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Effect of Chain Length Compatibility on Monolayers, Foams, and Macro- and Microemulsions

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The effect of chain length compatibility of various surfactants on molecular packing, foams, macro- and microemulsion structures, solubilization and oil displacement efficiency in porous media has been studied using different techniques. Moreover, the solubilization of water in microemulsions was studied in detail as a function of alkyl chain length of oils and cosurfactants. The solubilization behavior is discussed in terms of partitioning of alcohol among oil, water and the interface depending upon the chain length of alcohol and oil, as well as in terms of molecular packing at the interface in relation to the disorder produced by the chain length compatibility effects. It is proposed that the chain length compatibility strikingly affects the properties of interfacial film, which in turn influences emulsion stability, foam stability, solubilization capacity, molecular packing at the interface, fluid displacement efficiency and effective gas mobility in oil recovery processes.

The formation and stability of foams and emulsions depend on the structure of surfactants and cosurfactants employed in these systems. It has been reported that the structure of alcohol strongly influences the properties of microemulsions (1-5). Moreover, the interfacial composition and alcohol partitioning between aqueous phase and oil are influenced by the alkyl chain length of oil and alcohol (6,7). The structural aspects of microemulsions using various techniques such as X-ray diffraction, viscometry, light scattering, ultracentrifugation, electron microscopy and electrical conductivity have been reported by previous investigators (8-10). From these studies, it is proposed that microemulsions are isotropic, clear or translucent and thermodynamically stable dispersions of oil, water and emulsifiers with the droplet diameter ranging from 100 - 1000 Å.

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Schick and Fowkes (11) studied the effect of alkyl chain length of surfactants on critical micelle concentration (CMC). The maximum lowering of CMC occurred when both the anionic and nonionic surfactants had the same chain length. It was also reported that the coefficient of friction between polymeric surfaces reaches a minimum as the chain length of paraffinic oils approached that of stearic acid (12). In order to delineate the effect of chain length of fatty acids on lubrication, the scuff load was measured by Cameron and Crouch (13). The maximum scuff load was observed when both hydrocarbon oil and fatty acid had the same chain length. Similar results of the effect of chain length compatibility on dielectric absorption, surface viscosity and rust prevention have been reported in the literature (14-16).

The gas/liquid and liquid/liquid systems are relevant to biomedical and engineering applications. The large interfacial area in foams, macro- and microemulsions is suitable for rapid mass transfer from gas to liquid or liquid to gas in foams and from one liquid to another or vice versa in macro- and microemulsions. The formation and stability of these systems may be influenced by the chain length compatibility which may also influence the flow through porous media behavior of these systems. Therefore, the present communication deals with the effect of chain length compatibility on the properties of monolayers, foams, macro- and microemulsions. An attempt is made to correlate the chain length compatibility effects with surface properties of mixed surfactants and their flow behavior in porous media in relation to enhanced oil recovery.

Experimental

Materials. Sodium dodecyl sulfate was supplied by Aldrich Chemical Company, Milwaukee, WI, and various alkyl alcohols were obtained from Supelco, Inc., Bellefonte, PA, with purity greater than 99%. For microemulsion preparation, sodium stearate (>> 99% pure) was supplied by Matheson, Coleman and Bell, Inc. and sodium myristate was supplied by K & K Laboratories, Inc. All the oils (>> 99% pure) were obtained from Chemical Samples Company. Double-distilled water was used in all experiments. For monolayer studies, the 4.0 mM solutions of all pure alkyl alcohols were prepared in a mixture of methanol, chloroform and n-hexane in a volume ratio 1:1:3.

The sand used as porous media was purchased from AGSCO Corp., Peterson, NJ. The transducer used for the measurements of pressure drop across the porous medium was supplied by (Validyne DP-15), Validyne Engineering Corporation, Northridge, CA. The recorder was obtained from (Heath/Schlumberger 225), Heath Company, Benton Harbor, MI. The water was pumped using Cheminert Metering Pump (Model EP-2), Laboratory Data Control, Riviera Beach, FL.

