Influence of Alkyl Chain Length Compatibility on Microemulsion Structure and Solubilization

V. K. BANSAL, D. O. SHAH,[1] AND J. P. O'CONNELL

Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, Florida 32611

Received October 19, 1979; accepted January 16, 1980

The solubilization capacity of water/oil microemulsions formed with fatty acid soaps and alcohols was studied as a function of alkyl chain length of oil (C_8 to C_{16}), soap (C_{14} and C_{18}), and alcohol (C_4 to C_7). For *n*-butanol with both soaps, the maximum amount of water solubilized in the microemulsion continuously decreased with increasing oil chain length whereas for *n*-heptanol the solubilization capacity continuously increased. For pentanol with both soaps and for hexanol with sodium stearate, the solubilization reached a maximum when the oil chain length, l_o, plus that of the alcohol, l_a, was equal to that of the surfactant, l_s, (i.e., $l_a + l_o = l_s$). When excess water was added to these systems, a birefringent aqueous phase in equilibrium with an isotropic upper phase formed if $l_a + l_o < l_s$ whereas a different phase behavior, namely, the formation of two isotropic phases, was observed if $l_a + l_o \geq l_s$. Both of these observations indicate a chain length compatibility effect similar to that observed in monolayers, foams, emulsions, and lubricants. The solubilization behavior is interpreted in terms of partitioning of alcohol among oil, water, and the interface depending upon the chain length of oil and alcohol, as well as in terms of molecular packing at the interface in relation to the disorder produced by the chain length compatibility effect. It was concluded from the oil–alcohol titration study that the molar ratio of alcohol to soap at the interface increases with oil chain length. We propose that the increase in the alcohol/soap molar ratio leads to increased spacing between carboxyl groups resulting in a greater degree of ionization. Electrical resistance and dielectric constant measurements yielded results consistent with this interpretation. At a given water/oil ratio, the electrical resistance of microemulsions decreases, the dielectric constant increases, and the thickness of ionic atmosphere within the water droplets increases as the oil chain length is increased. These phenomena are consistent with the concept that microemulsions form, and vary their structure, under the influence of surfactant and alcohol partitioning between aqueous and oleic phases and the consequent interfacial activity of both species. Here, the partitioning of alcohol and soap is subtly varied by changing the oil chain length.

INTRODUCTION

Ever since their introduction, microemulsions have been studied extensively theoretically as well as experimentally by various investigators (1–21). It has been reported that the formation and various physicochemical properties of the microemulsions are influenced by the alkyl chain length of alcohol and hydrocarbons (22–27). For example, the interfacial composition and distribution of alcohol in the oil and aqueous phases are influenced by the alkyl chain length of alcohol and oil (22, 26, 27). Moreover, we have shown previously (26) that the electrical resistance, dielectric constant, interfacial polarization, and ESR order parameter are strongly influenced by the alkyl chain length of alcohol.

While it is clear that the nature of the alcohol strongly influences the properties of the microemulsions, the influence of the

[1] Currently a Visiting Professor of Chemical Engineering, Petroleum Engineering and the Institute for Energy Studies at Stanford University, Stanford, California 94305.

0021-9797/80/060462-14$02.00/0
Copyright © 1980 by Academic Press, Inc.
All rights of reproduction in any form reserved.

nature of the oil is not well documented. In the earlier work on aerosol OT systems, it was reported that the solubilization limit of water is a function of the alkyl chain length of hydrocarbons (23, 24). In contrast, it was reported recently that the maximum water solubilization capacity of microemulsions is independent of hydrocarbon nature (28).

Microemulsions have been used for enhanced oil recovery from petroleum reservoirs (29–31). Under appropriate conditions, a microemulsion can exhibit an ultralow interfacial tension ($\leq 10^{-3}$ dyn/cm) with excess oil or excess brine (31–33). The addition of ethoxylated surfactants in microemulsions can strikingly improve their stability at high salinity (≈30% salt concn) even in the presence of bivalent cations (34–36).

In the present study, the water solubilization capacity of water/oil microemulsions has been studied as a function of alkyl chain length of oil (C_8–C_{16}), surfactant (C_{14} and C_{18} fatty acid soaps), and alcohol (C_4–C_7). The electrical resistance and dielectric constant of the microemulsions have also been measured as a function of alkyl chain length of the oil.

EXPERIMENTAL

Materials. Sodium stearate of 99% purity, supplied by Matheson, Coleman and Bell, Inc., and sodium myristate of technical grade, supplied by K & K Laboratories, Inc., were used as surfactants for preparing microemulsions. All the alcohols and oils were purchased from Chemical Samples Company and were of 99% purity or greater. Triple-distilled water was used in making all the microemulsions.

Water solubilization limit. The microemulsions were prepared by mixing surfactant (1 g), alcohol (4 or 8 ml), oil (10 ml), and water (1 ml) to get a clear solution. The water solubilization capacity was determined by mixing additional water slowly from a graduated 1-ml pipette to the microemulsion, until turbidity was observed and two-phase formation occurred. In all cases, the endpoint was sharp (within ±0.1 ml of added water). At the endpoint the systems were initially turbid, but after a few minutes of standing two clear phases formed.

Electrical resistance measurement. The low-frequency electrical resistance measurements were made on a Beckman Model RCB2 conductivity bridge. The instrument employs a transformer ratio–arm bridge circuit with a vacuum tube oscillator and an electronic-eye null detector. The measurements can be made at the line frequency (60 Hz) or at 1 kHz. All measurements reported in this paper were carried out at 1 kHz. Beckman conductivity cells with cell constants 0.1 and 1.0 cm^{-1} were used. All measurements were made at 25 ± 0.1°C.

Dielectric properties measurement. The dielectric properties of the microemulsions were obtained using an R-X Meter Type 250 B (Boonton Radio Corp., Division of Hewlett–Packard), as reported previously (26). Dielectric cells with variable electrode distances were designed similar to that of Sachs *et al.* (37) to operate in the frequency range of 0.5 to 150 MHz.

