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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Solubilization and Fluorescence Behavior of Petroleum Sulfonate Containing Microemulsions

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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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theory by various researchers (1-8). The formation and physicochemical properties of a microemulsion are influenced by the alkyl chain length of alcohol and oil. For example, the interfacial composition and partitioning of alcohol in the oil and aqueous phases are influenced by the carbon chain length of alcohol and oil (9,10). Moreover, we have shown previously that electrical resistance, dielectric constant and ESR order parameter are strongly influenced by the alkyl chain length of alcohol (11). Fluorescence measurements have been extensively used for investigations of microenvironments of proteins and membranes, as well as systems containing surfactants (12-14). Using the fluorescence technique, the critical micelle concentration (15), size of the micelle (16), interior of the micelle (17,81) and microviscosity (19) of the micellar solutions have been determined. Various models are reported in the literature (20,21) describing the distribution of fluorescence probes on the basis of their kinetic interactions with the host micelles. The structural aspects of microemulsions are also studied using fluorescence measurements (22,23).

Although the amount of oil and brine solubilization have been shown to correlate with the interfacial tension (the higher the solubilization the lower the interfacial tension), the mechanism of high solubilization is not well understood. In this paper we report a possible explanation for this correlation by the fluorescence technique. The effect of chain length of the alcohol as well as the oil on the solubilization and fluorescence behavior has also been investigated.

EXPERIMENTAL

Petroleum sulfonate TRS 10-410 (Witco Chemical Co., New York, NY) was used as received. This surfactant has an average molecular weight of 418. All the alcohols and oils were purchased from Chemicals Samples Company and were of 99% purity or greater.

Brine Solubilization Limit

The microemulsions were prepared by mixing 1 g TRS 10-410, 0.8 g alcohol and 8 g oil. The brine solubilization limit was determined by mixing the brine slowly from a graduated 1 mL pipette to the microemulsions, until turbidity was observed and two phases formed. In all cases, the end point was sharp (within 0.1 mL of brine). At the end point the systems were initially turbid, but after a few minutes of standing, two clear phases formed.

Fluorescence Measurements

The fluorescence behavior of these microemulsions was studied using a Perkin Elmer MPF-44B fluorescence spectrophotometer with differential correction unit (DCSU-2). The surfactant-type fluorescent dye used in this study was 4-heptadecyl umbeliferrone (Fig. 1), which was synthesized in our laboratory. The dye was dissolved in isopropanol and added to each microemulsion sample to make its concentration the same (10^{-4} *M/L*) for all samples. The samples were excited at 366 nm and emission spectra were obtained. The maximum emission was found to be at 486 nm. Samples were also run without the addition of the dye and we found that TRS 10-410 has its own fluorescence characteristics when it is dissolved in water. When excited at 366 nm, the maximum in emission occurred around 480 nm.

RESULTS AND DISCUSSION

Effect of Oil Chain Length on Brine Solubilization in Oil External Microemulsions

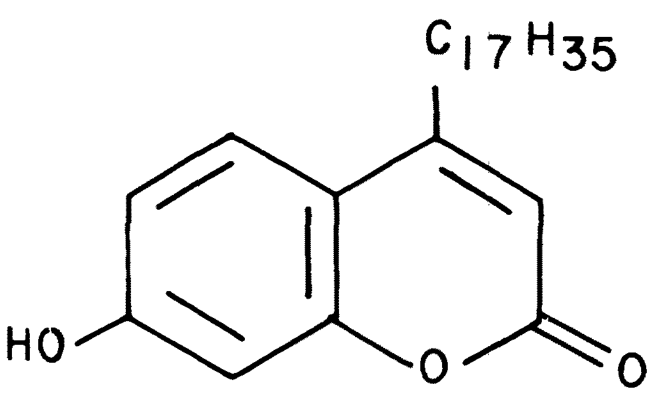

FIG. 1. Structure of a surfactant-type fluorescent dye, 4-heptadecyl umbeliferone.