Methods. Using an Agla microsyringe, alkyl alcohol solution (0.025 ml) was spread on the subsolution of 0.01 M HCl. A time interval of 5 minutes was allowed for spreading solvents to evaporate or diffuse in the subsolution from the monolayers. The monolayer was compressed at a constant rate by an electrically operated motor. The surface pressure area curve for a monolayer was recorded automatically by x-y recorder. Three to five monolayers of each mixture were studied and the results reported are average values. The reproducibility of data was $\pm$ 0.15 $Å^2$/molecule. The detailed discussion of the apparatus is given elsewhere (17).

The macroemulsions were prepared by mixing an aqueous surfactant solution and oil in a volume ratio 3:1. Oil phase also contained an equimolar alkyl alcohol. The emulsions were produced by using an ultrasonic device (Model W185) for two minutes. The volumes of the emulsions were recorded at different time intervals. 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 adding more water slowly from a graduated 1 ml pipette to the microemulsion, until turbidity was observed and two-phase formation occurred upon standing. The surface tension of freshly prepared aqueous solutions was measured by Wilhelmy plate method (18) and surface viscosity was measured by a single knife-edge rotational viscometer (19).

For flow through porous media studies, the sandpacks used as porous media were flushed vertically with carbon dioxide for an hour to replace interstitial air. Distilled water was pumped and the pore volume (PV) of the porous medium was determined. By this procedure, the trapped gas bubbles in the porous media can be easily eliminated because carbon dioxide is soluble in water. For determining the absolute permeability of the porous medium, the water was pumped at various flow rates and the pressure drop across the sandpack as a function of flow rate was recorded. After the porous medium was characterized, the mixed surfactant solutions of known surface properties were injected. This was followed by air injection to determine the effect of chain length compatibility on fluid displacement efficiency, breakthrough time and air mobility in porous media.

Results and Discussion

Mixed Monolayers. Figure 1 shows the excess area/molecule when C_{18} alkyl alcohol was mixed with alkyl alcohols of various chain lengths. In this figure, A_{20} represents the molecular area at surface pressure of 20 dynes/cm, whereas A_c and A_e represent the area/molecule at zero surface pressure in the condensed and expanded states of the mixed monolayers. The excess area/molecule is the difference between the experimentally measured area/molecule in the mixed monolayers and that expected from the simple additivity rule (17). The comparison of the results of area/molecule in pure and mixed monolayers indicates that the mixed alkyl alcohols of different chain lengths form a

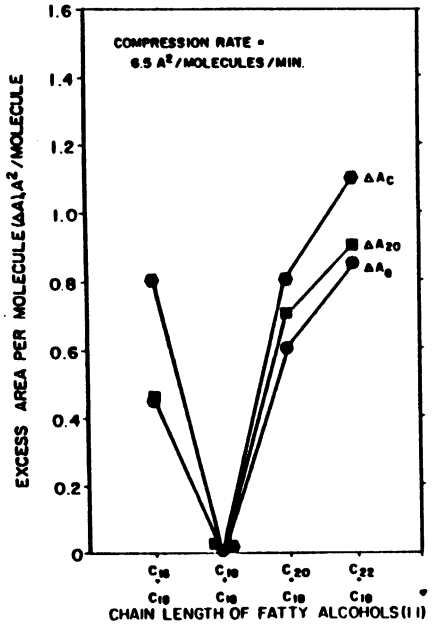

Figure 1. Excess Area per Molecule for Various Alkyl Alcohol Mixtures (1:1) with $C_{18}H_{37}OH$ as the Common Component at pH 2.0.

considerably expanded mixed monolayer. It is also evident that as the difference between the alkyl chain length of the components increased, the molecular area in the mixed monolayers also increased. Among excess area/molecule measured at different states of the monolayers, the excess area/molecule in the condensed state is most strikingly influenced by the differences in chain length. Similar results were also observed when the common components in the mixed monolayers were C_{16}, C_{20} and C_{22} alkyl alcohols (17).