RESULTS AND DISCUSSION

Solubilization Study

The water solubilization capacity of sodium stearate microemulsions as a function of alkyl chain lengths of oil and alcohol is shown in Figs. 1 and 2. In the first case (Fig. 1), 4 ml of alcohol was used in preparing the microemulsions, whereas in the second case (Fig. 2) 8 ml of alcohol was used. It was found that for *n*-butanol microemulsions the maximum amount of water solubilized in the microemulsion decreased continuously with increasing oil chain length, whereas for *n*-heptanol it increased continuously. For *n*-pentanol and *n*-hexanol systems, water solubilization reached a maximum when the oil chain length, l_o, plus that of the alcohol, l_a, was equal to that of

the surfactant, l_s. This effect was found to be more pronounced when 8 ml of alcohol was used in making microemulsions (Fig. 2). The water solubilization capacity of sodium myristate microemulsions as a function of alkyl chain length of oil and alcohol was also studied and is shown in Fig. 3. It can be seen from Fig. 3 that for butanol microemulsion systems the solubilization capacity continuously decreased with increasing oil chain length, whereas for *n*-hexanol microemulsions it abruptly increased at C_{10}. The comparison of the water solubilization behavior of the two microemulsion systems (Figs. 2 and 3) reveals that the butanol and pentanol microemulsions behave exactly the same way in both systems. However, the solubilization behavior of hexanol microemulsions of sodium myristate (Fig. 3) is similar to the heptanol microemulsions of sodium stearate systems (Fig. 1). From these studies, it can be concluded that when the oil chain length is increased, the solubilization capacity of microemulsions can increase, decrease, or show a maximum, depending upon the structure of the alcohol used.

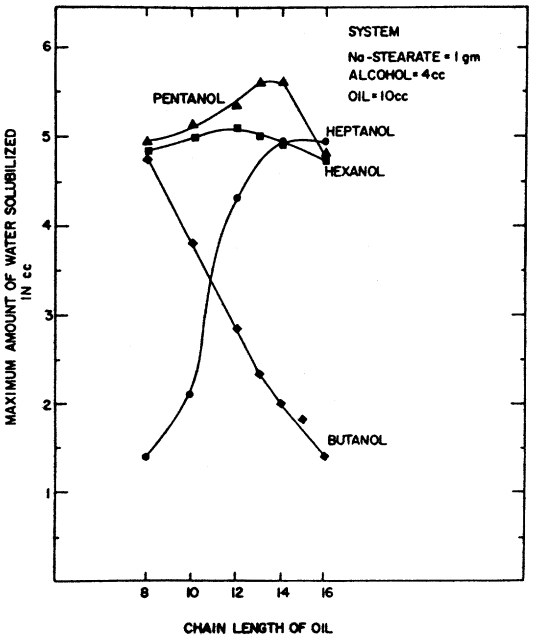

FIG. 1. Effect of oil and alcohol chain length on water solubilization capacity of microemulsions.

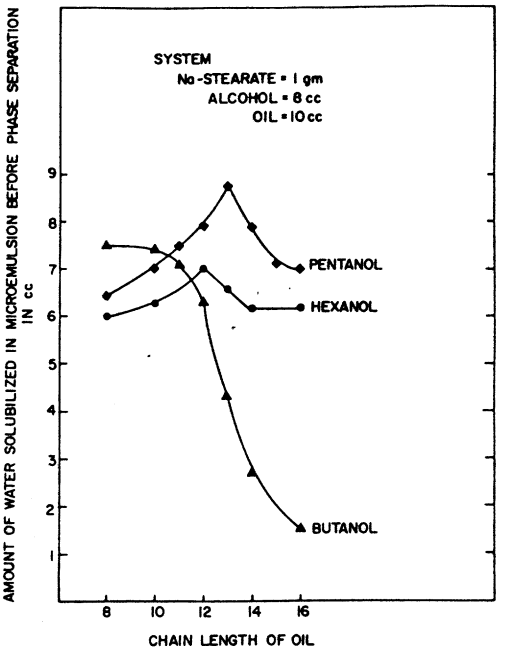

FIG. 2. Effect of oil and alcohol chain length on water solubilization capacity of microemulsions.

Figure 4 schematically illustrates our proposed explanation for the maximum solubilization and chain length compatibility effect observed for pentanol- and hexanol-containing systems in Fig. 2. Upon addition of water, the size of water 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 into 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 due to an increase in the area per molecule and thus destabilize the microemulsion, and hence prevent further solubilization of water. Ruckenstein (19) has shown theoretically that microemulsions cannot form if the interfacial tension at the oil/water interface is high (0.1 dyn/cm) as compared to the value of 10^{-3} dyn/cm where they do form.

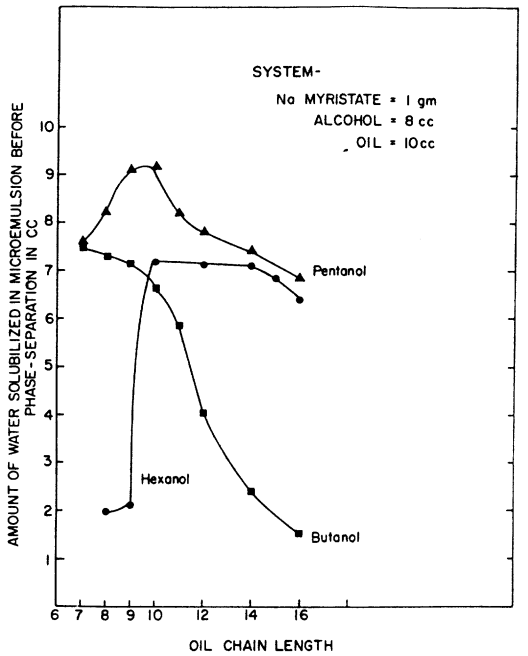

FIG. 3. Effect of oil and alcohol chain length on water solubilization capacity of microemulsions.

When $l_a + l_o \gtrless l_s$, there will be a region of disordered hydrocarbon chains near the terminal methyl groups around the droplet as shown in Fig. 4. Using mixed monolayers, we have shown (38) that the thermal motion of the terminal segment produces a disruptive effect on the packing of surface-active molecules and increases the area per molecule at the interface. It was further shown (39) that this disruptive effect causes an increase of about 0.05 Å in the intermolecular distance between surfactant molecules at the interface, which in turn influences the evaporation of water through mixed monolayers, surface viscosity, surface tension, contact angle, boundary lubrication, melting point of crystals, and stability of foams and emulsions of mixed surfactant systems. Therefore, we propose that the maximum solubilization observed at $l_a + l_o = l_s$ is due to the maximum cohesive interaction between hydrocarbon chains (or due to minimum disruptive effect in the interfacial region) under these conditions (Fig. 4). Similar chain length compatibility effects in other systems have been observed by various investigators (40–42).

