensol-53 (C ₁₉)	275	315 to 341	13.0	43.0	36.0	8.0

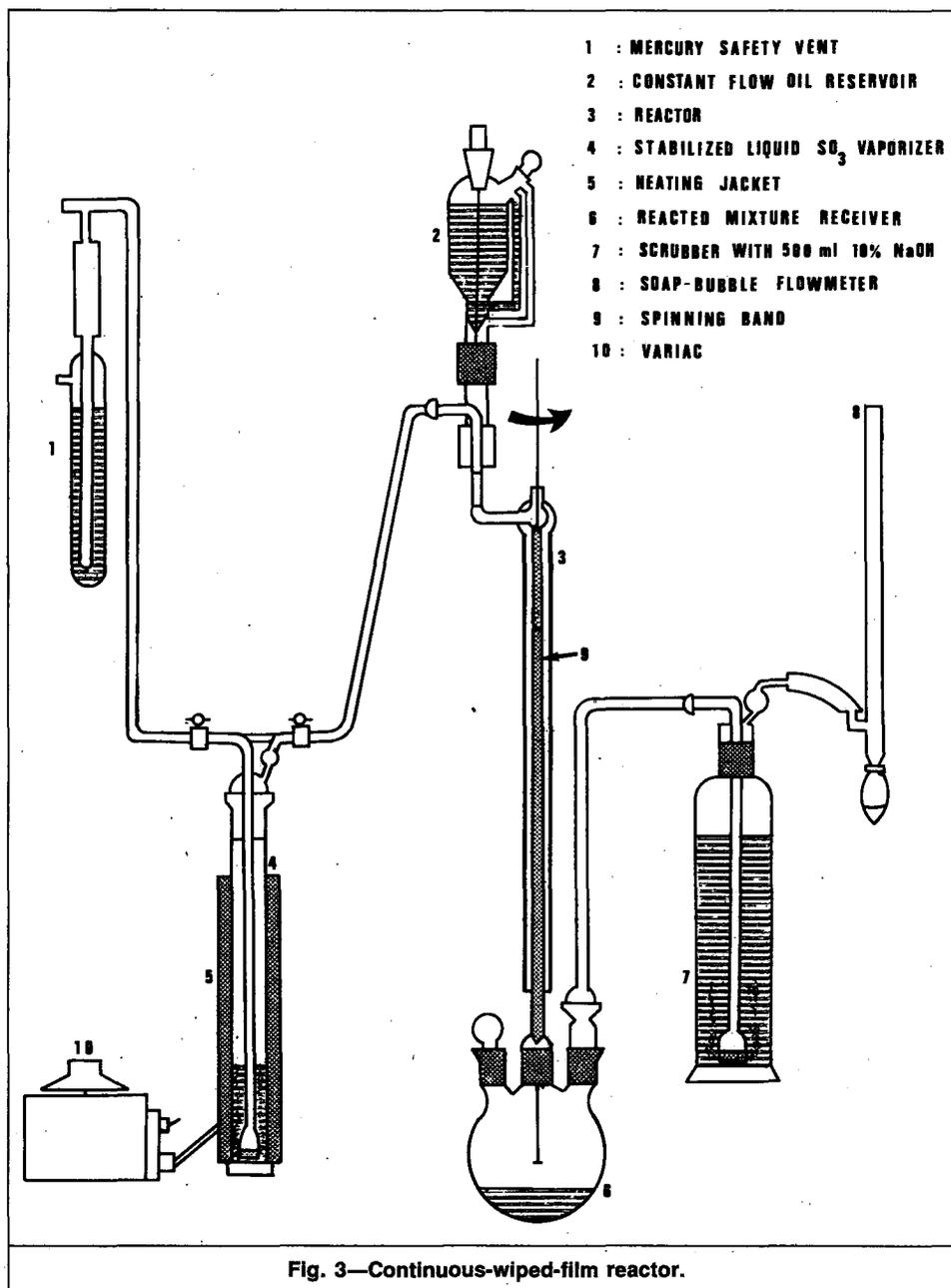


Fig. 3—Continuous-wiped-film reactor.

ing the sulfonates is similar to the procedure developed by Ashcraft and Saunders.⁷ Considerably more inorganic sulfate is found than in the production of conventional sulfonates because the SO₃ dehydrates the cyclic ethers, as described in the Introduction. The sulfate resulting from the dehydration forms inorganic salt. The product is dissolved in 40% isopropanol and is held in an ice bath to crystallize the salts. It is then filtered to obtain a final product with only 2 to 3 wt% inorganic salt.

Feedstocks with different molecular size distribution (C₁₉, C₂₂, and C₂₆) were used to produce sulfonates with different average EW's. In most cases, the sulfonation products were separated into two fractions by extraction with 85% isopropanol. The alcohol-soluble fraction has been designated as mono and contains mostly mono- and disulfonates (higher-EW fraction). The alcohol-insoluble fraction consists primarily of di- and trisulfonates and has been designated as poly (lower-EW fraction). The

average EW of sulfonates reflects their hydrophilic or lipophilic nature.⁸

An additional factor that may affect hydrophilicity is the sulfonate structure. A study by Maag *et al.*⁴ shows that 1,2 sultones are likely to be formed by sulfonation of olefins. 2-hydroxysulfonic acid produced by hydrolysis of this sultone can form a stable six-member ring by intramolecular hydrogen bonding, resulting in very low water-solubility.⁹ Thus, if the amount of this 2-hydroxyolefin sulfonate is substantial, the sulfonate mixture may be less water-soluble than expected from its EW. An example of a lower-EW sulfonate with lower hydrophilicity is discussed in the Results section.