The brine solubilization capacity of microemulsions containing TRS 10-410 as a function of brine concentration is shown in Figure 2 for oils ranging from hexane to hexadecane. For every oil, as the electrolyte concentration is increased, the solubilization limit increases, passes through a maximum, and then decreases. On addition of brine, the size of the droplets is expected to increase, resulting in a concomitant increase in interfacial area. Up to a certain extent, the alcohol from the oil phase can partition the interface to stabilize the additional interfacial area. However, as the alcohol in the oil phase is depleted, further growth of water droplets would increase the interfacial tension at the oil-water interface because of an increase in area per molecule and thus destabilize the microemulsion and prevent further solutilization of brine. The electrolyte concentration at which the largest amount of brine is solubilized is a function of the extent of the partitioning of alcohol in the oil phase, interphase and brine phase. The critical electrolyte concentration depends on the oil chain length. A similar observation is reported in enhanced oil recovery literature for surfactant/oil/alcohol/brine systems. Here, on increasing the salinity, a transition occurs from the lower-phase to the middle-phase to the upper-phase microemulsion. At low salinity, a surfactant-rich micro-

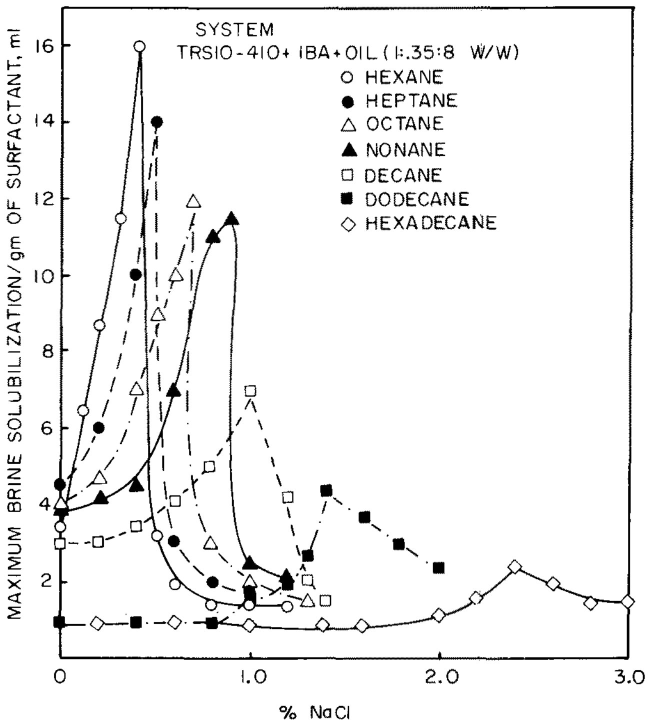

FIG. 2. Maximum brine solubilization capacity of microemulsions containing different oils at various electrolyte concentrations.

emulsion phase or the lower phase is in equilibrium with the excess oil. As the salinity is increased, a middle-phase microemulsion is formed that is in equilibrium with excess oil and excess brine. At high salinities, a surfactant-rich upper phase is formed that is in equilibrium with the excess brine. The salinity at which there is an equal solubilization of oil and brine in the middle phase is defined as the optimal salinity of the system. Research has shown (24) that the critical electrolyte concentration at which the most brine is solubilized in a single-phase microemulsion corresponds to the optimal salinity of the formulation, hence this critical electrolyte concentration will be referred to as the optimal salinity. When brine is added beyond the maximum brine solubilization limit, the system becomes turbid and, on standing, excess oil phase remains in equilibrium with the lower-phase microemulsions for all salinities below optimal salinity, whereas above optimal salinity, excess brine remains in equilibrium with the upper-phase microemulsion. The increase in the optimal salinity can be explained in terms of the stronger van der Waals attraction forces between the chains for longer-chain hydrocarbons. These data are consistent with reported results (25) for systems containing petroleum sulfonate where the optimal salinity was determined either as the salinity at which equal volume of oil and brine was solubilized in the middle phase in 3 phase regions or as the salinity at which interfacial tension at the middle-phase microemulsion/excess oil and excess brine/middle-phase microemulsion was found to be equal.