We propose that not only the molecular packing, but also the total amount of soap and alcohol at the interface influence the solubilization behavior of microemulsions. The higher the amount of soap and alcohol at the interface, the higher is the solubilization capacity of microemulsions. Our explanation for the solubilization behavior of heptanol- and butanol-containing microemulsions is illustrated in Fig. 5. From a study on the surfactant partitioning in various oil/water systems, we have shown (31, 32) that as the oil chain length was increased from *n*-hexane to *n*-hexadecane, the surfactant partitioning in oil decreased. Similar behavior is expected for *n*-heptanol. Since *n*-heptanol has a negligible solubility in

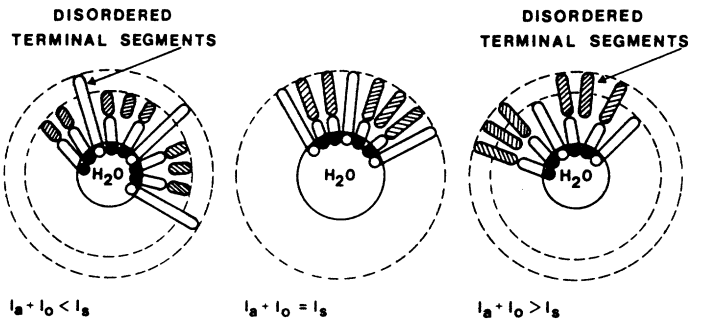

FIG. 4. A schematic illustration of the disordering effect of the terminal segment of alkyl chain protruding out of the interfacial film and the solubilization capacity of microemulsions. l_a, l_o, and l_s are the chain lengths of alcohol, oil, and soap molecules, respectively.

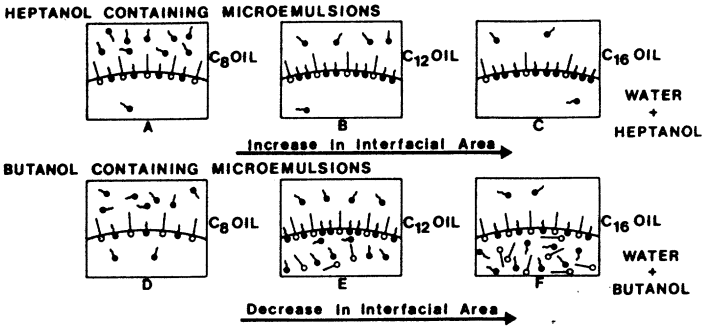

FIG. 5. A schematic presentation of the effect of increasing oil chain length on the partitioning of alcohol in the oil, water, and interfacial region.

water, the heptanol concentration at the interface would increase due to decreased partitioning in oil as the chain length of the oil is increased from C_8 to C_{16}. In other words, the alcohol/soap molar ratio at the interface increases as the oil chain length increases from C_8 to C_{16} (Fig. 5). This indeed was confirmed by a titration study carried out according to Bowcott and Schulman (43) (Fig. 6). The intercept, which represents the molar ratio of alcohol to soap at the interface, increased as the oil chain length increased.

For butanol-containing microemulsions, the solubilization capacity decreased as the oil chain length increased (Figs. 1–3). Our

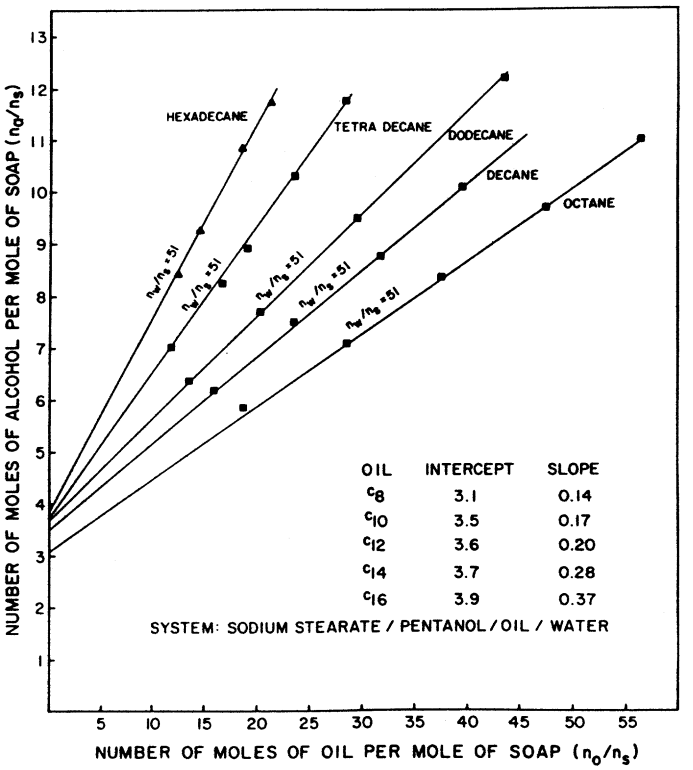

FIG. 6. Effect of oil chain length on the oil/alcohol titration plots for microemulsions.