Slug Design and Optimization Criteria

Penn State sulfonates were evaluated for use in both low-concentration micellar solutions and in microemulsions. In this paper, a distinction between a micellar solution

TABLE 2—SLUG COMPOSITIONS

System	Composition	Type	EW	Concentration (%)	Water/Oil Ratio	Electrolytes (%)	Cosurfactants (%)	Oil
A	TRS-18 + TRS-40	Aromatic sulfonates	381	5	1.0	1.5 NaCl	0.325 t-butanol 0.20 t-amyl alcohol	cyclohexane
B	TRS-18 + TRS-40	Aromatic sulfonates	381	5	15.7	0.89 NaCl	0.325 t-butanol 0.20 t-amyl alcohol	cyclohexane Isopar-M + HAN (9/1)
C	TRS-18 + DI-128 (C ₁₉) (1/2)	Aromatic sulfonates and mainly paraffinic Penn State sulfonates	363	13	1.0	1.5 NaCl	0.37 t-butanol 0.20 t-amyl alcohol	Isopar-M + HAN (9/1)
D	SI-122 (C ₂₆) (3/1-mono/poly)	Mainly paraffinic Penn State sulfonates	354	0.5	Micellar, no oil	2.0 NaCl 0.75 Na ₂ CO ₃ 0.75 Na ₂ SO ₄	0.3 C ₁₉ oxy 3 C ₁₉ oil	50% cyclohexane + 50% Bradford crude
E	DII-14 (C ₂₂) (mono)	Mainly paraffinic Penn State sulfonates	340	0.5	Micellar, no oil	1.4 NaCl 1.1 NaCl 0.5 Na ₂ CO ₃	None	Isopar-M + HAN (9/1)

HAN = heavy aromatic naphtha

and a microemulsion is made. An aqueous solution of surfactant slightly above critical micelle concentration but containing no oil is referred to as a micellar solution. A surfactant solution at high concentration (e.g., 5 wt%) that contains both oil and water is called a microemulsion. Chemical slugs were also formulated with commercial aromatic sulfonates to provide a standard for comparison. Table 2 lists the average EW of the sulfonates and the slug compositions that subsequently were used in solution-behavior and core-test studies.

The primary criterion⁵ to determine whether a surfactant solution will effectively displace residual oil is that both slug/oil and slug/brine IFT's should be low, preferably less than 10^{-2} dynes/cm [10^{-2} mN/m]. With this criterion, the concentration of surfactant in solution and its ability to solubilize oil are secondary considerations. Some surfactants are capable of solubilizing considerable amounts of oil into the aqueous phase (or water into the oil phase). These surfactants typically are high-concentration surfactant solutions and generally exhibit low-IFT behavior. Some surfactant systems have been observed, however, that cannot solubilize significant amounts of oil and water yet still exhibit low IFT's. Thus solubilization behavior alone does not determine the usefulness of a surfactant. The IFT is the ultimate criterion. It is important to keep this distinction in mind while the two screening procedures outlined below are considered.

In screening high-concentration surfactant solutions, the relationship between IFT and solubilization frequently has been useful.¹⁰ The basis for this relationship is the hydrophilicity and lipophilicity of the surfactant, which can be altered by a change in the solution parameters, such as average EW of the surfactant and the type and concentration of the cosurfactants and electrolytes. When the hydrophilic/lipophilic balance is optimum, the surfactant favors neither the oil phase nor the aqueous phase, and it becomes most concentrated at the interface. Then the oil/water IFT is minimum and the amount of oil and water solubilized by the surfactant is a maximum. Thus for a specific surfactant/oil/water system with high surfactant

concentration, solution parameters may be optimized by studying the solubilization behavior.

When high surfactant concentrations (greater than 2 wt% active surfactant) were used in oil/brine systems, two or three stable coexisting phases were formed. In these systems, surfactants were equilibrated with equal volumes of oil and brine until no further change in phase volumes occurred. These systems were optimized to maximize the solubilization parameters V_o/V_s and V_w/V_s (the volume ratios of oil to surfactant and of water to surfactant, respectively) in the microemulsion phase. In calculating these ratios, we assumed that the cosurfactant volume had a negligible effect on the observed volume ratios and that almost all the surfactant partitioned into the microemulsion phase. Healy¹⁰ established that for surfactant solutions that do solubilize large amounts of oil and water, solubilization parameters greater than 2 will ensure satisfactory IFT's.

Dilute surfactant slugs were formulated by minimizing the IFT between oil and aqueous phases. IFT measurements were used to find the optimum composition because the amount of surfactant was not sufficient to solubilize appreciable amounts of oil and water. In these experiments, 0.5 wt% active surfactant was dissolved in the brine and equilibrated with an equal volume of oil. The surfactants were also tested for salt tolerance, which was determined by increasing the salinity at fixed temperature until the solution became turbid.

Following these two types of slug formulation methods, if IFT's were less than 10^{-2} dynes/cm [10^{-2} mN/m] and solubilization parameters were greater than 2 to 3, the system was considered suitable for core testing.

Results

Five surfactant systems were formulated and used for core tests. Compositions of the slugs are given in Table 2.

Middle-Phase-Microemulsion Slug With Commercial Surfactants. The equilibrated middle-phase microemulsion is an oil/brine/surfactant solution that is immiscible

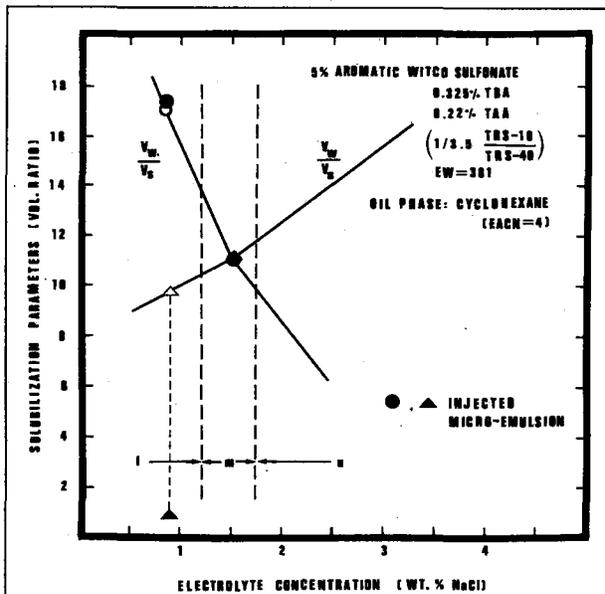


Fig. 4—Solubilization parameters vs. electrolyte concentration of TRS-18 and TRS-40 sulfonate mixture.

with both oil and water. High concentration of surfactant and large solubilization parameters are typical of middle-phase microemulsions. In these solutions, the surfactant mixture favors neither the oil nor the aqueous phase. Therefore, this type of microemulsion has the most desirable solution behavior.