Effect of Oil Chain Length on the Fluorescence Behavior of Microemulsions

The maximum emission intensity of different microemulsion samples at 486 nm is shown (Fig. 3) as a function of sodium chloride concentration with corresponding maximum brine solubilization for various oils. As the salinity is increased, the fluorescence intensity increases, passes through a maximum and then decreases for all the oils studied. The maximum in the fluorescence intensity was found to be at the optimal salinity for every oil. The similarity in Figures 2 and 3 suggest a correlation between the brine solubilization and fluorescence intensity of the microemulsions. The maximum in the fluorescence intensity can be interpreted in terms of maximum surface charge density at the oil/water interface of the microemulsion droplet or in terms of the maximum number of microemulsion droplets in the system. We have observed that petroleum sulfonate molecules used in this study exhibit fluorescence when present at the interface or dissolved in the aqueous phase. Research has shown (26) that for crude oil/brine interface, higher electophoretic mobility is responsible for ultralow interfacial tension. The lowering of intefacial tension at the oil/brine interface is caused by higher interfacial area or crowding of surfactant molecules at the interface. This leads to higher oil or brine solubilization by the microemulsion (27).

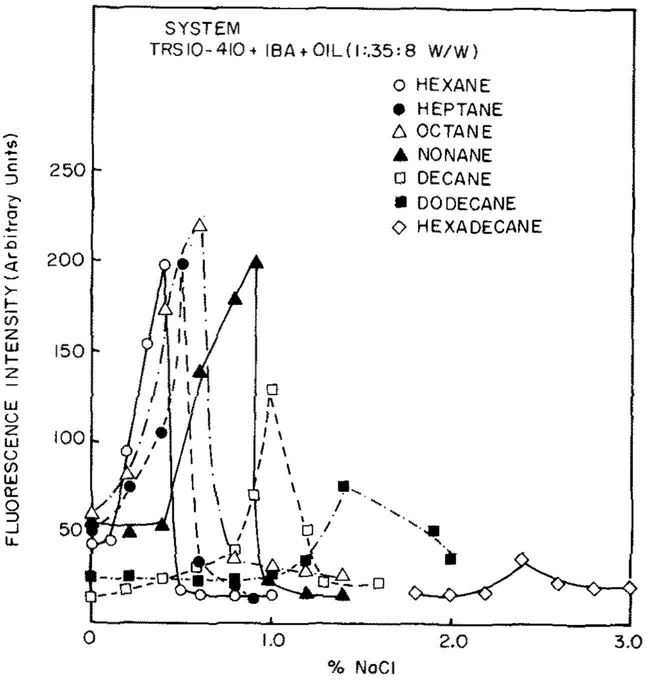

FIG. 3. Effect of NaCl concentration on the fluorescence intensity of microemulsions containing maximum solubilized brine.