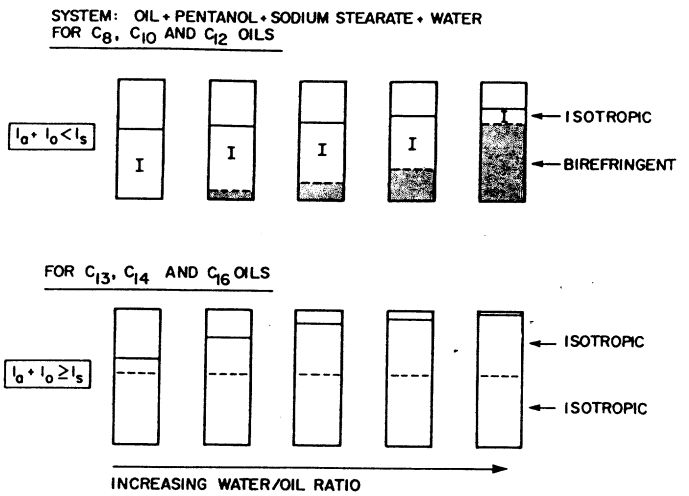

FIG. 7. A schematic representation of phase behavior of microemulsions upon addition of excess water beyond the solubilization limit for oils of various chain length.

proposed explanation for this effect is schematically shown in Fig. 5. As the oil chain length is increased, less partitioning of butanol will occur in the oil phase. Since the total amount of butanol is constant in each system, a concomitant increase in the butanol concentration at the interface and in water phase will occur. Unlike heptanol systems, the water pool in butanol systems gradually becomes water plus butanol pool as this alcohol has substantial solubility in water. The water plus butanol as solvent will solubilize soap molecules in the pool and remove them gradually from the interface. This will decrease the total interfacial area and hence the concomitant decrease in solubilization capacity.

The above interpretation and explanations lead to the following conclusions regarding the formation and solubilization capacity of the microemulsions studied in this paper: (i) The soap stabilizes the interface and alcohol partitions (or penetrates) in this interfacial film of soap; (ii) the soap must remain at the interface to be effective as a microemulsion-stabilizing agent; (iii) if the soap desorbs from the interface into the water pool due to increasing concentration of water-soluble alcohol or in the oil phase due to increasing concentration of oil-soluble alcohol, the total interfacial area and solubilization capacity decrease; (iv) if the soap and alcohol remain predominantly adsorbed at the oil/water interface and if the disruptive effect of the motion of terminal segments of hydrocarbon chains is minimized, the maximum solubilization capacity can be obtained (i.e., $l_a + l_o = l_s$); (v) the chain length of soap influences the partitioning behavior of alcohol at the interface.

It was thought that perhaps the properties of the phases separating beyond the solubilization limit might also reveal the chain length compatibility effect observed for solubilization behavior of the microemulsions. Figure 7 schematically shows the optical appearance of the phases separated out upon addition of water beyond the solubilization limit of the pentanol-containing microemulsions. It was interesting that when excess water was added to the microemulsion, a birefringent aqueous phase separated out at the bottom when $l_a + l_o < l_s$ whereas an isotropic oil-rich phase separated out at the top when $l_a + l_o \geq l_s$. The volume, interfacial tension, and optical appearance of separated phases of the sodium stearate–pentanol microemulsions

as a function of excess water are summarized in the Tables I and II. It can be noted from Table I that for those systems when $l_a + l_o < l_s$ (C_8–C_{12}), the volume of the birefringent phase increases, with an increase in the water/oil ratio. It can also be noted that the volume of birefringent phase increases dramatically upon increasing the water/oil ratio. An increase of 0.01 in the water/oil ratio can cause a factor of 5 to 10 increase in the volume of the birefringent phase. It was also found that the interfacial tensions between the birefringent lower phase and the isotropic upper oil phase were too low to be measured by a spinning drop interfacial tensiometer (44). Table II summarizes the properties of separated phases of the microemulsions when $l_a + l_o \geq l_s$. Both of the phases were isotropic and clear, and the volume of the upper phase (oil) increased upon increasing the water/oil ratio. It can also be noted from the Table II that the interfacial tension between the two separated phases increased with added water. Very similar results were obtained for the sodium myristate and pentanol microemulsion systems. A birefringent aqueous phase separated out at the bottom for $l_a + l_o < l_s$ systems ($<C_9$ oil) and an isotropic upper oil phase separated out for nonane and higher chain length oil systems upon adding the excess water to the microemulsion. A typical photograph for $l_a + l_o < l_s$ and $l_a + l_o \geq l_s$ systems is shown in Fig. 8. (The samples were placed between cross-polarized plates.)

The properties of separated phases in pentanol microemulsions were not observed

TABLE I

Effect of Oil Chain Length on the Properties of Phases Separated Out from Microemulsions after Their Water Solubilization Limit[a]

Water/oil ratio[b]	Volume of upper phase (V_U) (ml)	Volume of lower phase (V_L) (ml)	V_U/V_L
	Oil: n-C_8H_{18}		
0.650	9.6	0.6	16.0
0.675	8.8	1.5	5.9
0.725	7.0	3.5	2.0
0.775	2.1	8.6	0.2
	Oil: n-$C_{10}H_{22}$		
0.725	9.0	1.5	6.0
0.750	4.5	6.1	0.7
0.775	0.8	9.9	0.1
	Oil: n-$C_{12}H_{26}$		
0.795	10.5	0.2	52.5
0.800	8.7	2.1	4.1
0.805	5.2	5.6	0.9
0.810	1.5	9.3	0.2

[a] Lower phases in all cases were anisotropic and strongly birefringent whereas the upper phases were isotropic. Interfacial tensions between the two phases were too low to be measured ($<10^{-4}$ dyn/cm).

[b] Initial system contained 2.4 ml water, 4 ml oil, 3.2 ml n-pentanol, 0.4 g sodium stearate, and water was then added to get the required water/oil ratio.

TABLE II

Effect of Oil Chain Length on the Properties of Phases Separated Out from Microemulsion after Their Water Solubilization Limit[a]

Water/oil ratio[b]	Volume of upper phase (V_U) (ml)	Volume of lower phase (V_L) (ml)	V_U/V_L	$\gamma_{U/L}$ (dyn/cm)
	Oil: n-$C_{13}H_{28}$			
0.850	1.4	9.7	0.14	$<10^{-3}$
0.900	2.5	8.7	0.29	4.0×10^{-3}
0.937	2.9	8.4	0.35	1.0×10^{-2}
0.975	3.5	8.4	0.42	1.1×10^{-2}
	Oil: n-$C_{14}H_{30}$			
0.775	2.1	8.6	0.24	8.55×10^{-4}
0.850	3.1	7.9	0.39	5.74×10^{-3}
0.900	3.4	7.8	0.44	1.35×10^{-2}
0.975	3.8	7.7	0.49	2.00×10^{-2}
	Oil: n-$C_{16}H_{34}$			
0.725	1.9	8.6	0.22	2.93×10^{-3}
0.775	2.4	8.3	0.29	5.88×10^{-3}
0.850	3.4	7.6	0.45	9.00×10^{-3}
0.975	4.4	7.1	0.62	1.90×10^{-2}

[a] All phases were isotropically clear.