It was reported by previous investigators (20-22) that a change of 0.3 to 1.5 Å in the intermolecular spacing between lipid molecules in the monolayer strikingly influences the rate of the enzymic hydrolysis and interaction of metal ions in the monolayers. By assuming a molecular area to be a circle, one can calculate the intermolecular spacing in the monolayers. The distance between the centers of adjacent molecules (2R) can be viewed as the intermolecular spacing in the monolayers. For example, at surface pressure of 20 dynes/cm, the excess area/molecule of 0.90 $Å^2$ was observed in the mixed monolayers. Moreover, the experimentally observed molecular area is 21.0 $Å^2$, whereas the average area per molecule according to simple additivity rule is 20.1 $Å^2$ at 20 dynes/cm in the mixed monolayers of C_{18} + C_{22} alkyl alcohols. The corresponding diameter for the circles (2R) or intermolecular spacing for these two areas are calculated to be 5.18 Å and 5.06 Å, respectively. The increase in the intermolecular spacing due to expansion of the monolayer would be 0.12 Å (5.18 - 5.06 = 0.12 Å). It is very likely that a change in the intermolecular spacing of the order of 0.12 Å may be of significant importance in determining the properties of mixed surfactant systems such as foams and macroemulsions.

Our explanation for these chain length compatibility effects is shown schematically in Figure 2. The equal chain length surfactant molecules form a condensed mixed monolayer as compared to the dissimilar chain length molecules. However, in mixed monolayers of different chain lengths, it is very likely that the portion of molecule above the height of the adjacent molecules exhibits thermal motion such as oscillational, vibrational and rotational modes. Moreover, if these thermal disturbances were limited to the portion above the height of the adjacent molecules, it would not expand the mixed monolayer and molecular area would remain the same. However, the thermal motion most probably propagates along the chain towards the polar group of the molecule which in turn causes expansion in the mixed monolayers and exhibits greater molecular area.

Figure 3 represents the effect of compression rate on excess area per molecule in mixed monolayers. As the rate of compression increases, the excess area per molecule in mixed monolayers increases. These results suggest that the disordered segments of alkyl chain may begin to orient themselves in a more ordered state with decreasing rate of compression, resulting in smaller excess area per molecule. Moreover, it is interesting to note that the rate of compression did not influence significantly the molecular area in the monolayers of pure components. Based on the

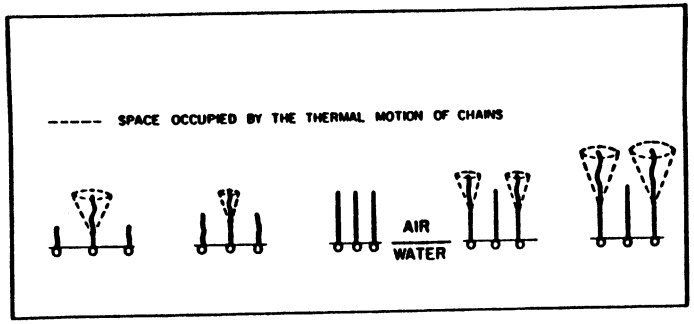

Figure 2. Schematic Diagram of the Chain Length Compatibility and the Thermal Motion of the Terminal Segments of Molecules.

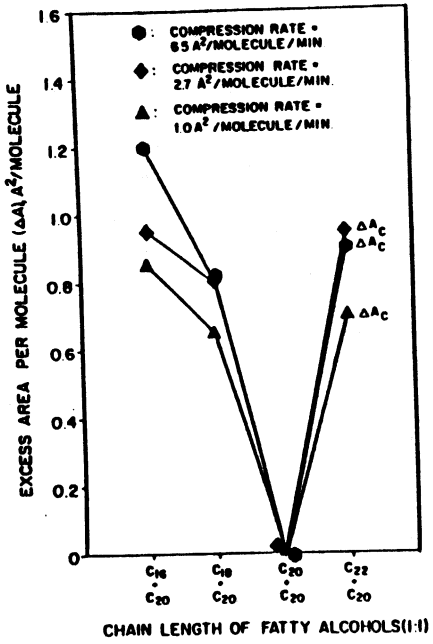

Figure 3. Effect of Compression Rate on the Excess Area/Molecule for Various Alkyl Alcohols with $C_{20}H_{41}OH$ Alcohol as a common Component at pH 2.0.