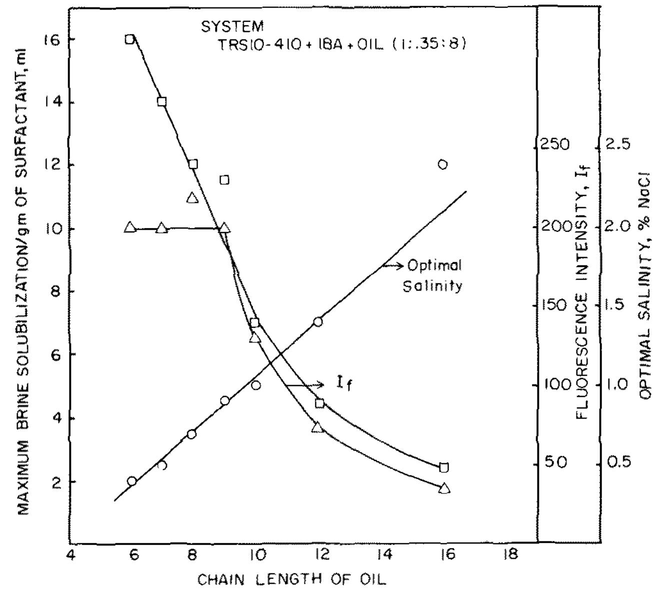

FIG. 4. Effect of chain length of oil on optimal salinity, maximum brine solubilization and fluorescence intensity of microemulsons.

Figure 4 summarizes the effect of oil chain length on optimal salinity, maximum brine solubilization and fluorescence behavior of petroleum sulfonate/isobutanol microemulsions. The optimal salinity increased linearly with the chain length of oil whereas the brine solubilization limit and fluorescence intensity decreased for all oils higher than octane. For reasons not known, the fluorescence intensity did not change significanly when the oils used were hexane, heptane and octane. The decrease in solubilization capacity for increasing oil chain length can be explained in terms of the partitioning of water-soluble isobutanol in different phases of the microemulsion. As the oil chain length is increased, the partitioning of isobutanol in the oil phase will be less. Because the amount of alcohol used for each system is the same, a concomitant increase in the alcohol concentration in the aqueous phase and at the interface will occur on increasing the oil chain length. The aqueous phase, which contains isobutanol, will solubilize surfactant molecules from the interface and create a condition of less crowding of surfactant molecules at the interface. This will increase the interfacial tension at the oil/brine interface and decrease the interfacial area, hence a corresponding decrease will in occur in the brine solubilization capacity of the microemulsion. The decrease in the fluorescence intensity could be explained in terms of a lower degree of ionization of the sulfonate group and decreased thickness of the electrical double layer on increasing the oil chain length.

Effect of Alcohol Chain Length on Solubilization and Fluorescence Behavior of Microemulsions

The effect of alcohol chain length on molecular motion, interfacial composition of surfactant and alcohol and the thickness of the double layer for soidum stearate/water/hexadecane is reported in our earlier publication (11). In this section, we describe the effect of different alcohols (butanol, pentanol, hexanol and heptanol) on optimal salinity, maximum brine solubilization and fluorescence intensity of systems containing petroleum sulfonate, brine and oil (octane, dodecane or hexadecane). These parameters were determined from experiments similar to those shown in Figures 2 and 3. The brine solubilization, optimal salinity and fluorescence behavior of TRS 10-410/brine/oil/alcohol is shown in Figures 5-7 for octane, dodecane and hexadecane. On increasing the chain length of alcohol, optimal salinity decreased for all oils. This agrees with results reported in oil recovery systems (25). Water-soluble alcohols are found to increase the optimal salinity, whereas water-insoluble alcohols decrease the optimal salinity, because a higher concentration of salt is required to cause the surfactant molecules to migrate from the pool of alcohol-containing aqueous phase to the oil phase. Optimal salinities are below 0.1% NaCl when insoluble alcohols, e.g., hexanol and heptanol, are used. The maximum brine solubilization limit also decreased drastically for hexanol and heptanol-containing microemulsions for all oils. This is again related to the solubility of alcohol in the aqueous phase and higher partitioning of surfactant molecules in the oil, thus providing less interfacial area for solubilization of brine. For hexadecane-containing microemulsions, the maximum brine solubilization was for pentanol microemulsions. n-Butanol is considerably more soluble in water than higher alcohols and partitions between aqueous phase, interface and the oil phase. The aqueous phase with butanol has the ability to solubilize surfactant molecules from the interface and creates higher oil/water interfacial tension while decreasing interfacial area. The latter decreases the solubilization parameter. In the case of pentanol-containing microemulsions, the partitioning of alcohol is much less in the aqueous phase than with butanol. Pentanol also partitions the oil phase much less than hexanol or heptanol in hexadecane. Thus, more pentanol molecules will be present at the interface than any other alcohol, which agrees with results in the literature (27). And since the aqueous phase containing a smaller amount of pentanol can not significantly solubilize surfactant molecules from the interface, a large interfacial area is available for brine solubilization. This preferred chain length of alcohol (pentanol) was only observed in the hexadecane system. In a dodecane-containing system, butanol and pentanol microemulsions were found to be equally capable of solubilizing brine, whereas in the octane-