Witco TRS-18TM (EW 510) and TRS-40TM (EW 344) were used to prepare a middle-phase microemulsion. These commercial surfactants were blended to optimize the solubilization parameters by changing the average EW of the mixture at fixed electrolyte and cosurfactant composition. A mixture of t-amylalcohol and t-butylalcohol was found to be a suitable cosurfactant. The salinity and cosurfactant concentrations were adjusted alternately until there was no further increase in solubilization parameters. Fig. 4 shows the final salinity scan for this system with cyclohexane [equivalent alkane carbon number (EACN)=4]. The EACN is a way of characterizing hydrocarbon and crude oil mixtures from their solution behavior with surfactant.¹¹⁻¹³ In Fig. 4, 1.5 wt% NaCl concentration corresponds to an optimum middle-phase microemulsion with maximum solubilization parameters. The same type and concentration of electrolyte and cosurfactants could be used with a different oil of a much higher EACN (90% Isopar-MTM+10% heavy aromatic naphtha, EACN-11). The only required change was to increase the average EW of the surfactant mixture from 381 to 426. In both cases, maximum solubilization parameters of 10.5 were obtained.

Lower-Phase-Microemulsion Slug With Commercial Surfactants. An equilibrated lower-phase microemulsion is an oil/brine surfactant solution that is immiscible with oil but miscible with water. In Fig. 4, the solid line represents how oil and water solubilization parameters in equilibrated microemulsions are changing as salinity increases. A lower-phase microemulsion forms at low salt

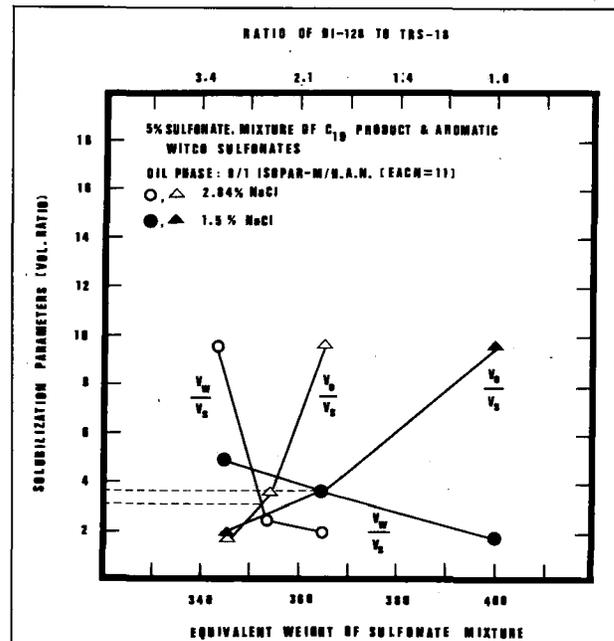


Fig. 5—Solubilization parameters vs. EW of DI-128 (C₁₉) and TRS-18 (aromatic) sulfonate mixture.

concentrations where surfactant favors the lower, aqueous phase. The particular slug designed was not equilibrated with oil. This solution contained a very small amount of oil, as shown in Fig. 4 with a broken line and indicated by its composition given in Table 2 (System B). This slug would therefore solubilize some oil in the core when contacted with residual oil and would approximately reach the composition of the equilibrated lower-phase microemulsion. This type of a slug is expected to lead to a partially miscible oil displacement mechanism. First, it would mobilize the residual oil by solubilizing it. After it is equilibrated with oil, displacement occurs through the production and maintenance of low IFT between the slug and reservoir fluids. Because it is a combination of both miscible and immiscible stages, the total displacement mechanism is called partially miscible.

Middle-Phase-Microemulsion Slug With C₁₉ Penn State Sulfonate. Penn State sulfonate DI-128 from C₁₉ oil was used without separation into mono and poly fractions. The relatively light feedstock yielded a sulfonate of low EW (290), which was highly water-soluble. This sulfonate was blended with TRS-18 (EW 510) to form a surfactant mixture with a wide EW distribution and a more suitable average EW to be used with a high-EACN oil. Fig. 5 shows the solubilization parameters vs. average EW of the surfactant mixture at two salinities. At 1.5 wt% NaCl concentration, an optimum average EW of 363 gave maximum solubilization parameters of 3.7. When NaCl concentration was increased to 2.84 wt% NaCl, the optimum average EW was decreased to 352. For this system, maximum solubilization parameters were slightly lower (3.2). Higher maximum solubilization parameters could have been obtained if the electrolyte concentration was decreased and the average EW of the surfactant mixture was increased. The optimization of this system was constrained, however, by limiting the amount of TRS-18