concept of chain length compatibility in monolayers, this study was further extended to investigate the surface chemical aspects of several colloidal systems such as foams, macro- and microemulsions.

Foams. In order to correlate the chain length compatibility with surface properties of foaming solutions and bubble size in foams, sodium lauryl sulfate ($C_{12}H_{25}SO_4Na$) and various alkyl alcohols ($C_8H_{17}OH$-$C_{16}H_{33}OH$) were used in a molar ratio 10:1 as mixed foaming agents. Figure 4 shows the photomicrographs of various foams containing sodium lauryl sulfate (5.0 m M) and different alkyl alcohols (0.5 m M) at 15 minutes after foams were produced. The mixed surfactants of equal alkyl chain length produced the smallest bubbles as compared to the mixed surfactants of unequal chain length (e.g. $C_{12}H_{25}SO_4Na + C_nH_{(2n+1)}OH$, where n = 8, 10, 14 and 16). It is evident that as the difference in chain length increases, the bubble size also increases.

Table I shows various surface and microscopic properties such as surface tension, surface viscosity, foaminess (i.e. foam volume generated in a given time) and bubble size in foams of the surfactant solutions as a function of chain length compatibility. The results indicate that a minimum in surface tension, a maximum in surface viscosity, a maximum in foaminess and a minimum in bubble size were observed when both the components of the mixed surfactant system have the same chain length. These results clearly show that the molecular packing at air-water interface influences surface properties of the surfactant solutions, which can influence microscopic characteristics of foams. The effect of chain length compatibility on microscopic and surface properties of surfactant solutions can be explained as reported in the previous section.

Macroemulsions. Figures 5 and 6 show the emulsion stability for various emulsions containing sodium alkyl sulfates (C_{12},C_{14}) and sodium alkyl soaps (C_{12},C_{14}) as the common hydrophilic emulsifiers, and various alkyl alcohols as the hydrophobic emulsifiers. The stability of various macroemulsions was measured by recording the volume of the unseparated emulsion in a given period of time. The volume of the emulsion was maximum when both mixed emulsifiers had the equal chain length (Figures 5 and 6). As the difference in alkyl chain length increases, the volume of the macroemulsion decreases. It clearly shows that the surfactant molecules with similar alkyl chain length pack tightly at liquid/liquid interface similar to that observed at gas/liquid interface. Moreover, the tight packing at the liquid/liquid interface seems to reduce the rate of water or oil separation from the macroemulsion phase. These results indicate that the gas/liquid (foams) and liquid/liquid (macroemulsions) systems behave in the same manner in the presence of mixed surfactants.

Table II shows the effect of chain length compatibility on oil recovery, fluid displacement efficiency, breakthrough time and effective gas mobility in porous media. For gas/liquid systems (e.g. foams), a maximum in fluid displacement efficiency, a