[b] Initial system contained 2.4 ml water, 4 ml oil, 3.2 ml n-pentanol, 0.4 g sodium stearate, and water was then added to get the required water/oil ratio.

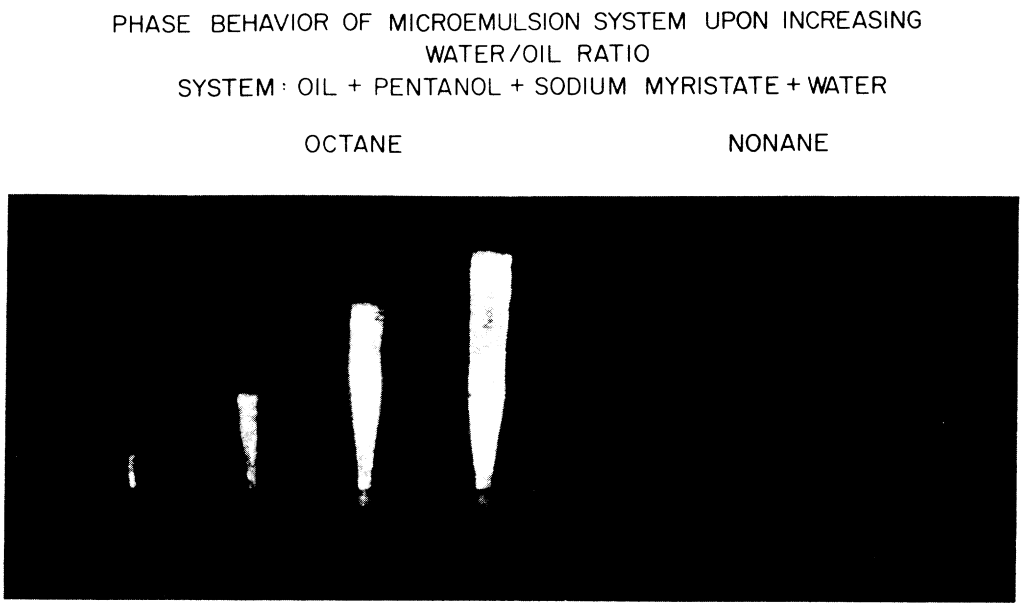

FIG. 8. The effect of one carbon atom difference in the oil chain length (C_8 vs C_9) on the phase behavior of microemulsions when excess water is added. The photo was taken by placing the samples between two cross-polarized plates.

in systems containing other alcohols. In the butanol microemulsion system, no birefringent phase was observed, whereas for hexanol and heptanol a white precipitate formed beyond the solubilization limit.

ELECTRICAL PROPERTIES OF MICROEMULSIONS

Electrical Resistance Behavior

The electrical resistance behavior of the pentanol microemulsions as a function of alkyl chain length of oil at different water/oil ratios is shown in Figs. 9 and 10 for stearic acid and myristic acid soap, respectively. In our view, the electrical resistance behavior can be explained on the basis of surface conductance model as suggested by O'Konski (45) for polyelectrolyte systems. According to this model, the effective volume conductivity can be considered as the sum of parallel bulk and surface conductivity contributions. The contribution due to the surface conductivity is a function of the size of the dispersed particles (water droplets) and the mobility of ions in the ionic atmosphere of water droplets. The increase in the specific resistance at a given water/oil ratio in the microemulsion (Figs. 9 and 10) with a decrease in the alkyl chain length of oil suggests that the contribution of surface conductance to the total volume conductance decreases. This can be attributed to the lower degree of ionization of soap at the interface and to a concomitant thinning of the ionic atmosphere at the interface. This hypothesis is confirmed by our dielectric constant measurements and will be discussed later.

The effect of oil chain length on the interfacial composition of alcohol and surfactant (N_a/N_s) was determined by the Bowcott and Schulman method (43) and was shown in Fig. 6. According to this model, the intercept on the y-axis represents the molar ratio of alcohol to soap at the interface (N_a/N_s) and the slope of each plot represents the critical molar ratio of alcohol/oil necessary to produce a microemulsion. As can be seen from Fig. 6, N_a/N_s and N_a/N_o

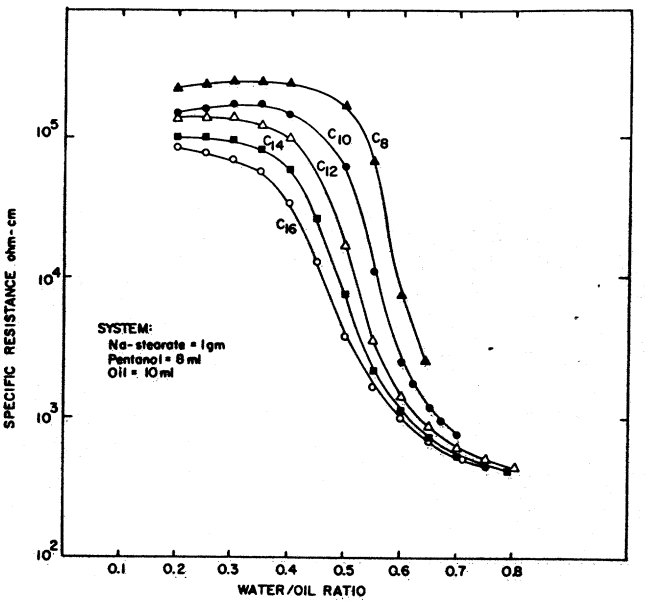

FIG. 9. Effect of oil chain length on the electrical resistance of microemulsion at different water/oil ratios.

increased with the oil chain length and there was no observed chain length compatibility effect. The increase in N_a/N_s should increase the intermolecular distance between soap molecules and cause a greater degree of ionization of soap molecules at the interface (26) and thus the surface contribution to the total conductance will increase, lead-