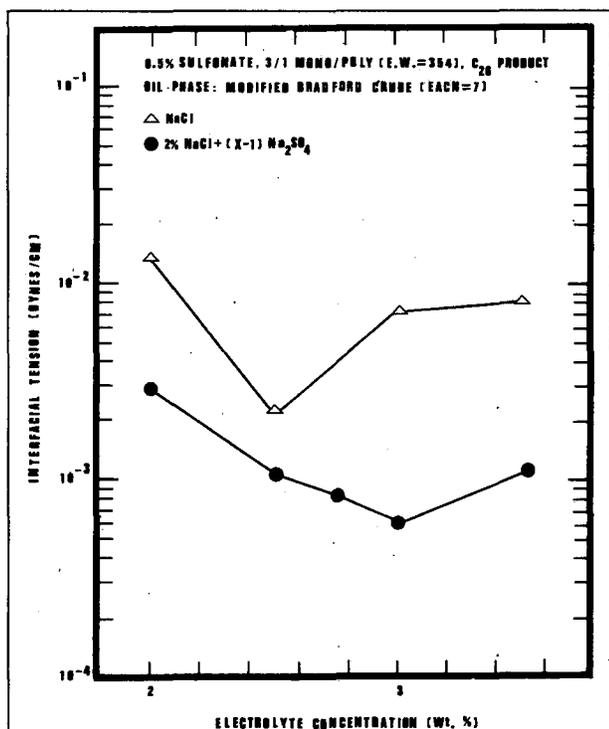


Fig. 6—IFT vs. electrolyte concentration of SI-122 (C₂₆) sulfonate system.

used in the blend. Furthermore, both of the maximum solubilization parameters obtained with the two blends are in a range considered potentially applicable for EOR.¹⁰ The blend with an average EW of 363 and 1.5 wt% NaCl was chosen as a slug composition (Table 2).

Dilute Micellar Slug With C₂₆ Penn State Sulfonate.

Penn State sulfonate SI-122 from C₂₆ oil was used to study the effect of sodium sulfate on surface activity of the surfactant. The sulfonate was separated into a mono fraction (EW 399) and a poly fraction (EW 219), which were then blended to optimize phase behavior. The optimum blend in equilibrium with an oil of EACN=7 had an EW of 354. Fig. 6 shows a salinity scan for this sulfonate and the effect of sodium sulfate on IFT's. The system produced IFT's of less than 1×10^{-2} dynes/cm [1×10^{-2} mN/m] with both sodium sulfate and NaCl. But the presence of sodium sulfate reduced the IFT by half an order of magnitude. The composition of the slug formulated with SI-22 is given in Table 2 (System D).

Dilute Micellar Slug With C₂₂ Penn State Sulfonate.

Sulfonate DII-4 synthesized from C₂₂ white oil was also separated into mono and poly fractions. We found that the mono fraction of DII-4 (EW 340) was less water-soluble than the higher-EW SI-122 mono fraction (EW 399). This behavior may be attributed to the molecular structure of some components of the sulfonate product, as mentioned earlier in the sulfonation part of the synthesis discussion. The mono fraction of DII-4 gave excellent IFT's against EACN=11 oil when optimized for electrolyte concentration (Fig. 7). It was used as a 0.5% solution without cosurfactants. The second curve on Fig. 7 shows a salinity scan with 0.5% Na₂CO₃ added. Ad-

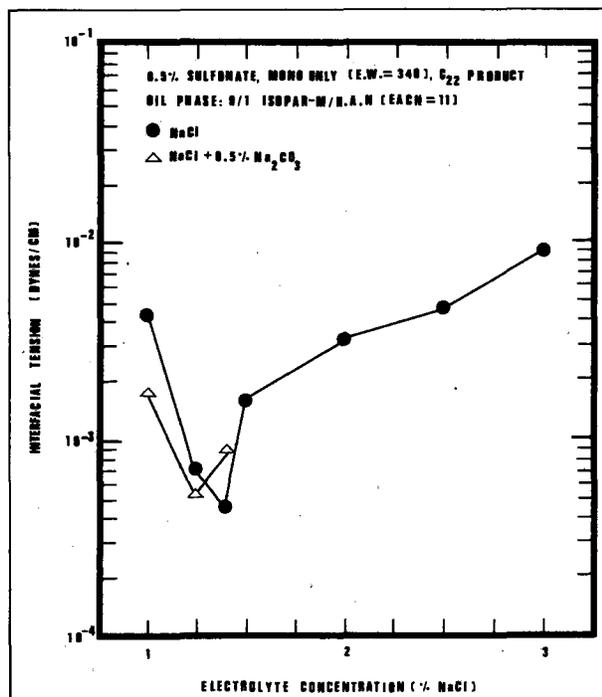


Fig. 7—IFT vs. electrolyte concentration of DII-4 (C₂₂) sulfonate system.

dition of Na₂CO₃ increases the pH of dilute solutions of Penn State sulfonate from about 6 to 11 but gives comparable IFT's. We decided to add Na₂CO₃ to slug formulations when adsorption studies showed that small amounts of Na₂CO₃ decreased adsorption losses.

DII-4 system also gave a high solubilization ratio of 12.5, indicating a potential for use in microemulsion slugs. The last slug composition given in Table 2 contains DII-4 surfactant.

Adsorption Studies. Surfactant loss in reservoirs is a major factor limiting the effectiveness of oil recovery. Studies of Hill *et al.*,¹⁴ Trushenski *et al.*,¹⁵ Bae and Petrick,¹⁶ and Novosad¹⁷ describe several mechanisms responsible for surfactant losses in porous media, including adsorption, precipitation, and entrapment of immiscible microemulsion phase. Adsorption is probably the most significant cause of slug retention, although other processes contribute to the problem.¹⁸ It is possible to compensate for the effect of adsorption in some cases; however. In this study, the purpose of adsorption experiments was to understand the significance of adsorption and to minimize it with some additives. Two types of adsorption experiments were conducted: static adsorption tests on crushed Berea sandstone, and effluent analysis of core tests using high-pressure liquid chromatography (HPLC).

