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Technical

Enhanced Oil Recovery Using Carboxylate Surfactant Systems

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ABSTRACT

Oil displacement tests in water wet Berea sandstone cores containing residual crude **oil** flooded with water have shown that high tertiary oil recoveries can be obtained using the sodium salts of readily available carboxylic acids. Using a 10% pore volume surfactant slug containing 3.0% sodium isostearate and 3.0% isopentyl alcohol followed by a polyacrylamide mobility buffer resulted in a 92% tertiary oil recovery, which compares well with recoveries using petroleum sotfonates. Oil recoveries were highly dependent on pH and added base. Aliphatic C18 carboxylates gave higher recoveries at lower pH using sodium bicarbonate as the added base (pH 8.5) rather than sodium hydroxide, sodium carbonate or sodium orthosilicate (pH 11-13). In contrast, aromatic earboxylates e.g., sodium p-(1-pentylnonyl)benzoate, gave higher recoveries at higher pH using sodium carbonate rather than sodium bicarbonate. Carboxylares with branched alkyl groups, e.g., isostearate, gave higher tertiary oil recoveries than unbranched carboxylates, e.g., oleate or stearate. Low cost tall oils and tall-oil fatty acids, when neutralized with base, gave oil recoveries of 60-80%. Carboxylates were found to give good oil recoveries even when significant amounts of calcium ion were present.

INTRODUCTION

Because many carboxylic acids are readily available at much lower prices than petroleum sulfonates, a study was carried

out to assess the potential of sodium carboxylates as surfactants for enhanced oil recovery. Previous reports (1-3) have shown that low interfacial tensions $(\sim 0.001$ dyne/cm) can be obtained between hydrocarbons and aqueous saline solutions of sodium carboxylates. Phase volume studies presented in the accompanying paper have shown that 3-phase systems are produced, often with large volume fraction middle-phase microemulsions. Although the possible use of carboxylates as surfactants for enhanced oil recovery are mentioned in several patents (4-6), very few examples are given where they are actually used. In this paper, results are presented of oil displacement tests in sandstone cores with a variety of carboxylate surfactants.

EXPERIMENTAL PROCEDURES

The sources and composition of the various surfactants, cosurfactants and other materials are listed in Table I. In cases where sodium carboxylates were not available, carboxylate solutions were prepared by using equimolar amounts of carboxylic acid and sodium hydroxide, which would give the desired weight percentage of sodium carboxylate. If the carboxylic acid sample was not pure, as in the case of tall oils, the amount of sodium hydroxide needed to neutralize the acid was calculated using the acid

TABLE I

Sources and Composition of Various Surfactants, Cosurfactants and Other Materials

aCosurfactants not listed were reagent grade.

bNorth Burbank Unit crude oil from Shelley-Thompson lease, which was centrifuged (15 hr, 1200 RPM), filtered through 1-2 in Berea sandstone, and purged with nitrogen overnight before addition of ethylbenzene.

value or neutralization equivalent of the sample. Optimal salinities used in the oil displacement tests were based on phase volume studies (7). The optimal salinity was defined as the salinity where the uptake of oil and water in the middle phase was equal. The optimal salinities were determined at 49 C using n-deeane rather than North Burbank Unit (NBU) crude oil with ethylbenzene added to simulate the oil before the natural gas is lost (EACN=10) because long-lasting macroemulsions often occurred using the oil.

Oil displacement tests were carried out in water wet epoxy-coated Berea sandstone cores (3 ft \times 3 in. dia.) at 49 C by the following procedure. The dry core was saturated with brine of the desired salinity in simulated Ark-Burbank water (Table I) and was then flooded with simulated NBU crude oil. The oil-saturated core was then flooded with water to irreducible oil saturation with brine of the desired salinity in simulated Ark-Burbank water.

