Carboxylate Surfactant Systems Exhibiting Phase Behavior Suitable for Enhanced Oil Recovery

J.E. SHAW, Phillips Petroleum Company, Research Center, Bartlesville, OK 74004

ABSTRACT

A large variety of aliphatic and aromatic carboxylate surfactants with alcohols as cosurfactants displayed phase behavior with n-decane that indicated they could be useful in enhanced oil recovery. Three-phase systems with large volume fraction middle-phase microemulsions were observed with sodium isostearate and sodium oleate. The interfacial tension between top and bottom phases was at a minimum (~0.001 dyne/cm) at the optimal salinity where the uptake of oil and water in the middle phase was equal. The phase behavior of carboxylates was affected by pH and added bases. In cases where a bicarbonate-carbonate buffer was used to control pH, the optimal salinity decreased as the pH decreased. Use of ethoxylated alcohols as cosurfactants increased optimal salinities markedly and caused formation of very large volume fraction middle phases. Neutralized tall oils and tall oil fatty acids with alcohols as cosurfactants gave 3-phase behavior with n-decane with large volume fraction middle-phase microemulsions.

INTRODUCTION

Because many carboxylic acids are readily available at much lower prices than petroleum sulfonates, the phase behavior of carboxylate surfactant systems has been investigated to assess their potential for enhanced oil recovery. Previous studies (1-3) have shown that ultralow interfacial tensions (~0.001 dyne/cm), which are desirable in surfactant flooding, can be obtained with carboxylates. This report describes the phase behavior of a large variety of synthesized and commercially available carboxylates and shows how changes in cosurfactant and pH affect the phase behavior. Interfacial tensions observed between phases are also reported. An accompanying paper describes oil displacement tests with these surfactant systems in Berea sandstone cores.

EXPERIMENTAL PROCEDURES

The 2-benzylalkanoic acids were prepared by the malonic ester method starting from diethyl benzylmalonate and the appropriate alkyl bromide. The procedure used was analogous to the reported for the preparation of 2-methyldecanoic acid (4). The alkylbenzoic acids were prepared by reacting the appropriate alkylbenzene (5) with oxalyl chloride in carbon disulfide using anhydrous aluminum chloride as catalyst by a procedure analogous to that reported by Sokol (6). Because the crude product obtained by this procedure consisted of the carboxylic acid and its acid chloride, refluxing the product with a solution of 4% sodium hydroxide in ethanol/water (9:1) was necessary. An acidic workup and distillation then gave the pure alkylbenzoic acid.

The following criteria were used to support the identity and purity of each synthesized compound: narrow melting or boiling point range, satisfactory elemental analysis, infrared (IR) and nuclear magnetic resonance (NMR) spectra, and gas liquid (GLC) or thin layer (TLC) chromatographic analysis. In the case of the alkylbenzoic acids, the NMR spectra showed only the existance of the para isomer. However, conversion of 4-(1-pentyloctyl)benzoic acid to its methyl ester (7), and analysis by GLC (silicone rubber OV-101) showed the acid to be 98.5% para and 1.5% ortho substituted.

The sources of other carboxylic acids, sodium carboxylates and cosurfactants were cited in reference 8. The n-decane was Phillips Pure Grade (⩾99%).

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 the tall oils, the amount of sodium hydroxide needed to neutralize the acid was calculated using the acid value or neutralization equivalent of the sample.

The phase behavior was determined over a range of salinities by equilibrating aqueous saline solutions of 3.0% sodium carboxylate, 3.0% cosurfactant and 0.3-0.6% sodium bicarbonate and/or other base in distilled water with an equal volume of n-decane at 49 C. After through mixing at 49 C, the mixtures were allowed to equilibrate until the phases separated and no further change occurred in their volumes. This usually required 2 weeks or more. Where 3 phases were formed, a middle-phase microemulsion occurred with an excess n-decane phase above and excess brine phase below. The optimal salinity was defined as the salinity where an equal volume was taken up of n-decane and water in the middle microemulsion phase. Interfacial tensions were measured using the spinning drop technique, which has been described elsewhere (9).