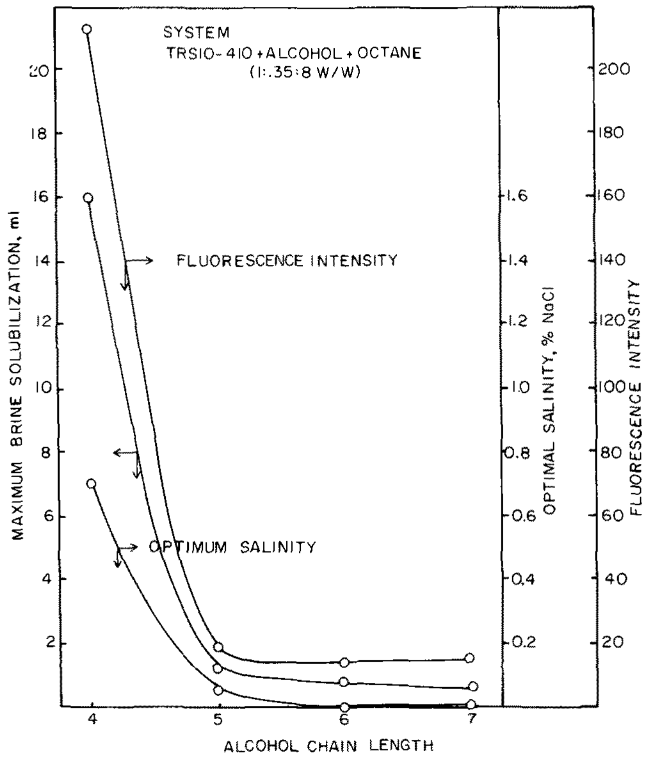

FIG. 5. Effect of chain length of alcohol on solubilization and fluorescence behavior of TRS 10-410/octane/brine system.

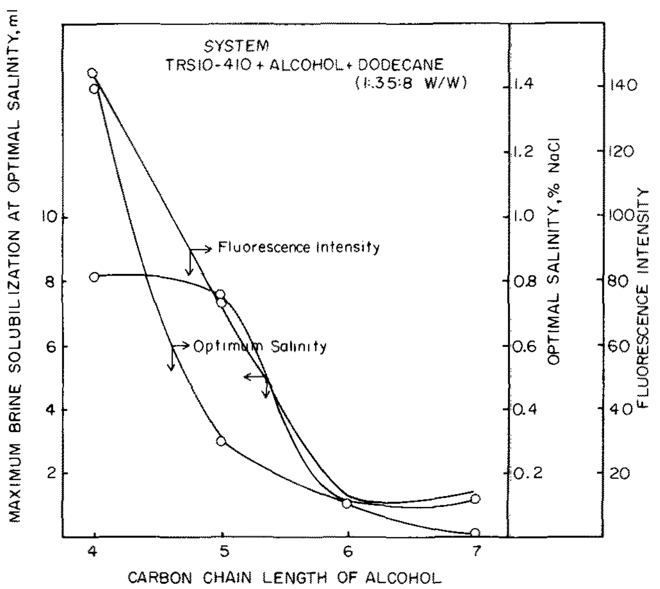

FIG. 6 Effect of chain length of alcohol on solubilization and fluorescence behavior of TRS 10-410/dodecane/brine system.