The following preflush, surfactant and mobility buffer slugs were used in the majority of the oil displacement tests (procedure A). Any variations in this procedure are noted in the discussion and tables. A preflush (10% pore volume, 20 mL/hr, 1.8 feet/day) containing 0.6% base at the desired salinity in distilled water was used. Bases used included sodium bicarbonate, sodium carbonate, sodium hydroxide and sodium orthosilicate. The surfactant slug (10% pore volume, 10 mL/hr, 0.9 feet/day) consisted of 3.0% sodium carboxylate, 3.0% Cosurfactant and 0.6% base at the desired salinity in distilled water. This was followed by a 50% pore volume mobility buffer slug of 40-45 centipoise (49 C) Betz Hi Vis polyacrylamide in Ark-Burbank water, which was graded back logarithimically with Ark-Burbank water (10 mL/hr, 0.9 feet/day). Ark-Burbank water is freshwater of very low salinity and hardness (Table I). In a few oil displacement tests, higher salinity mobility buffers and mobility buffer diluents (prepared in distilled water) were used. These cases are noted in the text and tables.

The following preflush, surfactant and mobility buffer slugs were used in the oil displacement tests described in Tables II and VIII (procedure B). Any variation in this procedure are noted in the discussion and tables. A preflush (25% pore volume) containing 0.3% sodium bicarbonatesodium carbonate at the optimal salinity and pH 9.4 was used. The surfactant slug (20% pore volume) consisted of 3.0% sodium carboxylate, 3.0% cosurfactant, and 0.3% sodium bicarbonate-sodium carbonate at the optimal salinity and pH 9.4. The preflush and surfactant solutions were prepared in distilled water. The surfactant slug was

followed by a mobility buffer that is the same as that described in procedure A.

Surfactant recoveries were determined by comparing the amount of carboxylic acid isolated from the core effluents with the amount that was injected The carboxylic acid was isolated by acidification of the effluents with dilute sulfuric acid to pH 2-3 and then extracting 3 times with ethyl ether. The combined ether extract was washed with distilled water until neutral, dried with anhydrous sodium sulfate and evaporated under reduced pressure. The amount of carboxylic acid in the resulting oil sample could be determined from its weight and neutralization equivalent.

RESULTS AND DISCUSSION

Oil displacement tests using sodium carboxylates were carried out in Berea sandstone cores containing residual NBU crude oil flooded with water. Initial displacement tests (procedure B) used a surfactant slug (20% pore volume) containing 3.0% sodium carboxylate, 3.0% alcohol cosurfactant and 0.3% sodium bicarbonate-sodium carbonate at the optimal salinity and pH 9.4. The results are shown in Table II. Tertiary oil recoveries of 85% and 90% were obtained using sodium isostearate with isopentyl alcohol and isohexyl alcohol. Isostearate is a complex mixture of 18:0 fatty acid carboxylates with branched alkyl groups. As will be discussed later, even better oil recoveries could be obtained using 10% pore volume surfactant slugs when the effect of pH was studied.

More oil soluble alcohols of 5 carbons or more are preferred as cosurfactants with aliphatic 18:0 carboxylates, e.g., sodium isostearate. Lower molecular weight alcohols, e.g., isobutyl alcohol were undesirable because the phase behavior was poor, as shown in the accompanying paper. An oil displacement test using isobutyl alcohol (3%) and sodium isostearate (3%) at the optimal salinity gave only a 19% tertiary oil recovery. The suffactant solution was difficult to inject into the core because of the precipitation of sodium isostearate. If a higher percentage of isobutyl alcohol was used, the surfactant solution would probably be more suitable for injection. Use of 5% isobutyl alcohol with isostearate did give improved phase behavior.

Sodium oleate, an unsaturated 18:1 fatty acid carboxylate, gave lower tertiary oil recoveries than isostearate. Oil recoveries of 59% and 76% were obtained using isopentyl alcohol and 1-hexanol as cosurfactants. For both

TABLE II

^aProcedure B used.

bEmery Emtall 729 neutralized with sodium hydroxide.

CFollowed procedure B except 60% PV surfactant slug containing 1% sodium stearate and 3% isopentyl alcohol was used.

dFollowed procedure B except preflush slug also contained 3% isopentyl alcohol and pH of preflush and surfactant slugs was 9.1.

 $\frac{e}{e}$ The pH of preflush and surfactant slugs was 9.9.

fwhen n-decane was displaced rather than NBU crude, the tertiary oil recovery was 92%.

TABLE III

Effect of pH and Added Base on Oil Displacements Using Sodium Isostearate^a

^aProcedure A used with isopentyl alcohol as cosurfactant.

bOptimal salinity unless otherwise noted.