RESULTS AND DISCUSSION

Phase volume studies were carried out using a large variety of synthesized and commercially available sodium carboxylates. Carboxylates used included isostearate, stearate, oleate, naphthenates, p-alkylbenzoates, 2-benzylalkanoates, abietate and neutralized tall oils. When aqueous saline solutions of these carboxylates (3%) and various cosurfactants (3%) were mixed with equal volumes of n-decane and allowed to equilibrate, 3-phase systems with middle-phase microemulsions were produced, as shown by the phase volume diagrams in Figures 1-5. Sodium isostearate, which is a complex mixture of 18:0 fatty acid carboxylates with branched alkyl groups, gave a large volume fraction (58%) middle-phase microemulsion when isopentyl alcohol was used as cosurfactant (Fig. 1). The optimal salinity where the uptake of oil and water was equal in the middle phase was at 2.5% sodium chloride at a pH of 9.4. Use of a more oil-soluble cosurfactant, isohexyl alcohol, gave lower optimal salinity and even larger volume fraction middle phase (Table I) as might be expected from previous phase volume studies with petroleum sulfonates (10). Use of isobutyl alcohol as cosurfactant at the same concentration (3%) resulted in poor phase behavior (Table I). Use of 5% isobutyl alcohol gave improved phase behavior (Table I), but the volume fraction of the middle phase was much less than when isopentyl or isohexyl alcohol were used. Other workers (2) have recently observed small volume fraction middle phases with sodium oleate and 5% isobutyl alcohol. Sodium stearate also gave a 3-phase system (Table I); however, a lower concentration (1%) of stearate was necessary because it is much less soluble than isostearate.

Sodium oleate, an unsaturated 18:1, fatty acid carboxylate, gave good phase behavior with large volume fraction middle phases using isopentyl alcohol, 1-pentanol and 1-hexanol as cosurfactants, as shown in Figure 2 and

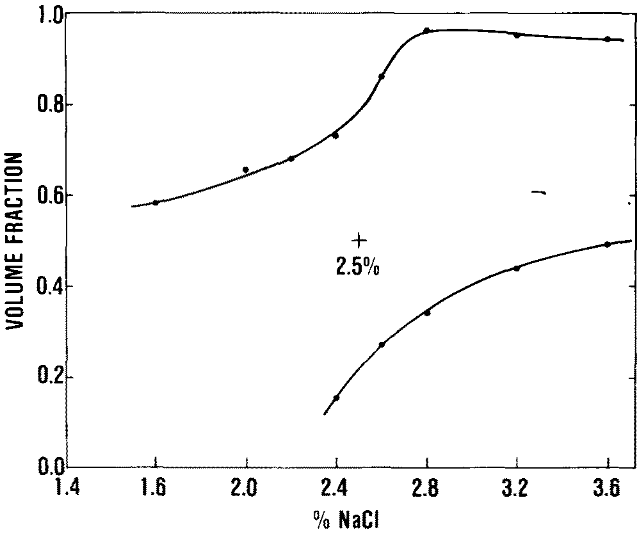

FIG. 1. Phase volume behavior vs salinity for aqueous solution containing 3% sodium isostearate, 3% isopentyl alcohol, 0.3% $NaHCO_3$-Na_2CO_3 and sodium chloride at pH 9.4 equilibrated with an equal volume of n-decane at 49 C.