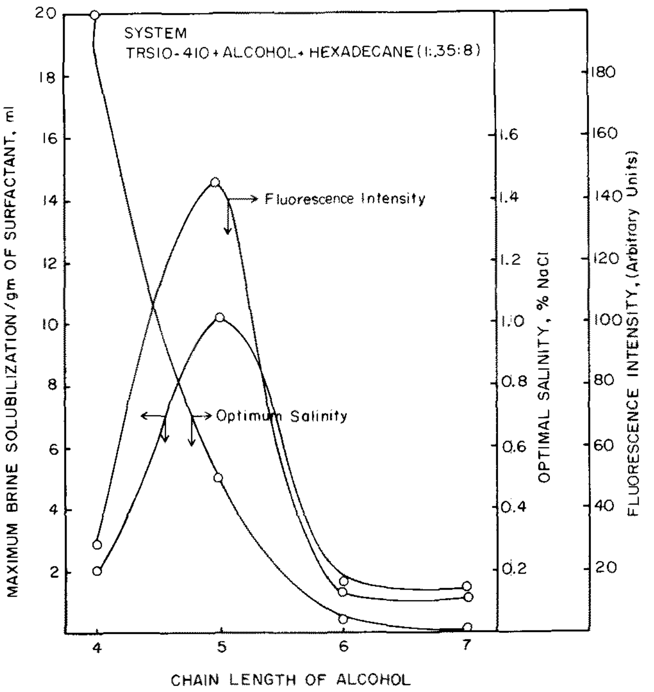

FIG. 7. Effect of chain length of alcohol on solubilization and fluorescence behavior of TRS 10-410/hexadecane/brine system.

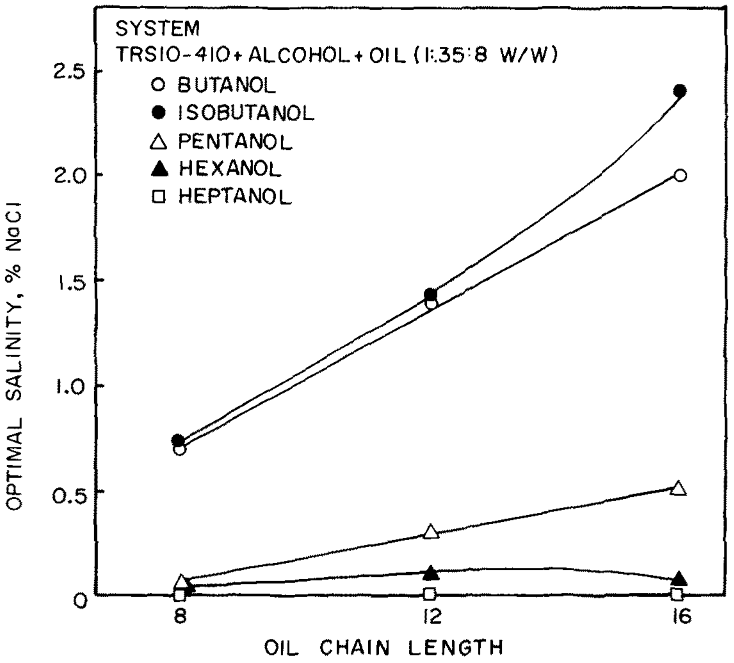

FIG. 8. Effect of chain length of oil on optimal salinity of microemulsions containing different alcohols.