A static adsorption study was conducted on the effect of electrolytes on adsorption of C₂₆ sulfonate in 0.5% solution. Crushed Berea sandstone was first preflushed with brine, then agitated for 24 hours with the surfactant solution. The IFT against 50% cyclohexane and 50% Bradford crude mixture and against a series of n-alkanes was measured before and after adsorption. In this proce-

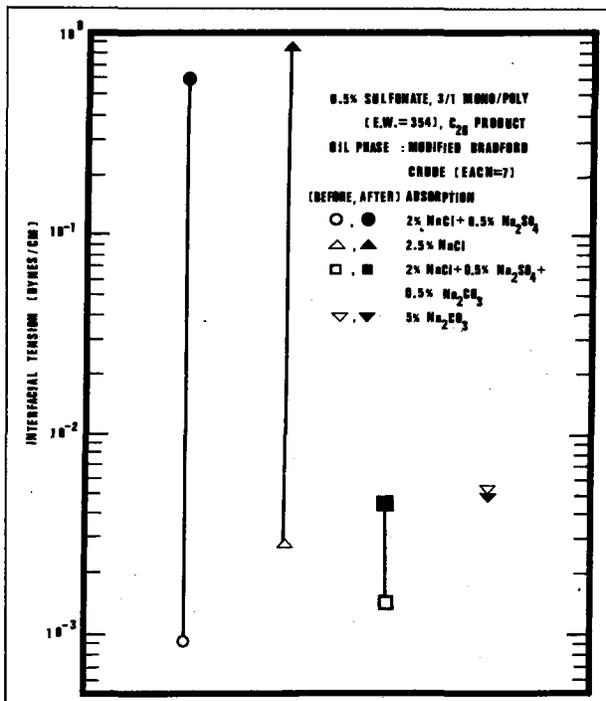


Fig. 8—IFT against oil of EACN-7 for SI-122 (C₂₆) sulfonate system before and after static adsorption tests.

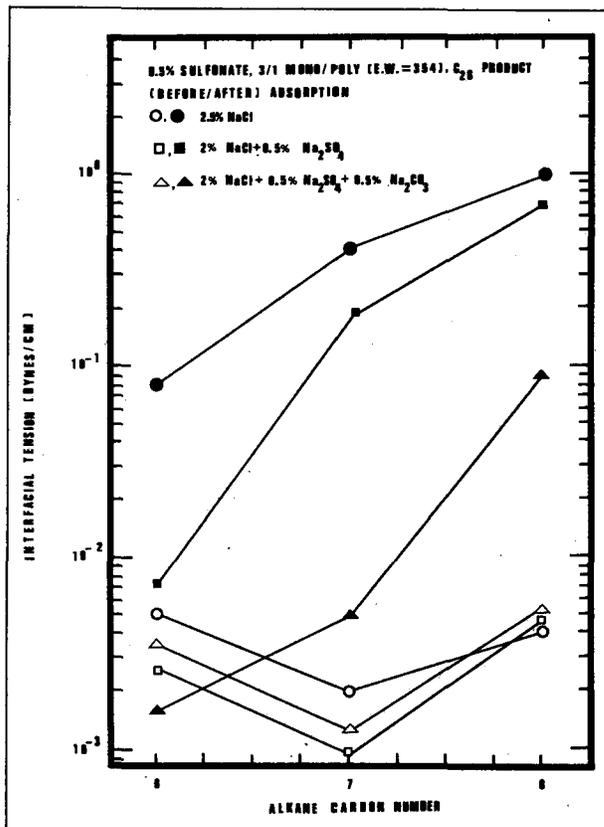


Fig. 9—IFT against ACN for SI-122 (C₂₆) sulfonate system.

TABLE 3—EFFLUENT ANALYSIS

Volume of Solution Injected in the Core, mL*	Volume of Effluent Collected, mL					
	Oil Phase	Water Phase	Microemulsion Phase			
33	50	393	54			
HPLC Analysis						
Sulfonates Recovered, %						
	Mono- 7.0	Di- 4.0	Mono- 10.0	Di- 29.0	Mono- 38.0	Di- 65.0
55% monosulfonates recovered						
97% disulfonates recovered						

*45% oil and 5% sulfonate microemulsion.

ture, surfactant adsorption was not measured quantitatively but only by its effect on IFT. Fig. 8 shows the change in IFT for four electrolyte compositions. Na₂CO₃ reduced surfactant loss while sodium sulfate had little effect. Fig. 9 shows the change in IFT against different alkanes. For similar sulfonates, the average EW of the sulfonates that gives a minimum IFT varies directly with the alkane carbon number (ACN) of the oil. Following adsorption, the minimum IFT occurred at a lower ACN, showing that the average EW of the sulfonate had decreased. This indicates greater adsorption of high-EW sulfonates.

Parallel to static adsorption tests, HPLC analysis was implemented to study surfactant losses in a series of core

tests with the commercial sulfonates. A sample of the injected microemulsion containing 1.0 mg of active sulfonate was diluted to form a 10-ppm solution, which was used to determine the HPLC detector response. The analysis conditions were those given by Zornes.¹⁹ Produced brine, oil, and microemulsions were analyzed separately for sulfonate content. The total monosulfonate and disulfonate in the produced fluids was calculated and the sulfonate retained in the core computed by difference. Table 3 shows an analysis for a typical core test. The higher-EW monosulfonates had larger losses in the core than the disulfonates. This agrees with the results of the static adsorption test.

Core Tests. All corefloods were conducted in 2-in. [5-cm]-diameter unfired Berea sandstone cores 1 ft [30 cm] long. Average permeability of the cores was 298 md (with a standard deviation of 78.7), while the average porosity was found to be 21.2% (with a standard deviation of 1.25). A fresh core was used for each run. Cores were preflushed, saturated with oil, then waterflooded to an average residual oil saturation of 31% with a standard deviation of 3.7. Note the small standard deviation in the residual oil saturation. In general it would appear that a high residual oil saturation would favor the conditions for a chemical flood because of the availability of large reserves of oil to form an oil bank. On the other hand, a low residual oil saturation attained after waterflooding indicates favorable pore-size distribution of each individual core. A small deviation in this property ensures that the cores had similar relative permeability and pore-size

	TRS-18/TRS-40		TRS-18/DI-128	SI-122	DII-4
	System A	System B	System C	System D	System E
EW	381	426	363	354	340
Concentration (wt%) × slug size (% PV)	78	70, 170*	78	35, 63*	32, 63*
Solubilization parameters					
(V_o/V_s)	10.5	8.5	3.6	—	12
(V_w/V_s)	10.5	17.0	3.6	—	12
(V_w/V_o)	1.0	2.0	1.0	—	1
IFT, dynes/cm	7×10^{-4}	1.8×10^{-3}	5.3×10^{-3}	1×10^{-3}	6×10^{-4}
Oil-in-place recovery, %	61	63, 87*	40	40, 37*	61, 73
Process efficiency (recovery/concentration × slug size)	78	90, 51*	51	114, 59*	191, 116*

*Corefloods with a larger slug size but the same composition for the systems studied.

distribution characteristics, and hence the effects of the variations of residual oil saturation on the tertiary recovery performance of the systems tested were minimal.