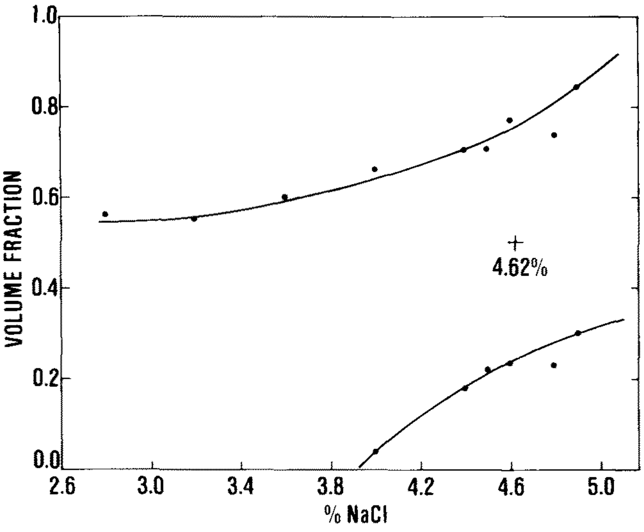

FIG. 2. Phase volume behavior vs salinity for aqueous solution containing 3% sodium oleate, 3% isopentyl alcohol, 0.3% $NaHCO_3$-Na_2CO_3 and sodium chloride at pH 9.4 equilibrated with an equal volume of n-decane at 49 C.

Table II. The sodium oleate-isopentyl alcohol system had a much higher optimal salinity (4.6%) than the corresponding isostearate-isopentyl alcohol system (2.5%). Note that sodium oleate is a potential low-cost surfactant for enhanced oil recovery because oleic acid is available in large quantities at $0.35 per pound (11). Sodium naphthenates, which are 7:0-14:0 aliphatic carboxylates containing saturated 5 or 6 carbon rings, also gave a 3-phase system (Table I) although the volume fraction of the middle phase was much less than that for isostearate or oleate. The aromatic carboxylates, sodium *p*-(1-pentylnonyl)benzoate and *p*-(1-pentyldecyl)benzoate, gave large middle-phase microemulsions, but using isopropyl alcohol as cosurfactant rather than isobutyl or isopentyl alcohol was necessary so that the optimal salinities would not be too low (Table I). The aromatic (benzoate) carboxylates are much more oil soluble than aliphatic carboxylates of similar molecular weight, e.g., 2-benzylhexadecanoate (Table III). In optimal salinity

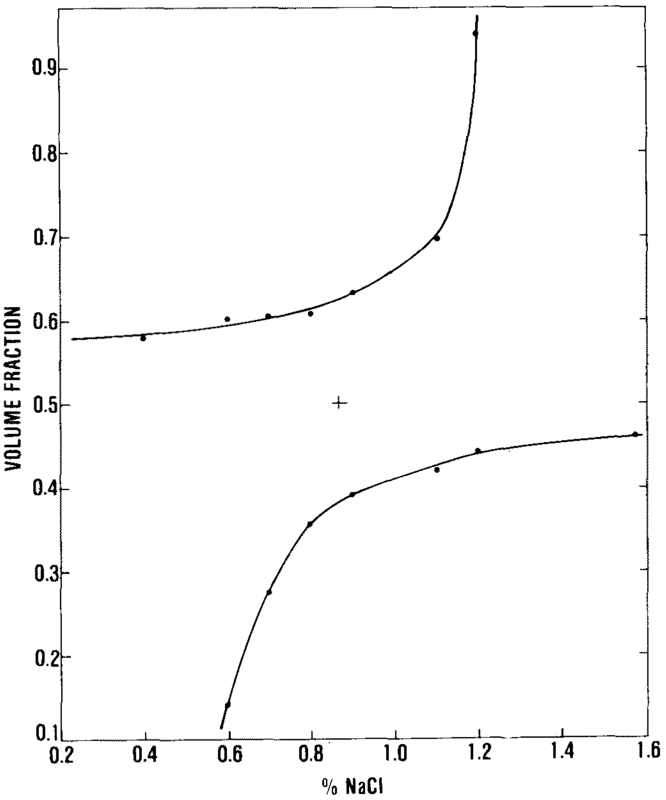

FIG. 3. Phase volume behavior vs salinity for aqueous solution containing 3% sodium 2-benzyloctadecanoate, 3% isobutyl alcohol, 0.3% $NaHCO_3$-Na_2CO_3 and sodium chloride at pH 9.9 equilibrated with an equal volume of n-decane at 30 C.