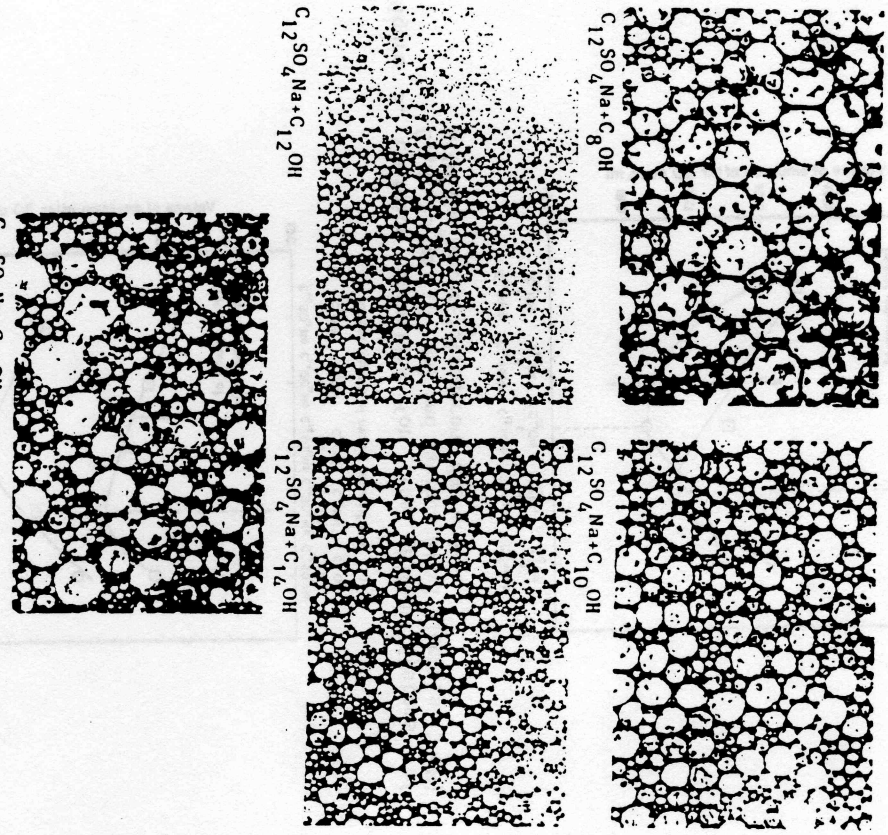

Figure 4. Photomicrographs of Various Foams Containing Sodium Lauryl Sulfate (5 mM) and Different Alkyl Alcohols (0.5 mM).

Table I. Effect of Chain Length Compatibility on Surface Properties of Mixed Surfactant Solutions

Systems / Surface Properties	$C_{12}H_{25}SO_4Na$ + $C_8H_{17}OH$	$C_{12}H_{25}SO_4Na$ + $C_{10}H_{21}OH$	$C_{12}H_{25}SO_4Na$ + $C_{12}H_{25}OH$	$C_{12}H_{25}SO_4Na$ + $C_{14}H_{29}OH$	$C_{12}H_{25}SO_4Na$ + $C_{16}H_{33}OH$
Surface Tension (dynes/cm)	25.8	24.3	22.9	25.6	30.3
Surface Viscosity (s.p.)	9.8×10^{-3}	14.5×10^{-3}	32.0×10^{-3}	26.2×10^{-3}	21.0×10^{-3}
Foam Volume in 1st Min. (ml)	284	310	480	298	260
Bubble Size Diameter (cm)	0.21	0.13	0.05	0.16	0.17

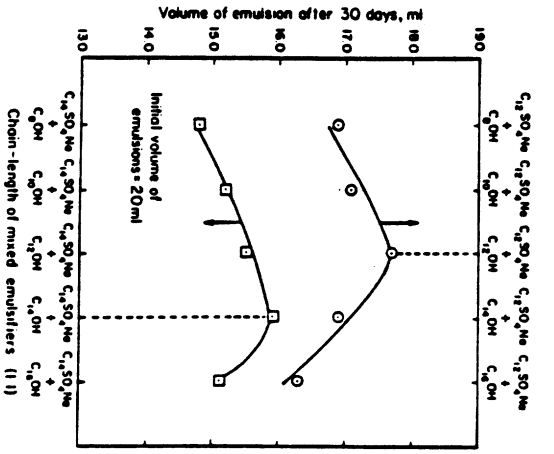

Figure 5. Emulsion Stability for the Mixed Systems of $C_{12}H_{25}SO_4Na$ (5 mM) and Various Alkyl Alcohols (5 mM) with the Water-Tetradecane Ratio 3:1.