In all the displacement tests, the same brine composition was used for preflush and secondary and tertiary drive water. All the fluids were injected at a constant superficial velocity of 1 ft/D [0.3 m/d]. Glycerine solutions of the desired viscosity were used as mobility-control buffers to avoid the effect of polymer/surfactant interactions. Several runs duplicated with 500 ppm xanthan gum in place of glycerine gave less produced emulsions; however, oil recoveries were virtually the same. Tables 2 and 4 give the slug compositions and a summary of displacement tests.

Initial core tests with commercial surfactants established a reference for comparison and tested the slug design procedure. System A in Table 2 was a middle-phase microemulsion at its maximum oil solubilization capacity. System B was a low-oil-content lower-phase microemulsion system. After corrections were made for the volume of oil injected, recoveries averaged about 12% greater with the low-oil-content slugs (Fig. 10). Although System A had a larger solubilization parameter for oil and water compared with System B, which had a lower oil

solubilization parameter, the fact that System B was not equilibrated with oil and could stabilize more oil within the core might be the reason for its better oil recovery performance.

System C of Table 2 was designed in an effort to replace the TRS-40 component of System B with Penn State surfactant DI-128 (C₁₉). The recovery performances of the system with DI-128 and its commercial counterpart are compared in Fig. 11. The production profiles indicate very similar production behaviors. Formation of the oil banks started after 0.26 PV injection, and both of the banks disappeared approximately after a total injection volume of 0.96 PV. Although the times that the oil banks started and disappeared are very similar, a significantly lower recovery with the TRS-18/DI-128 system was achieved. The higher recovery performance of the commercial system is attributed to its higher interfacial activity. Thus observed recovery performances are consistent with the results obtained in the phase-behavior studies.

System D was designed with a pure Penn State surfactant (SI-122 [C₂₆]). This system yielded recoveries between 28.5 and 39.7% when used as a 0.5%-concentration aqueous solution. Because concentration and slug size were small, process efficiencies were somewhat higher

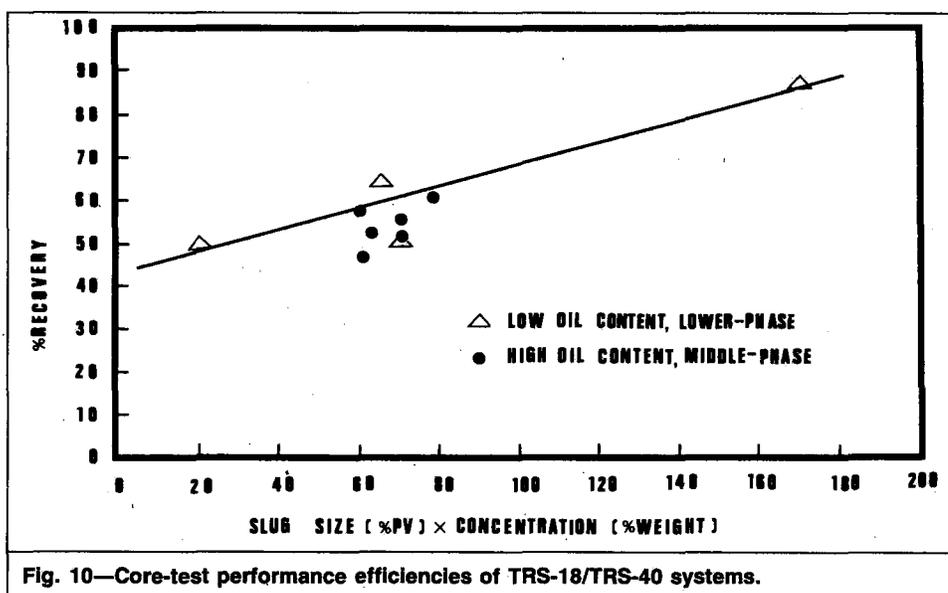
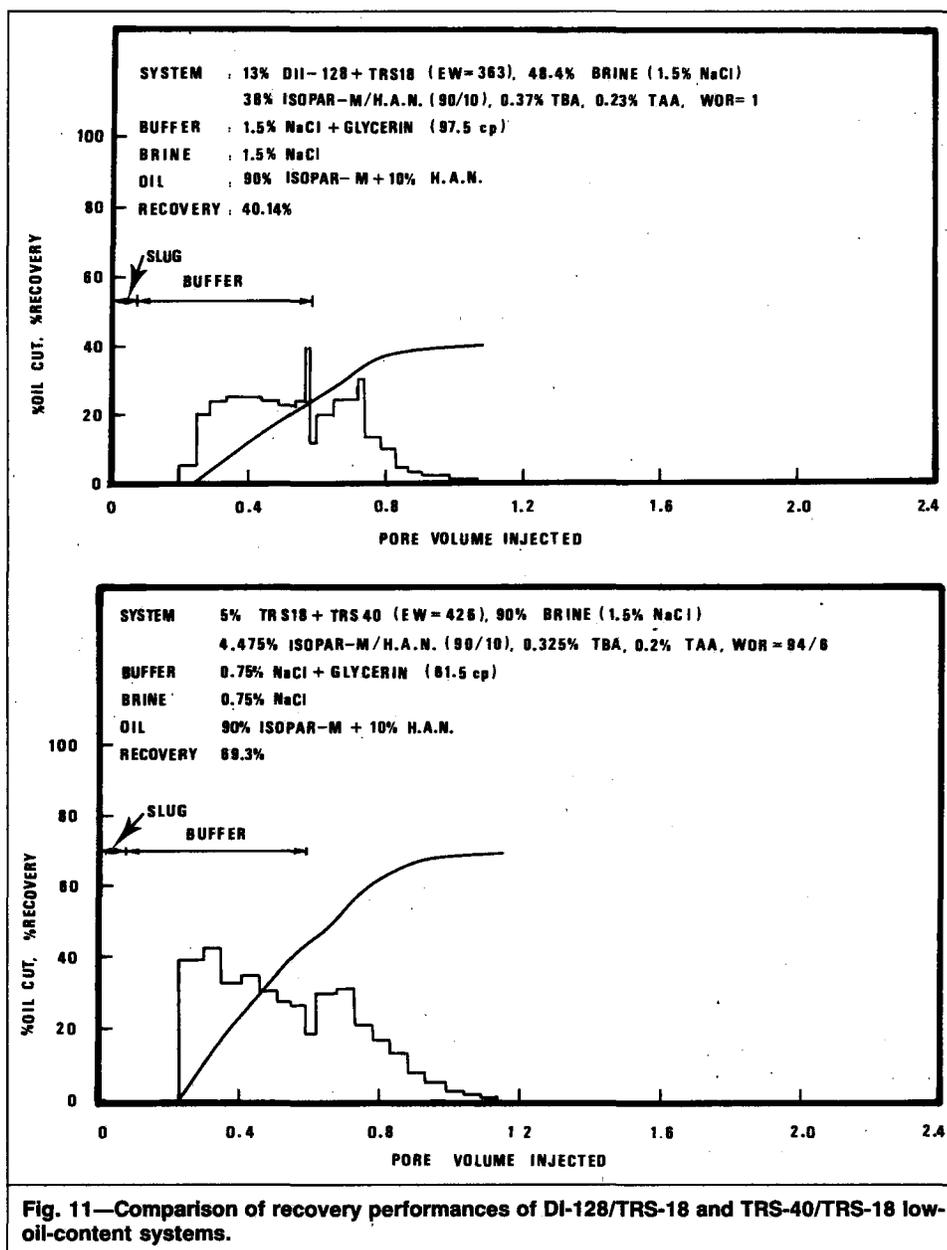