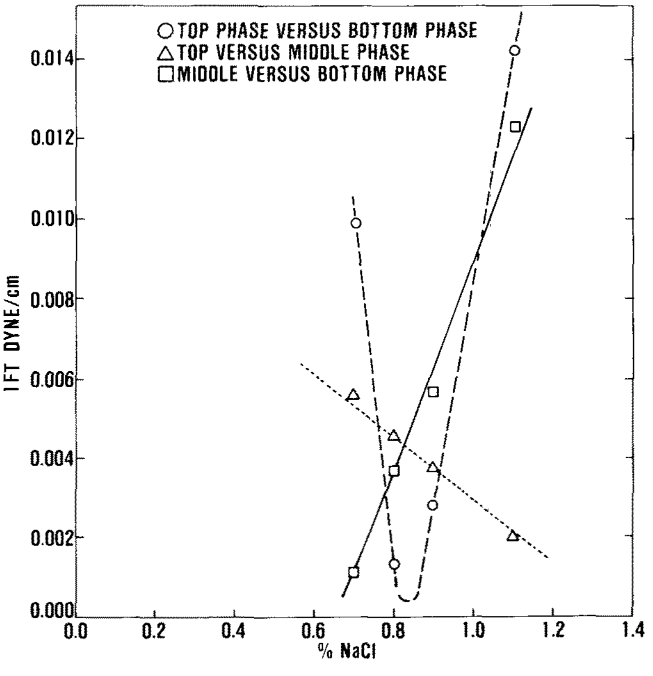

FIG. 4. Interfacial tension vs salinity for phase volume behavior of sodium 2-benzyloctadecanoate shown in Figure 3.

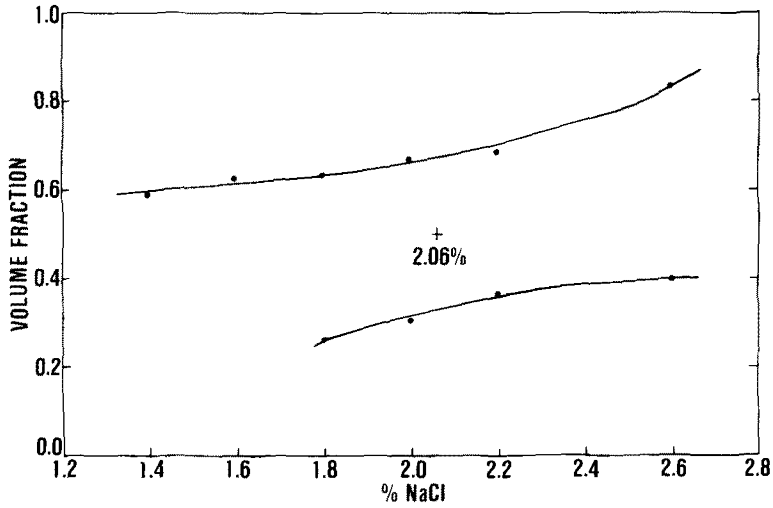

FIG. 5. Phase volume behavior vs salinity for aqueous solution containing 3% neutralized distilled tall oil, 3% 1-pentanol, 0.6% $NaHCO_3$ and sodium chloride at pH 8.7 equilibrated with an equal volume of n-decane at 49 C.

TABLE I

Phase Behavior of Sodium Carboxylates with n-Decane[a]

Sodium carboxylate	Cosurfactant	pH	Optimal salinity (% NaCl)	Volume fraction[b] of middle phase (%)
Isostearate	Isopentyl alcohol	9.4	2.5	57
Isostearate	Isohexyl alcohol	9.4	0.93	89
Isostearate	Isobutyl alcohol	9.4	~4.6[c]	~15[c]
Isostearate	Isobutyl alcohol[d]	8.5[e]	3.8	30
Stearate[f]	Isopentyl alcohol	8.2[e]	3.2	24
Oleate	Isopentyl alcohol	9.4	4.6	51
Naphthenate	Isopentyl alcohol	9.1	5.3	8
p-(1-Pentylnonyl)benzoate	Isopropyl alcohol	11.0	0.88[g]	30
p-(1-Pentyldecyl)benzoate	Isopropyl alcohol	11.5	0.50[g]	35
2-Benzyloctadecanoate	Isobutyl alcohol	9.9	0.85[h]	24
Abietate	Isopentyl alcohol	11.0	3.0	5