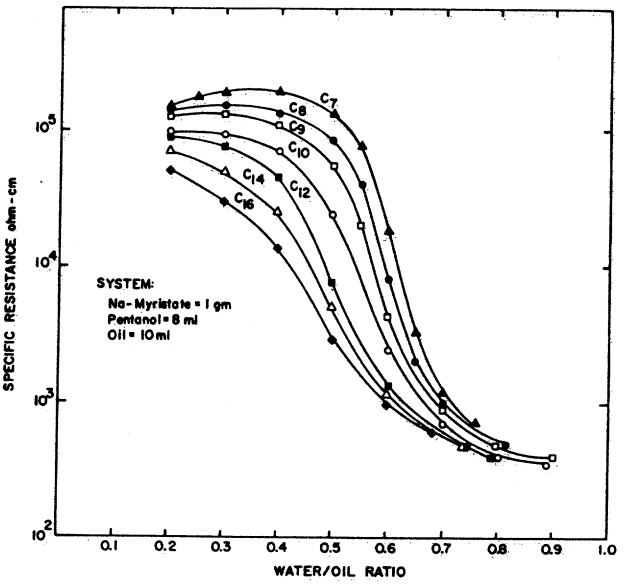

FIG. 10. Effect of oil chain length on electrical resistance of microemulsions at different water/oil ratios.

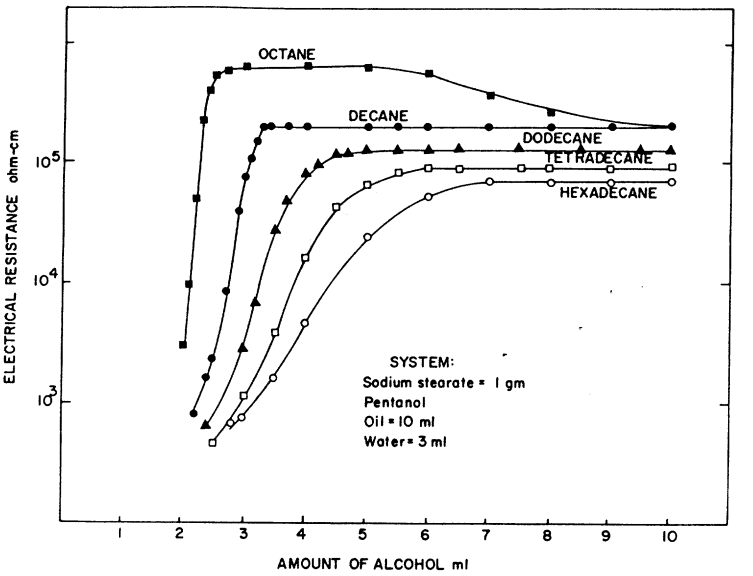

FIG. 11. Effect of alcohol concentration on the electrical resistance of microemulsions.

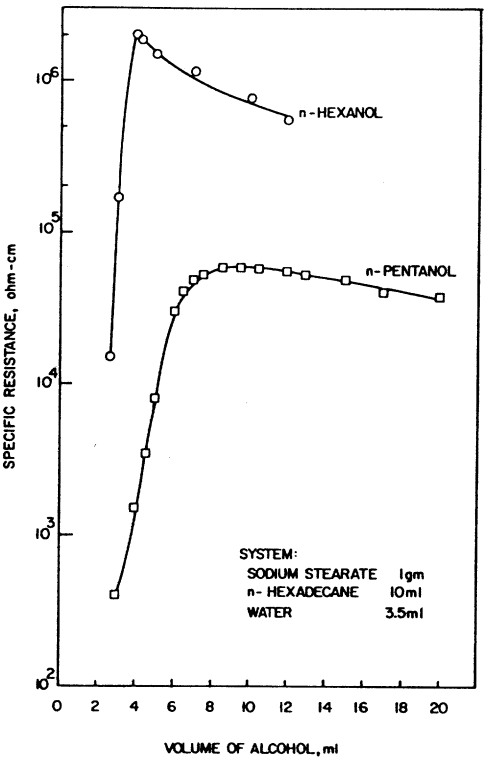

FIG. 12. Effect of alcohol concentration on specific resistance of microemulsions at a water/oil ratio of 0.35.

ing to a decrease in specific resistance. This indeed was observed in Figs. 9 and 10.

Figure 11 shows the electrical resistances of the microemulsions as a function of alcohol concentration in the microemulsion. The electrical resistance increases sharply with increased amount of alcohol up to a critical amount of alcohol where the electrical resistance becomes constant. The critical amount of alcohol is a function of the oil chain length. It is evident that the higher the oil chain length, the higher is the critical concentration of alcohol (e.g., the sharp break around 2.5 ml for octane microemulsions in Fig. 11). At the saturation limit, the absolute value of the electrical resistance is lower for the higher chain length oils. This is in agreement with the proposition that there is a greater degree of ionization in the microemulsions of greater oil chain length. It should be emphasized that the oil chain length influences the alcohol/surfactant ratio at the interface (Fig. 6) which, in turn, determines the intermolecular spacing between soap molecules and hence the degree of ionization. The increase in the degree of ioniza-

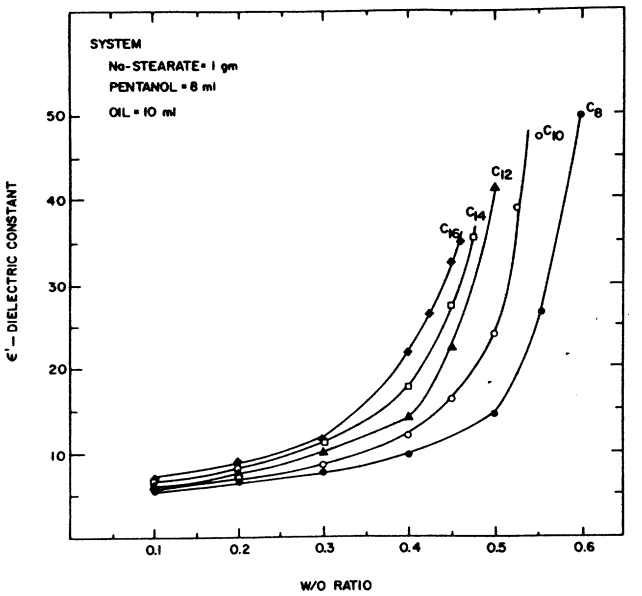

FIG. 13. Effect of oil chain length on the dielectric constant of microemulsion at 1-MHz frequency at various water/oil ratios.

tion of a cationic surfactant upon addition of an alcohol has been reported also by Zana (46). Recently (47), a percolation mechanism has been invoked to account for the electrical conductivity of microemulsions. Accordingly, one can view the addition of the alcohol in microemulsions as a process interfering with the percolation mechanism resulting in an increase in the electrical resistance (Fig. 11).