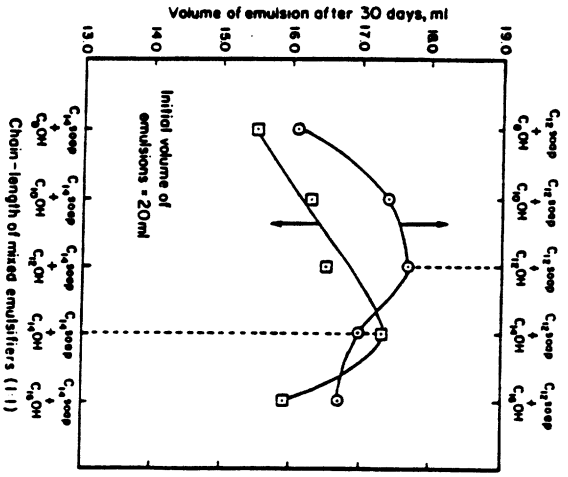

Figure 6. Emulsion Stability for the Mixed Systems of $C_{12}H_{25}SO_4Na$ (4.5 mM) and Various Alkyl Alcohols (4.5 mM) with the Water-Tetradecane Ratio 3:1.

Table II. Effect of Chain Length Compatibility on Flow Through Porous Media Behavior of Foams and Macroemulsion Systems

Systems / Measured Parameters	$C_{12}H_{25}SO_4Na$ + $C_8H_{17}OH$	$C_{12}H_{25}SO_4Na$ + $C_{10}H_{21}OH$	$C_{12}H_{25}SO_4Na$ + $C_{12}H_{25}OH$	$C_{12}H_{25}SO_4Na$ + $C_{14}H_{29}OH$	$C_{12}H_{25}SO_4Na$ + $C_{16}H_{33}OH$
Foams					
Fluid Displacement Efficiency, %	77.8	78.1	83.0	69.6	68.9
Breakthrough Time (min.)	25.1	41.3	46.8	30.6	27.2
Oil Recovery, %					
Air Foam	36.5	38.7	43.3	39.1	35.9
Steam Foam	49.8	51.5	55.0	49.5	47.6
Surfactant Flooding					
Oil Recovery, %	33.2	35.8	41.1	36.8	35.0

maximum in breakthrough time, a minimum in effective gas mobility and a maximum in oil recovery were observed when both the components of mixed surfactant system had the same chain length. Similar results were also observed by displacing oil with solutions of surfactants of equal chain length (Table II). These results can be utilized to design the surfactant formulations for optimum performance in enhanced oil recovery processes.

Microemulsions. The effect of chain length compatibility on microemulsion formation was studied by measuring the amount of water solubilized in the system. The amount of water solubilized as a function of oil chain length for sodium stearate system in the presence of various alcohols is shown in Figure 7. It was observed that for n-butanol containing microemulsions, the maximum amount of water solubilized decreased continuously with increase in oil chain length, whereas for n-heptanol it increased continuously. For n-pentanol and n-hexanol containing microemulsions, water solubilization reached a maximum value for tridecane and dodecane systems. Similar results were also observed for sodium myristate system (Figure 8). A maximum in water solubilization was observed when microemulsion contains n-hexanol and decane. From the observed findings, one can conclude that when the oil chain length is increased, the solubilization capacity of microemulsions can decrease, increase or exhibit a maximum, depending upon the structure and chain length of alcohol used. From the results of sodium stearate and sodium myristate systems, it is inferred that the water solubilization reached a maximum when alcohol chain length (l_a) plus that of the oil (l_o) is equal to that of the surfactant (l_s).