CBrookfield viscosity (6 RPM) was 71.5 cp at 49 C.

dThis is above the optimal salinity.

eViscosity was 51.5 cp at 49 C.

sodium oleate and sodium isostearate, oil recoveries were higher when the optimal salinities were lower, which was the case when more oil soluble alcohols were used. Note that sodium oleate is a low-cost surfactant because oleic acid is available at \$0.35 per pound (8). Neutralized tall oil, which contains a large percentage of sodium oleate and sodium linoleate, was used in an oil displacement test and gave a tertiary oil recovery of 74%. Use of neutralized tall oils and tall oil fatty acids will be discussed in more detail later.

Sodium stearate, which does not have a branched alkyl group like isostearate, gave a tertiary oil recovery of 77%, but this result can not be directly compared with sodium isostearate or oleate because a much larger pore volume surfactant slug was used. The reason for this was that a lower concentration (1%) of sodium stearate was used because it is much less soluble in water than isostearate or oleate.

Sodium naphthenates, which are 7:0-14:0 aliphatic carboxylates containing saturated 5 or 6 carbon rings, were also investigated for utility in oil displacement tests. The tests were carried out as described for isostearate and oleate except that the preflush slug also contained 3%

isopentyl alcohol. A tertiary oil recovery of 50% was observed. Three-phase systems had been observed in phase volume studies (see accompanying paper) with sodium naphthenate, but the volume fraction of middle phase was much smaller than that observed for isostearate or oleate indicating that interfacial tensions were not as low. This could account for the lower oil recovery.

Effect of pH and Base

The effect of pH and added base on oil displacements with carboxylates was investigated. Oil displacement tests using sodium isostearate were carried out in the presence of bases such as sodium hydroxide, sodium orthosilicate, sodium carbonate and sodium bicarbonate and gave tertiary oil recoveries varying from 47-92% as shown in Table III. A 10% pore volume preflush slug containing 0.6% base at the desired salinity was used in each case. The surfactant slug (10% pore volume) consisted of 3% sodium isostearate, 3% isopentyl alcohol and 0.6% base at the desired salinity. This was followed by a mobility buffer as previously described (procedure A). The results indicate that pH may be an important factor in these displacements because the core tests using sodium bicarbonate or no added base (pH

8.4-8.5) gave much higher tertiary oil recoveries than those using sodium carbonate (pH 11.0), sodium hydroxide (pH 12.4), or sodium orthosilicate (pH 12.8). Although the optimal salinity for the isostearate-bicarbonate system was 1.6%, the tertiary oil recovery at a salinity of *2.8%* was just as good (92% vs 90%), and was much better than those obtained (47-78%) where other bases or no added base were used at comparable salinities. Note that in all cases the surfactant slug was followed by a very low salinity mobility buffer that was graded back with low salinity water (Ark-Burbank water). Figure 1 shows how pH varied with volume of core effluent for several of the displacement tests shown in Table III. The pH values of the effluents were about as expected considering the bases used in the preflush and surfactant slugs.

Interfacial tensions obtained in carboxylate systems were found to vary considerably with pH, and this could account for the differences in the tertiary oil recoveries just described. Interfacial tensions were determined between ndecane and aqueous saline solutions of sodium isostearate (no cosurfactant) at different pH values. The results are plotted in Figure 2. The lowest interfacial tension was at pH 9.2, which is much closer to the pH (8.4) when sodium bicarbonate was used in the displacement tests than the pH (11.0-12.8) when sodium hydroxide, orthosilicate, or carbonate were used. Although interfacial tensions **with** fatty acid (aliphatic) carboxylates, e.g., isostearate, were lower at lower pH, interfacial tensions for benzoate (aromatic) type carboxylates were found to be lower at higher pH values. Interfacial tensions were determined between n-decane and aqueous solutions containing 0,15% sodium p-(1-pentylnonyl)benzoate and 0.6% sodium chloride (no cosurfactant) at different pH values. The lowest interfacial tension (5 \times 10⁻⁴ dyne/cm) was observed at pH 11.0. When oil displacement tests were carried out using this benzoate and sodium bicarbonate and sodium carbonate as added bases, the tertiary oil recoveries were 53% and 69%, respectively (Table IV). The higher recovery for the carbonate case agrees with the interfacial tension studies.