Fig. 10—Core-test performance efficiencies of TRS-18/TRS-40 systems.



than the high-concentration SI-122 surfactant slugs. Although these results were encouraging, addition of 0.3% oxygenated C₁₉ and 0.10% C₁₉ oil accelerated the process of establishing a reasonably high interfacial activity, but it did not alter the recovery significantly. Increasing the slug size did not help to increase the recovery, but a long, steady deviation of oil bank (up to 2.08 PV) was observed.

The mono fraction of Penn State DII-4 surfactant system (System E of Table 2), which was produced from C₂₂ white oil, was examined in three core tests. The first slug tested did not contain any Na₂CO₃ and gave a recovery of 22.7%. The production profile in this run contrasted with the excellent IFT and phase behavior of the system. The late start of production and relatively weak oil cuts were indications of more-pronounced sulfonate losses by adsorption. The HPLC analysis of effluent showed that 90% of the mono fraction was lost in the core.

The beneficial effect of Na₂CO₃ on adsorption was tested with the same surfactant by optimizing the electro-

lyte concentrations at 1.1% NaCl and 0.5% Na₂CO₃. The interfacial activity started at 0.32 PV of slug injection (Fig. 12). Two strong oil banks were formed during 1.8 PV of fluid injection. The recovery was 61% of residual oil saturation. The formation of a secondary oil bank was related to the chromatographic separation of sulfonates and the desorption of sulfonate by the low-saline mobility buffer injection. Fig. 12 compares the production profiles of Penn State sulfonate, DII-4 (C₂₂), and Witco sulfonate, TRS-16/TRS-40. Both of the coreflows were conducted under similar conditions of concentration, slug size, and mobility control. As can be seen from Fig. 12, production profiles from the perspectives of oil bank formation, oil cuts, and duration of oil production are almost duplicates of each other. Considering the high process efficiency of DII-4 (C₂₂) system, another run was carried out with the slug size doubled. Fig. 13 shows the production profile of this run, which yielded an oil recovery of 72.5%. The formation of a secondary oil bank during low-saline mobility drive indicated that the desorption