Our proposed explanation for the maximum water solubilization and chain length compatibility effect observed for pentanol and hexanol containing systems is schematically shown in Figure 9. The size of microemulsion droplets is expected to increase with increasing water content which in turn increases the interfacial area. Up to a certain extent, the alcohol from the oil phase can partition into the interface to stabilize the additional interfacial area. As the alcohol in the oil phase is depleted, further growth of water droplets would result in an increase of interfacial tension at the oil/water interface due to an increase in the area per molecule. This will destabilize the microemulsion as well as prevent further solubilization of water. It has been shown theoretically (23) that for microemulsion formation, the interfacial tension at the oil/water interface should be about 10^{-3} dynes/cm. When the chain length of oil plus alcohol is not equal to that of the surfactant ($l_a + l_o < l_s$), there will be a region of disordered hydrocarbon chains near the terminal methyl groups around the globules (Figure 9) due to thermal motion which produces a disruptive effect on the packing of surfactant molecules and increases area per molecule at the interface. It was suggested (17) that the thermal motion of alkyl chains which causes disruptive effect can increase the intermolecular distance between surfactant molecules by about 0.05 A. This change influences various properties of the systems such as evaporation of

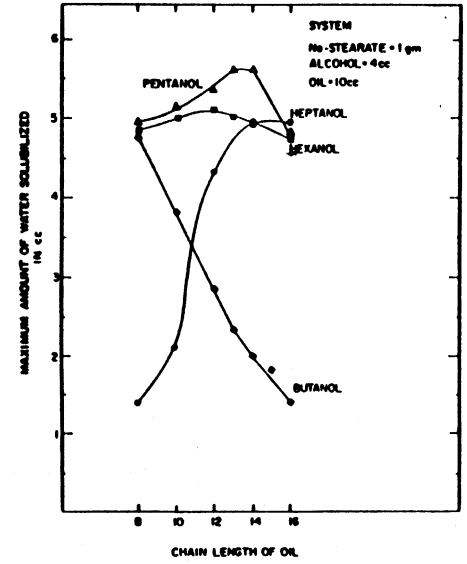

Figure 7. Effect of Alcohol and Oil Chain Length on Water Solubilization Capacity of Sodium Stearate Containing Microemulsions.

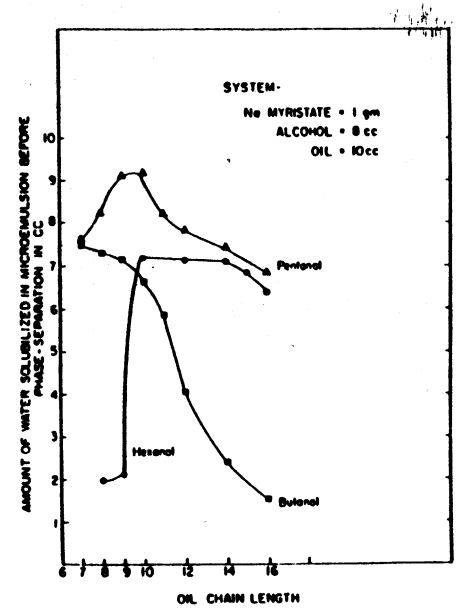

Figure 8. Effect of Alcohol and Oil Chain Length on Water Solubilization Capacity of Sodium Myristate Containing Microemulsions.

water through monolayers, contact angle, surface tension, boundary lubrication, surface viscosity, bubble size in foams and emulsion stability of mixed surfactant systems. Therefore, our proposed explanation based on chain lengths of oil, alcohol and surfactant, is that the maximum water solubilization in microemulsion occurred at $l_o + l_a = l_s$, which is due to the maximum cohesive interaction between hydrocarbon chains (or due to minimum disruptive effect in the interfacial region) under these conditions (Figure 9).