Effect of Alkyl Group Branching of the Carboxylates

The effect of alkyl group branching in the carboxylate surfactant was also investigated. Sodium isostearate, which is a mixture of branched 18:0 carboxylates, gave higher tertiary oil recoveries than the unbranched sodium oleate at comparable salinities as shown in Table II. Also, sodium isostearate gave a higher tertiary oil recovery (70%) than **the** unbranched sodium stearate (47%) under identical conditions as shown in Table V. The 3.4% sodium chloride concentration was the optimal salinity for the unbranched stearate, but was above the optimal salinity for the branched isostearate. Note that the mobility buffer following the surfactant slug contained very low salinity water and was graded back with low salinity water (Ark-Burbank water).

FIG. 1. pH vs volume of effluent for oil displacement tests (Table III) using sodium orthosilicate, sodium carbonate and sodium bicarbonate as the added base.

FIG. 2. Interracial tension rs pH for sodium isostearate with n-decane (0.3% sodium isostearate and 1.25% sodium chloride in distilled water vs n~lecane at 30 C, no cosurfactant).

TABLE IV

Effect of pH and Added Base on Oil Displacements with Sodium p-(1-Pentylnonyl)be nzoate^a

Base added	pH of Surfactant slug	Salinity ^b $(%$ \mathcal{N} Ω \mathcal{N} Ω \mathcal{N}	Tertiary oil recovery (%)	Surfactant recovered $(\%)$
Sodium carbonate	11.4	1.0	69	17
Sodium bicarbonate	8.5	1.0	53	31

aprocedure A used with isobutyl alcohol as cosurfactant. bThis is above the optimal salinity in both cases.

TABLE V

Effect of Alkyl Group Branching of Carboxylates on Tertiary Oil Recoveries^a

aFollowed procedure A except 20% PV surfactant slug containing 1% sodium carboxylate, 3% isopentyl alcohol, 0.6% sodium bicarbonate and 3.4% sodium chloride was used. bOptimal salinity.

CAbove optimal salinity.

TABLE VI

Effect of Salinity of Mobility Buffer and Its Diluent **on oil Displacements with Sodium Oleate a**

aprocedure A used except for changes in salinity of mobility buffer and mobility buffer diluent. Surfactant slug contained 3% sodium oleate, 3% isopentyl alcohol and 0.6% sodium bicarbonate.

bSee Table I for composition of Ark-Burbank water.

Effect of the Salinity of the Mobility Buffer

The salinity of the mobility buffer and mobility buffer diluent were varied to determine the effect on tertiary oil recoveries with a sodium oleate surfactant system. In each core run the same surfactant slug (10% pore volume), containing 3% sodium oleate, 3% isopentyl alcohol, 0.6% sodium bicarbonate and 4.3% sodium chloride (optimal salinity), was used. Betz Hi Vis polyacrylamide mobility buffers (50% pore volume) of the same viscosity (40 centipoise) containing various salt concentrations (Table VI) followed the surfactant slugs. The mobility buffer was graded back logarithmically with a diluent that had the same salt concentration. As shown in Table VI the tertiary oil recovery when the mobility buffer and its diluent had a sodium chloride concentration of 2.5% was almost the same as when the mobility buffer and diluent had very low salt content (Ark-Burbank water). This shows that a freshwater mobility buffer is not necessary for good oil recovcry, although a high salt concentration (4%) will reduce recovery, probably because of poor solubility of the alcohol and carboxylate in the brine as the surfactant slug loses its integrity. At higher salinities, maintaining certain relative concentrations of surfactant and cosurfactant may be more critical for achieving good oil recoveries.

Use of Neutralized Tall Oils as Surfactant

A series of oil displacement tests were carried out with neutralized tall oils because of their low price. Crude tall oil, distilled tall oil and tall oil fatty acids cost \$0.07, \$0.19, and \$0.18 per pound (8). Distilled tall oil contains ca. 60% oleic and related fatty acids, 35% abietic and related rosin acids and 5% unsaponifiable matter. The tall oils were neutralized with sodium hydroxide to give their sodium salts. Core runs were carried out using surfactant slugs (10% pore volume) containing 3% neutralized tall oil or tall oil fatty acid, 3% 1-pentanol and 0.6% sodium bicarbonate at optimal salinity. The results are shown in Table VII. Tertiary oil recoveries of 71% and 80% were

obtained with the neutralized distilled tall oil and tall oil fatty acids. Neutralized crude tall oils gave lower tertiary oil recoveries (54-61%) because they contain lower percentages of fatty acid carboxylates (Table VII). Southern crude tall oils gave higher recoveries than northern crude tall oils because they have a higher fatty acid content. A phase volume study of the sodium salt of abietic acid (7) indicated that it would not be nearly as effective for tertiary oil recovery as the fatty acid carboxylates would be.