[a] Aqueous solution of 3% sodium carboxylate, 3% alcohol cosurfactant, 0.3% $NaHCO_3$-Na_2CO_3 and sodium chloride equilibrated with equal volume of n-decane at 49 C unless otherwise noted.

[b] At the optimal salinity.

[c] Middle phase poorly defined.

[d] Concentration of isobutyl alcohol was 5% rather than 3%.

[e] Surfactant slug contained 0.6% $NaHCO_3$.

[f] Concentration of sodium stearate was 1% rather than 3%.

[g] Temperature was 25 C.

[h] Temperature was 30 C.

TABLE II

Interfacial Tensions Observed Between Phases at the Optimal Salinity for Carboxylate Surfactant Systems[a]

Carboxylate	Cosurfactant	Optimal salinity (% NaCl)	Volume fraction middle phase (%)	Interfacial tension (dyne/cm)		
				Top phase versus middle phase	Middle phase versus bottom phase	Top phase versus bottom phase
Oleate	Isopentyl alcohol	4.6	51	0.0013	0.0008	0.0010
Oleate[b]	Isopentyl alcohol	4.0	45	0.0006	0.0008	0.0006
Oleate[b]	1-Pentanol	3.5	53	0.0005	0.0006	0.0002
Oleate	1-Hexanol	1.9	71	–	–	–
Oleate	Ethoxylated 2-Ethylhexanol (2 mol E.O.)	8.1	78	–	–	–
Oleate	Tergitol 25-L-3	6.4	96	–	–	–
Isostearate	Tergitol TMN-6	7.8	76	0.0005	0.0006	0.0010

[a] Aqueous solution of 3% sodium carboxylate, 3% cosurfactant, 0.3% $NaHCO_3$-Na_2CO_3 and sodium chloride at pH 9.4 equilibrated with equal volume of n-decane at 49 C.

[b] Contained 0.6% $NaHCO_3$ (pH 8.4) rather than 0.3% $NaHCO_3$-Na_2CO_3 (pH 9.4).

they behave more like the aromatic petroleum sulfonates (10).

Interfacial tensions were determined at various salinities between the phases obtained when equal volumes of n-decane and an aqueous solution of 2-benzyloctadecanoate and isobutyl alcohol were equilibrated at 30 C (Fig. 3). The interfacial tensions between top and bottom, middle and bottom and top and middle phases are plotted against salinity in Figure 4. As has been observed with petroleum sulfonates (10), the interfacial tension between the top and bottom phases was minimal at the optimal salinity. The minimum value was about 0.001 dyne/cm. Interfacial tensions between phases at the optimal salinity were obtained for several other systems and are presented in Table II. Interfacial tensions for the oleate and isostearate systems were usually 0.001 dyne/cm or less. These values are of the magnitude needed for good tertiary oil recovery. Interfacial tensions at the optimal salinity were determined for sodium 2-benzylhexadecanoate using different alcohol cosurfactants. The results (Table III) show that as the optimal salinity decreases when using more oil soluble alcohols, the volume fraction of the middle phase increases, and the interfacial tensions between phases decrease. This result agrees with those observed with petroleum solfonates (10). Large volume fraction middle phases are desirable because interfacial tensions will be lower.

Optimal salinities for carboxylate systems were greatly affected by pH and added base as shown in Table IV. When a bicarbonate-carbonate buffer was used to control pH in the isostearate-isopentyl alcohol and 2-benzyloctadecanoate-isobutyl alcohol systems, the optimal salinity always decreased as the pH decreased. Optimal salinities observed for the isostearate system were much higher when strong bases, e.g., sodium hydroxide, sodium carbonate and sodium orthosilicate, were used (pH 11-13) than when sodium bicarbonate was used (pH 8.5). Although the optimal salinity changed with pH, the volume fraction of the middle phase at the optimal salinity varied little with pH (Table IV).