Figure 12 shows the effect of *n*-hexanol and *n*-pentanol concentration on electrical resistance behavior of hexadecane microemulsions. The higher values of electrical resistance for hexanol microemulsions are in agreement with our previous (26) results which showed that a higher alcohol/soap ratio for pentanol causes a greater degree of ionization in the pentanol-containing microemulsions, as compared to hexanol-containing microemulsions.

Dielectric Behavior of Microemulsions

Dielectric constants of the microemulsion as a function of the alkyl chain length of oil and the water/oil ratio are shown in Fig. 13. For a given oil, as the water/oil ratio increases, the dielectric constant increases

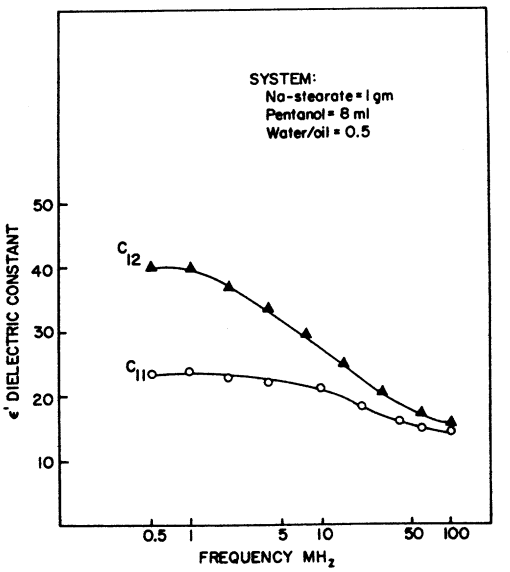

FIG. 14. Effect of one carbon atom difference in the oil chain length (C_{11} vs C_{12}) on the dielectric constant of microemulsions at various frequencies.

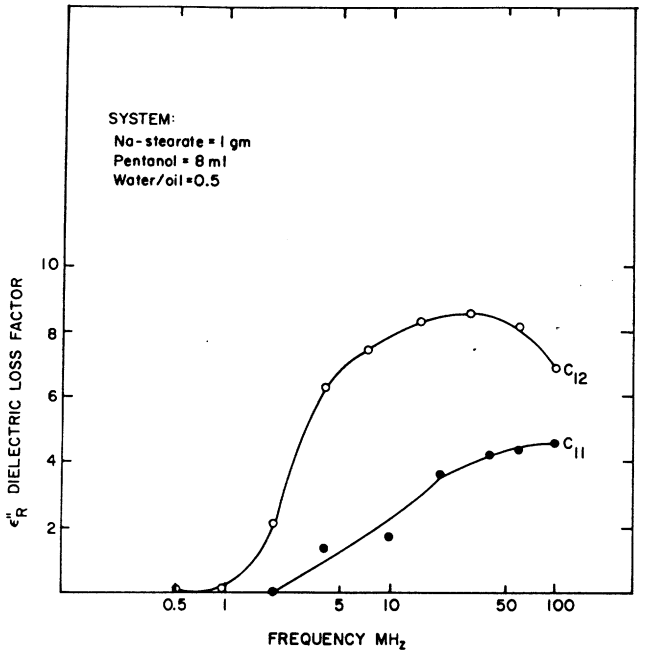

FIG. 15. Effect of one carbon atom difference in the oil chain length (C_{11} vs C_{12}) on the dielectric loss factor of microemulsions at various frequencies.

slowly until a critical value of water in the microemulsion (V_c) is reached. It was found (26, 48) that systems with volume fractions of water close to V_c exhibit dielectric relaxation and a sudden increase in dielectric constant. The increase in dielectric constant was explained on the basis of interfacial polarization. It was also concluded that the critical frequency in these systems is inversely related to the thickness of the ionic atmosphere in the dispersed water droplets. As can be seen from Fig. 13, at a given water/oil ratio, the dielectric constant increased with the chain length of oil. This suggests that the contribution due to the interfacial polarization, i.e., ionization of the carboxyl group at the interface, increases with the oil chain length. It is also evident from Fig. 13 that the value of V_c increases as the chain length of oil decreases.

Figures 14 and 15 show the dielectric relaxation behavior of the microemulsions for two oils at a given water/oil ratio of 0.5. It is evident that one carbon difference in the oil chain length can strongly influence the dielectric properties of the microemulsions. There is a large increase in the dielectric loss factor and a decrease in the critical frequency with an increase in the chain length of oil. This suggests that a thicker ionic atmosphere (i.e., electrical double layer) is associated with water droplets in microemulsions of longer chain length oil. This is also in agreement with our views on the degree of ionization and electrical resistance of microemulsions discussed earlier in this paper. A lack of correlation between solubilization capacity and electrical or dielectric behavior of microemulsions suggests that the former is probably a much more sensitive indicator of molecular packing and partitioning behavior of soap and alcohol as compared to electrical or dielectric characteristics of microemulsions.

ACKNOWLEDGMENTS

The authors are grateful to the Department of Energy (Grant EY-77-S-05-5341) and the consortium of 20 major oil and chemical companies for their support of this research which was carried out as a part of the Enhanced Oil Recovery Research Program at the University of Florida.