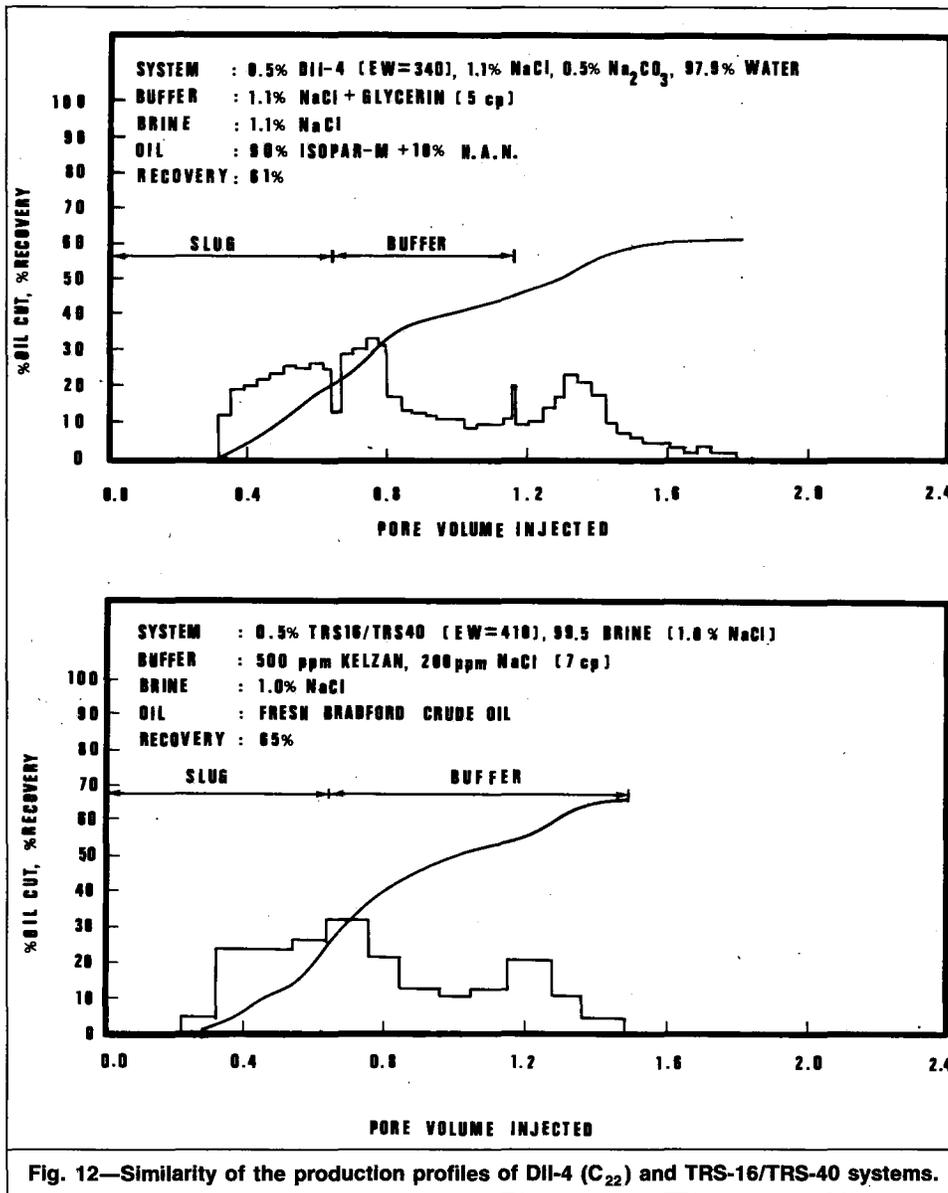


Fig. 12—Similarity of the production profiles of DII-4 (C₂₂) and TRS-16/TRS-40 systems.

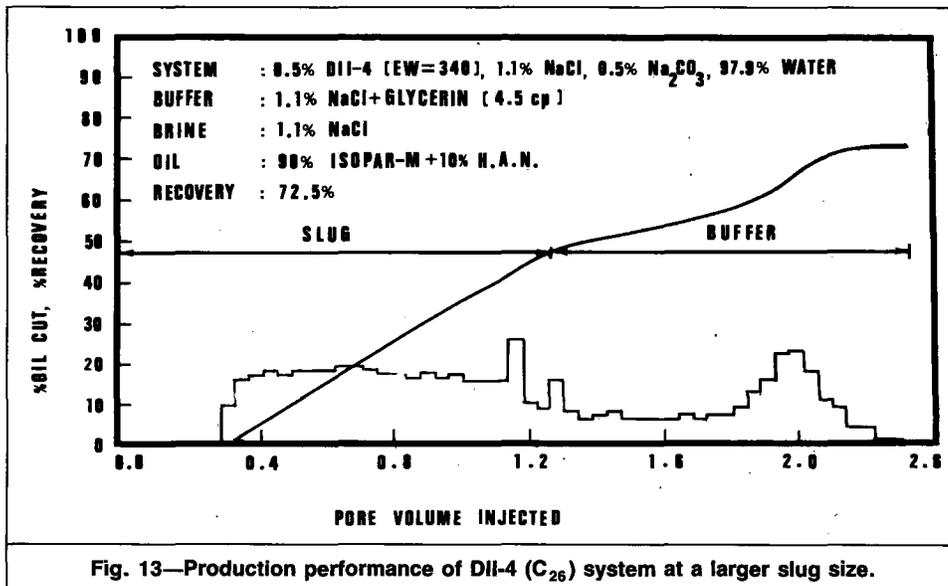


Fig. 13—Production performance of DII-4 (C₂₆) system at a larger slug size.

of the sulfonate molecule is important. This extremely simple system had only sulfonate and NaCl and Na₂CO₃ salts with no cosurfactant. This strongly water-soluble sulfonate solution had high solubilization capacity and very low IFT characteristics. Phase-behavior studies indicated that the DII-4 (C₂₂) system shows good partitioning of sulfonate in oil and brine.

Conclusions

1. Pure Penn State dilute surfactant systems proved effective in recovering tertiary oil from Berea sandstone cores.

2. Observed tertiary oil recoveries were consistent with the results of phase behavior and IFT studies.

3. Na₂CO₃ at low concentrations reduces the adsorption of Penn State sulfonates from dilute slugs. Adsorption studies and effluent analysis also showed that high-EW sulfonates are preferentially adsorbed.

4. The EW of surfactants from oxidized hydrocarbons does not always reflect their relative oil solubility.

Nomenclature

V_o = volume of oil in microemulsion phase

V_s = volume of surfactant in microemulsion phase

V_w = volume of water in microemulsion phase

Acknowledgments

We express our appreciation to the following organizations that provided support to our Enhanced Oil Recovery Research Project: Amoco, Conoco, Exxon, Marathon, Mobil, Penn Grade, Pennzoil, Sohio, Stauffer, Texaco, and Witco.

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SI Metric Conversion Factors

cp × 1.0*	E-03 = Pa·s
dynes/cm × 1.0*	E+00 = mN/m
°F (°F-32)/1.8	= °C
in. × 2.54*	E+00 = cm

*Conversion factor is exact.

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Original manuscript received in the Society of Petroleum Engineers office Sept. 16, 1984. Paper accepted for publication Dec. 21, 1984. Revised manuscript received May 12, 1986. Paper (SPE 12308) first presented at the 1983 SPE Eastern Regional Meeting held in Champion, PA, Nov. 9-11.