Phase volume studies were carried out using equal volumes of n-decane and solutions of sodium carboxylates containing cosurfactants other than common alcohols. Using sulfolane, nitrobenzene and acrylonitrile (3%) with 18:0 aliphatic carboxylates, e.g., isostearate or oleate (3%), did not cause formation of middle-phase microemulsions, and the sodium carboxylate precipitated out at high salt concentration. Using dimethylformamide or sulfolane with 2-benzylhexadecanoate gave 3-phase systems with much higher optimal solinities than those observed using isobutyl alcohol as cosurfactant (Table III).

Ethoxylated alcohols have also been used as cosurfactants with carboxylates for phase volume studies. Ethoxyated 2-ethylhexanol and various Tergitols (Union Carbide) were used that average 2-6 ethylene oxide units per molecule. Tergitol 25-L-3 is a mixture of 12:0-15:0 primary alcohols ethoxylated with 3 mol ethylene oxide, and Tergitol TMN-6 is 2,6,8-trimethylnonanol ethoxylated with 6 mol ethylene oxide. Using these cosurfactants with sodium oleate or isostearate caused high optimal salinities (6-8%) and formation of large volume fraction middle

TABLE III

Effect of Cosurfactant on Phase and Interfacial Tension Behavior of Sodium 2-Benzylhexadecanoate with n-Decane[a]

Cosurfactant	Optimal salinity (% NaCl)	Volume fraction middle phase[b] (%)	Interfacial tension (dyne/cm)[b] Top phase versus middle phase	Middle phase versus bottom phase	Top phase versus bottom phase
Isopentyl alcohol	0.28	34	0.0019	0.0027	0.0017
2-Pentanol	1.26	15	0.0069	0.0190	0.0100
Isobutyl alcohol	1.43	12.5	0.0168	0.0169	0.0114
Dimethyl formamide	2.7	10	–	–	–
Sulfolane	3.2	12	–	–	–

[a] Aqueous solution of 3% sodium 2-benzylhexadecanoate, 3% cosurfactant, 0.3% $NaHCO_3$-Na_2CO_3 and sodium chloride at pH 9.7 equilibrated with equal volume of n-decane at 30 C.
[b] At the optimal salinity.

TABLE IV

Effect of pH and Added Base on Phase Behavior of Carboxylate Surfactant Systems[a]

Carboxylate	Alcohol	Base	pH	Optimal salinity (% NaCl)	Volume fraction middle phase[b] (%)
Isostearate	Isopentyl alcohol	0.6% $NaHCO_3$	8.5	1.6	65
Isostearate	Isopentyl alcohol	0.6% $NaHCO_3$-Na_2CO_3	9.4	2.3	60
Isostearate	Isopentyl alcohol	0.6% $NaHCO_3$-Na_2CO_3	10.5	2.5	59
Isostearate	Isopentyl alcohol	0.6% Na_2CO_3	11.0	3.0	56
Isostearate	Isopentyl alcohol	0.6 NaOH	12.6	2.9	52
Isostearate	Isopentyl alcohol	0.6% Na_4SiO_4[c]	13.0	2.7	64
2-Benzyl octadecanoate	Isobutyl alcohol	0.3% $NaHCO_3$-Na_2CO_3	9.5	0.3[d]	25
2-Benzyl octadecanoate	Isobutyl alcohol	0.3% $NaHCO_3$-Na_2CO_3	10.4	0.9[d]	20

[a] Aqueous solution of 3% sodium carboxylate, 3% alcohol, 0.3-0.6% base and sodium chloride equilibrated with equal volume of n-decane at 49 C.
[b] At the optimal salinity.
[c] Sodium orthosilicate.
[d] Temperature was 30 C rather than 120 F (49 C).