Use of Ethoxylated Alcohols as Cosurfactants

Oil displacement tests were carried out with sodium carboxylates using ethoxylated 8:0-15:0 alcohol cosurfactants because phase volume studies had shown that high optimal salinities (4.8-8.2% NaC1) and large volume fraction middle phases were obtained. The results are shown in Table VIII. The procedure used was the same as that described for the core runs described in Table II (procedure B) except that the salinities of the mobility buffer and its diluent were sometimes different. Tertiary oil recoveries of 38-62% were obtained if the mobility buffer was graded back logarithmically with freshwater (Ark-Burbank water). If the mobility buffer was graded back with a higher salinity mobility buffer diluent (4.0-5.0% NaC1), the tertiary oil recoveries were poorer (24-27%).

Surfactant Recoveries

In most core runs the percentage of surfactant recovered was determined. As shown in Tables II and III, the percentage of surfactant recovered was quite high (71-89%) for 18:0 and 18:1 carboxylates e.g., sodium isostearate and sodium oleate. The use of different bases with sodium isostearate did not affect surfactant recoveries because all were 74- 82%. Surfactant recoveries were lower (17-51%) for carboxylates containing aromatic rings e.g., 2-benzyloctadecanoate (Table II) and p-(1-pentylnonyl)benzoate (Table IV). For comparison, petroleum sulfonates, e.g., Witco

TABLE VII

NBU Crude Oil Displacement Tests Using Neutralized Tall Oils and Tall Oil Fatty Acids a

aprocedure A was used. Surfactant slug contained 3% neutralized tall oil, 3% 1-pentanol and 0.6% sodium bi, carbonate.

bTall oils were neutralized with sodium hydroxide.

CTypical values.

TABLE VIII

Oil Displacement **Tests Using** Sodium Carboxylates with Ethoxylated Alcohols as **Cosurfactants a**

aprocedure B used.

bTergitol 15-S-5 consists of 11:0-15:0 secondary aliphatic alcohols ethoxylated with 5 mol ethylene oxide. Tergitol 25-L-3 and 25-L-5 are 12:0-15:0 primary aliphatic alcohols ethoxylated with 3 and 5 mol ethylene oxide, respectively.

CFor composition of Ark-Burbank water, see Table 1.

TRS 10-410, gave surfactant recoveries of 34-73% under conditions similar to those used for the aliphatic and aromatic carboxylates.

Effect of Calcium Ion on Oil Displacements

The effect of calcium ion on oil displacements with sodium carboxylates was briefly investigated. When the core run using sodium isostearate and isopentyl alcohol (Table II, 85% TOR) was carried out in exactly the same manner, except that 1760 ppm of calcium ion (1:2 mol ratio of $CaCl₂$ to carboxylate) and 1% n-decane was added to the surfactant slug, the tertiary oil recovery was still high (72%). When the same displacement test was carried out, except that the mobility buffer and mobility buffer diluent used higher salinity water (1.5% NaC1) than the low salinity Ark-Burbank water, the oil recovery was 54%. Because bicarbonate and carbonate were present in the previous tests and could act as sacrificial agents for the calcium ions, an additional oil displacement test was carried out where these materials were not present. Using a 20% pore volume surfactant slug containing 3.0% calcium isostearate, 3.0% isopentyl alcohol, 5.0% sodium chloride and 1.5% n-decane gave a 54% tertiary oil recovery. The surfactant slug was preceded by a preflush slug containing 3.0% isopentyl alcohol and 5.0% sodium chloride and was followed by the usual mobility buffer, which was graded back logarithmically with Ark-Burbank water.

In all displacement tests involving calcium ion, the surfactant slugs were stirred during injection because on standing they tended to separate into 2 liquid phases. The core tests show that carboxylates give appreciable tertiary oil recoveries even in the presence of significant amounts of calcium ion.

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