REFERENCES

1. Hoar, T. P., and Schulman, J. H., *Nature (London)* **152,** 102 (1943).
2. Prince, L. M., *J. Colloid Interface Sci.* **23,** 165 (1967).
3. Adamson, A. W., *J. Colloid Interface Sci.* **29,** 261 (1969).
4. Gerbacia, W., and Rosano, H. L., *J. Colloid Interface Sci.* **44,** 242 (1973).
5. Friberg, S., and Burasczenska, I., *Progr. Colloid Polym. Sci.* **63,** 1 (1978).
6. Reiss, H., *J. Colloid Interface Sci.* **52,** 182 (1975).
7. Ruckenstein, E., and Chi, J. C., *J. Chem. Soc. Faraday Trans. II* **71,** (1960).
8. Prince, L. M., *in* "Microemulsion: Theory and Practice" (L. M. Prince, Ed.). Academic Press, 1977.
9. Shinoda, K., and Kuneida, H., *J. Colloid Interface Sci.* **42,** 381 (1973).
10. Shah, D. O., and Hamlin, R. M., Jr., *Science* **171,** 483 (1971).
11. Shah, D. O., Tamjeedi, A., Falco, J. W., and Walker, R. D., Jr., *AIChE J.* **18,** 1116 (1972).
12. Falco, J. W., Walker, R. D., Jr., and Shah, D. O., *AIChE J.* **20,** 510 (1974).
13. Shah, D. O., Bansal, V. K., Chan, K. S., and Hsieh, W. C., *in* "Improved Oil Recovery By Surfactant and Polymer Flooding" (D. O. Shah and R. S. Schechter, Eds.). Academic Press, New York, 1977.
14. Eicke, H. F., and Shepherd, J. C. W., *Helv. Chim. Acta* **57,** 1951 (1974).
15. Clausse, M., and Rager, R., *in* "Colloid and Interface Science" (M. Kerker, A. C. Zettlemoyer, and R. L. Rowell, Eds.), Vol. 2, p. 217. Academic Press, London/New York, 1976.
16. Ahmed, S. I., Shinoda, K., and Friberg, S., *J. Colloid Interface Sci.* **29,** 261 (1969).
17. Lagiies, M., Ober, R., and Taupin, C., *J. Phys. Lett. Fr.* **39,** L487 (1978).
18. Overbeek, J. T. G., *Faraday Discuss.* **65,** 7 (1978).
19. Ruckenstein, E., *in* "Micellization, Solubilization and Microemulsions" (K. L. Mittal, Ed.), Vol. 2, pp. 755–778. Plenum, New York, 1977.
20. Gillberg, G., Lehtinen, H., and Friberg, S., *J. Colloid Interface Sci.* **4,** 281 (1975).
21. Shinoda, K., and Friberg, S., *Advan. Colloid Interface Sci.* **4,** 281 (1975).
22. Cooke, C. E., and Shulman, J. H., *in* "Surface Chemistry" (P. Ekwall, K. Groth, and V. Runnström-Reio, Eds.), pp. 231–251. Academic Press, New York, 1965.
23. Higuchi, W. I., and Misra, J., *J. Pharm. Sci.* **51,** 455 (1962).
24. Frank, S. G., and Zografi, G., *J. Colloid Interface Sci.* **29,** 28 (1965).
25. Shah, D. O., Walker, R. D., Jr., Hsieh, W. C., Shah, N. J., Dwivedi, S., Nelander, J., Pepinsky, R., and Dermer, D. W., SPE Paper 5815, presented at Improved Oil Recovery Symposium of SPE of AIME, Tulsa, Oklahoma, March 22–24, 1976.
26. Bansal, V. K., Chinnaswamy, K., Ramachandran, C., and Shah, D. O., *J. Colloid Interface Sci.* **72,** 524 (1979).
27. Sjoblom, E., and Friberg, S., *J. Colloid Interface Sci.* **67,** 16 (1978).
28. Prince, L. M., *J. Colloid Interface Sci.* **57,** 182 (1975).
29. Bansal, V. K., and Shah, D. O., *in* "Micellization, Solubilization, and Microemulsions" (K. L. Mittal, Ed.), Vol. 1, pp. 87–113. Plenum, New York, 1977.
30. Hsieh, W. C., and Shah, D. O., SPE Paper 6594, Proc. SPE International Symposium on Oilfield and Geothermal Chemistry, La Jolla, California, June 27–28, 1977.
31. Chan, K. S., and Shah, D. O., SPE Paper 7869, Proc. SPE International Symposium on Oilfield and Geothermal Chemistry, Houston, Texas, January 22–24, 1979.
32. Chan, K. S., and Shah, D. O., *J. Dispersion Sci. Technol.* **1,** 55 (1979).
33. Chan, K. S., Ph.D thesis, University of Florida, 1978.
34. Bansal, V. K., and Shah, D. O., *J. Amer. Oil Chem. Soc.* **55,** 367 (1978).
35. Bansal, V. K., and Shah, D. O., *Soc. Petrol. Eng. J.* 167–172, June 1978.
36. Bansal, V. K., and Shah, D. O., *J. Colloid Interface Sci.* **65,** 451 (1978).
37. Sachs, S. B., Katchalsky, A., and Spiegler, K. S., *Electrochim. Acta* **15,** 693 (1970).
38. Shah, D. O., and Shiao, S. Y., *Advan. Chem. Ser.* **144,** 153 (1975).
39. Shiao, S. Y., Ph.D thesis, University of Florida, 1976.
40. Schick, M. J., and Fowkes, F. M., *J. Phys. Chem.* **61,** 1062 (1957).
41. Fort, T., Jr., *J. Phys. Chem.* **66,** 1136 (1962).
42. Cameron, A., and Crouch, R. F., *Nature (London)* **198,** 475 (1963).

43. Bowcott, J. E. L., and Schulman, J. H., *Z. Electrochem.* **59,** 283 (1955).
44. Cayias, J. L., Schechter, R. S., and Wade, W. H., *in* "Adsorption at Interfaces" (K. L. Mittal, Ed.), ACS Symposium Series No. 8. Amer. Chem. Soc., Washington, D. C., 1975.
45. O'Conski, C. T., *J. Phys. Chem.* **64,** 605 (1968).
46. Zana, R., *in* "Surface Phenomena in Enhanced Oil Recovery" (D. O. Shah, Ed.). Plenum, New York, in press.
47. Lagourette, B., Peyrelasse, J., Boned, C., and Clausse, M., *Nature (London)* **281,** 60 (1979).
48. Bansal, V. K., Chinnaswamy, K., and Shah, D. O., *Ber. Bunsenges. Phys. Chem.* **82,** 979 (1978).