TABLE V

Phase Behavior of Neutralized Tall Oils with n-Decane[a]

Tall oil neutralized[b]	Cosurfactant	pH	Optimal salinity (% NaCl)	Volume fraction[c] of middle phase (%)
Crude tall oil[d]	1-pentanol	8.5	2.4	20
Distilled tall oil[e]	1-pentanol	8.7	2.1	34
Tall oil fatty acids[f]	1-pentanol	8.6	2.3	52

[a] Aqueous solution of 3% neutralized tall oil, 3% 1-pentanol, 0.6% $NaHCO_3$ and sodium chloride equilibrated with equal volume of n-decane at 49 C.
[b] Tall oils were neutralized with NaOH.
[c] At the optimal salinity.
[d] Reichhold Chemical, Oakdale, LA.
[e] Emery Emtall 731.
[f] Union Camp Unitol 1090.

phases (80-95%), as shown in Table II. Low interfacial tensions were observed at the optimal salinities (Table II). Using carboxylate-ethoxylated alcohol systems for oil displacements at high salinities is reported in reference 8.

The phase behavior of neutralized tall oils and tall oil fatty acids was also investigated (Fig. 5, Table V). Crude tall oils, distilled tall oils, and tall oil fatty acids, which are by-products from the pulping of wood, cost ca. \$0.07, \$0.19 and \$0.18 per pound (10). Distilled tall oil contains ca. 60% oleic and related fatty acids, 35% abietic and related rosin acids and 5% unsaponifiable matter. Phase volume studies using sodium oleate (Fig. 2 and Table II) and sodium abietate (Table I) with alcohol cosurfactants indicated that the fatty acid carboxylates rather than the rosin acid carboxylates are responsible for the desired 3-phase behavior. Neutralized crude tall oil, distilled tall oil and tall oil fatty acids have increasing percentages of fatty acid carboxylates and, as shown by the phase volume studies (Table V), the volume fraction of middle phase increased correspondingly. Oil displacement tests using these low cost surfactants are reported in reference 8.

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[Received January 10, 1984]

Solubilization and Fluorescence Behavior of Petroleum Sulfonate Containing Microemulsions

Y.K. PITHAPURWALA[+] and **D.O. SHAH***, Departments of Chemical Engineering and
Anesthesiology, University of Florida, Gainesville, FL 32611

ABSTRACT

The effects of various oils and alcohols on the brine solubilization and fluorescence behavior of oil-external microemulsions were investigated. At a critical electrolyte concentration, referred to as optimal salinity, the brine solubilization capacity of microemulsions containing petroleum sulfonate is maximum for C_6-C_{10} oils and C_4-C_7 alcohols. Moreover, at this salinity, the fluorescence intensity was found to be maximal. As the chain length of oil is increased, the optimal salinity increased for all the alcohols studied. However, the increase in optimal salinity was much greater for water-soluble alcohols than for pentanol, hexanol or heptanol. The brine solubilization limit decreased as the oil chain length increased for microemulsions containing n-butanol and iso-butanol. The solubilization behavior is explained in terms of solubility of alcohols in various phases of microemulsions and the ability of the aqueous phase to solubilize surfactant molecules from the interface. The fluorescence behavior is explained by higher surface charge density around the water droplet near optimal salinity. A simple correlation is given between the solubilization and fluorescence behavior of microemulsions that is independent of type and chain length of the alcohols or hydrocarbons.

INTRODUCTION

Microemulsions are clear or translucent, kinetically or thermodynamically stable systems containing microdomains of oil or water stabilized by a mixed film of surfactant and alcohol. Microemulsions and micellar solutions containing petroleum sulfonates in brine or oil have been used as injection fluids for a number of tertiary oil recovery processes. These systems produce ultralow interfacial tension at oil/microemulsion or microemulsion/brine interfaces under appropriate conditions. Microemulsions have been studied extensively in experiments as well as in

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*To whom correspondence should be addressed.
[+] Present Address: Alcon Laboratories Inc., Fort Worth, TX.