Further studies indicated that not only the molecular packing, but also the total amount of alcohol and surfactant at the interface influence the water solubilization capacity of the microemulsions (25). As the amount of alcohol and surfactant at the interface increases, the water solubilization capacity in microemulsions also increases. Figure 10 schematically illustrates the proposed explanation for the solubilization behavior of heptanol and butanol containing microemulsions. Previous study (24) on the surfactant partitioning in various oil/water systems indicates that the surfactant partitioning in oil phase decreases with increasing alkyl chain length of oil from n-hexane to n-hexadecane. Similar trend is also expected for n-heptanol. Since the solubility of n-heptanol in water is negligible, the decrease in n-heptanol partitioning in oil phase as the chain length of oil is increased from C_6 to C_{16} would result in an increase in the heptanol concentration at the interface (e.g. increase in the alcohol/soap molar ratio at the interface, Figure 10). This indeed was confirmed by the titration method (Figure 11) as described by Bowcott and Schulman (24). As the chain length of oil is increased, the intercept, which represents the molar ratio of alcohol to soap at the interface, increases.

For microemulsion systems containing butanol, the solubilization capacity decreased with increasing oil chain length (Figures 7 and 8). Our proposed explanation for this observation is schematically shown in Figure 10. As the oil chain length is increased, a decrease in butanol partitioning occurs in the oil phase. Since the total amount of butanol is constant in each system, a concomitant increase in the butanol concentration in the water phase and at the interface occurs. Unlike heptanol containing microemulsions, the water pool in butanol systems gradually becomes water plus butanol pool as the butanol has substantial solubility in water. Therefore, the water plus butanol pool as a solvent will solubilize some of the soap molecules in the pool and remove them gradually from the interface, which results in a decrease in the total interfacial area and hence the concomitant decrease in the capacity of water solubilization. This study suggests that the maximum water solubilization occurs when the soap and alcohol molecules remain predominantly adsorbed at the interface as well as when the chain length of oil plus alcohol equals to that of the surfactant.

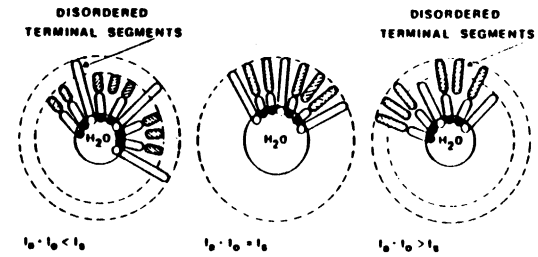

Figure 9. Schematic Diagram of the Disordering of the Terminal Segment of Alkyl Chain Protruding out of the Interfacial Film and the Solubilization Capacity of Microemulsions l_a, l_o and l_s are the Chain Lengths of Alcohol, Oil and Surfactant Molecules, respectively.

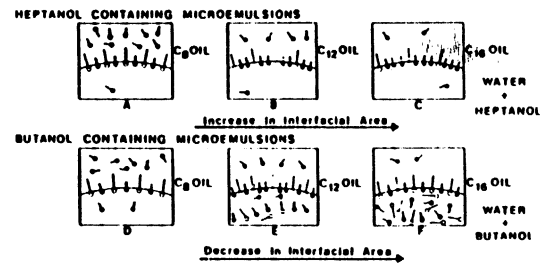

Figure 10. Schematic Illustration of the Effect of Increasing Oil Chain Length on the Partitioning of Alcohol in the Water, Oil and Interfacial Region.

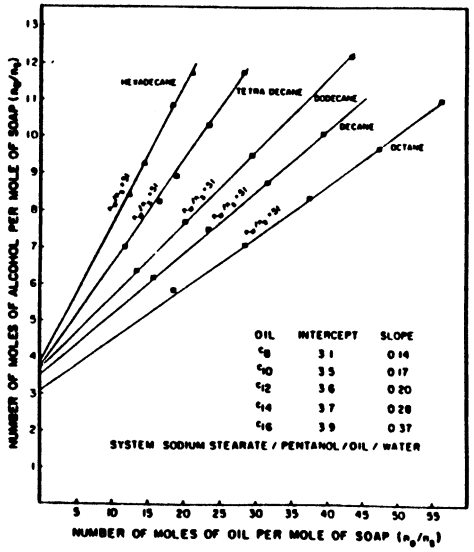

Figure 11. Effect of Oil Chain Length on the Oil/Alcohol Titration Plots for Microemulsions.

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