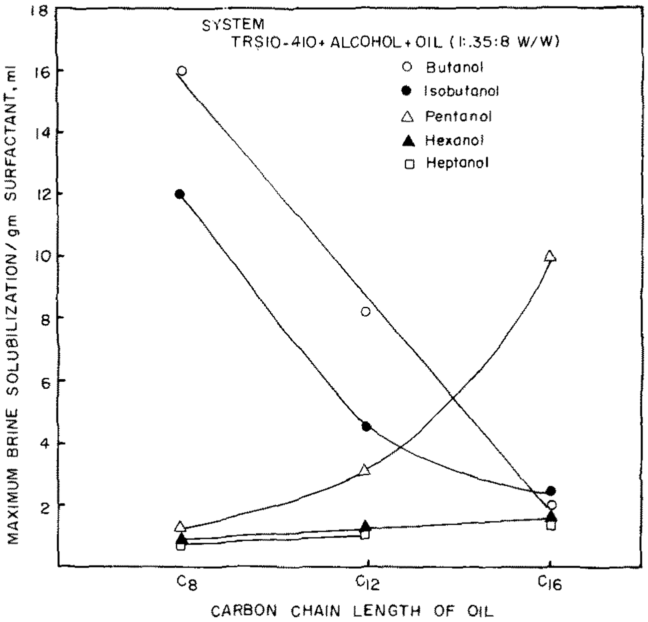

FIG. 9. Effect of chain length of oil on maximum brine solubilization of microemulsions containing different alcohols.

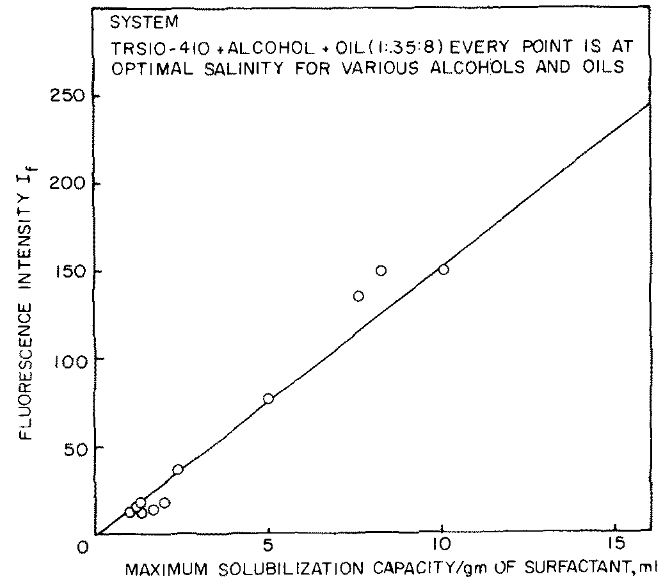

FIG. 10. A correlation between the fluorescence and the solubilization behavior of petroleum sulfonate containing microemulsions.

containing system, the brine solubilization limit was drastically lowered when pentanol or higher alcohols were used in place of butanol. The fluorescence behavior of these microemulsions was similar to their solubilization behavior.

Figures 8 and 9 show the optimal salinity and brine solubilization as a function of oil chain length of oil for various alcohols. Optimal salinity increased approximately linearly with the oil chain length (Fig. 8). As explained earlier, water-soluble alcohols (butanol and iso-butanol) gave high values of optimal salinities, whereas microemulsions containing water-insoluble alcohols had low values of optimal salinities. The brine solubilization limit decreased with increasing oil chain length for butanol and iso-butanol (Fig. 9) whereas it increased for pentanol and did not change significantly for hexanol- and heptanol-containing microemulsions.

A good correlation was found between the fluorescence intensity and the brine solubilization limit of microemulsions containing petroleum sulfonate. This correlation is independent of the type or carbon chain length of alcohol or oil used in preparing the microemulsions. Figure 10 shows the fluorescence intensity of microemulsion as a function of maximum brine solubilization of microemulsions at optimal salinity. A linear relationship exists between these 2 parameters as follows: $I = 15\ S_b$; where I is the fluorescence intensity of the microemulsion samples, and S_b is the brine solubilization limit of this microemulsion at its optimal salinity. We have also shown (not reported here) that the same correlation applies to microemulsions containing any other salinity brines. However, the fluorescent intensity is expressed in arbitrary units. The value of fluorescent intensity depends on settings of the fluroescence spectrophotometer, e.g., slit width and signal gain. For the same spectrophotometer setting, a linear relationship between fluorescent intensity and brine solubilization limit of microemulsions is expected.

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