Interfacial Instability and Spontaneous Formation of Microemulsions

Microemulsions, which are optically transparent oil-water dispersions, were spontaneously produced upon mixing hexadecane, hexanol, potassium oleate, and water in specific proportions. The drop-volume measurements of hexadecane-water interface in the presence of hexanol or potassium oleate revealed that these surfactants decrease the interfacial tension of the hexadecane/water interface. It is proposed that the interaction between these two emulsifiers at the oil-water interface causes spontaneous negative interfacial tension resulting in interfacial instability and the formation of microemulsions.

As the amount of water is increased, the microemulsion exhibits a clear to turbid to clear transition. Unlike the clear regions, the turbid region possesses birefringence. The development of birefringence is also accompanied by a sharp decrease in electrical resistance. High-resolution (220 Mc) nuclear magnetic resonance data suggest that water exists in two distinct environments or structures in the birefringent region. The electrical, birefringence, and nuclear magnetic resonance data agree with the proposed mechanism of phase-inversion of microemulsions, which can be described as water spheres to water cylinders to water lamellae to a continuous water phase. The spontaneous formation of such structures (for example, water cylinders and lamellae) presumably depends upon the phase-volume ratio and the interfacial tension at the oil-water interface.

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SCOPE

Microemulsions which are optically transparent isotropic oil-water dispersions, can be formed spontaneously by using a combination of emulsifiers. Such oil-in-water or water-in-oil microemulsions consist of droplets 100-600 Å in diameter. The objectives of the present study were to elucidate the structure, the mechanism of formation and of phase-inversion process of microemulsions using electrical, birefringence, nuclear magnetic resonance, and the interfacial tension measurements.

Since microemulsions form spontaneously and exhibit low viscosity, they have been considered promising for secondary recovery from oil wells. Microemulsions can have applications in the areas such as microdispersions of drugs, cosmetics, paints and pigments, formulation of scintillation liquids, and reactions in which the rate is dependent upon the interfacial area since the microemulsions offer the maximal surface/volume ratio in oil-water systems. Microemulsions can be formed by adding an appropriate combination of an ionic and a nonionic surfactants at concentrations which generate a spontaneous interfacial instability in the oil-water mixture.

CONCLUSIONS AND SIGNIFICANCE

The following major conclusions were made from electrical, NMR, birefringence, and interfacial tension measurements.

1. Electrical resistance measurements can distinguish between the oil-continuous and the water-continuous microemulsions. Upon increasing the water to oil ratio, the oil-continuous microemulsion undergoes a series of structural changes as follows. Oil-continuous microemulsion → water cylinders in oil → lamellar structure of surfactants, oil and water → water-continuous microemulsion.

2. The formation of cylindrical and lamellar structures in the phase inversion region abruptly decreases the electrical resistance. The formation of these structures appears to depend upon the phase volume ratio of water and oil and also on the interfacial tension.

3. Drop-volume measurements of water in oil indicate that the combination of the surfactants, that is, hexanol and potassium oleate, strikingly decreases the interfacial tension of the oil-water interface, causing the interfacial instability and spontaneous formation of microemulsions.

PREVIOUS WORK

Microemulsions are optically transparent stable dispersions of oil and water, usually obtained by using a combination of surface-active agents (Schulman et al., 1959; Stoeckenius, 1960). Such oil-in-water or water-in-oil microemulsions have been examined by low angle x-ray measurements (Schulman-Riley, 1948), light scattering techniques (Schulman-Friend, 1949), ultracentrifugation (Bowcott-Schulman, 1955), electron microscopy (Stoeck-

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enius, 1960), and viscosity measurements (Cook-Schulman, 1965) and have been shown to consist of droplets 100-600 Å in diameter. In contrast to alcohol-water mixtures (for example, ethanol-water) which involve miscibility at the molecular level, microemulsions consist of discrete droplets of one liquid dispersed in the other. Although the interface of the microemulsion droplet should have a finite positive interfacial tension, it is generally believed that the process of spontaneous breakdown of the oil-water interface leading to the formation of microemulsion droplets involves negative interfacial tension (Prince, 1967). It should be emphasized that the formation of microemulsions is not the same process as that of solubilization within micelles. The ratio of the number of water or oil molecules to a surfactant molecule is much greater in microemulsions than that in micellar solubilization (McBain-Hutchinson, 1955).

In several oil-water emulsions, it is possible to convert water-in-oil type to oil-in-water type emulsions by increasing the water/oil ratio. However, the mechanism of this phase-inversion process is not well understood. Schulman (1940) proposed that the phase-inversion process involves mutual contact of emulsion droplets. However, Zlocchower and Schulman (1967) later showed that the phase-inversion region consists of a lamellar structure exhibiting birefringence and restricted mobility of hydrocarbon chains, as suggested by nuclear magnetic resonance (NMR) spectroscopy. The present paper reports the effect of hexanol and potassium oleate on the interfacial tension of hexadecane-water interface and proposes a mechanism of phase-inversion for microemulsions from the effect of phase-volume ratio on the electrical, optical, and NMR characteristics.

METHODS

Interfacial Tension Measurements

A thin platinum blade suspended from a surface tensiometer was used to measure interfacial tension of hexadecane-water interface. The effect of hexanol on interfacial tension was studied by adding it to hexadecane, whereas the effect of potassium oleate was investigated by dissolving it in water. The buoyancy correction for the blade was determined experimentally by measuring the interfacial tension of known oil-water systems (Davies-Rideal, 1963). The effect of hexanol and potassium oleate on the interfacial tension was determined also by measuring the average drop-volume of water in hexadecane using a microsyringe with an 18 gauge blunt tip needle.

For electrical, birefringence, and NMR measurements, microemulsions were produced by mixing the components in the following proportions: for 1 ml of hexadecane, 0.4 ml of hexanol, and 0.2 g of potassium oleate were added. Water was added in small amounts to this mixture, which was then shaken vigorously. Two polarizing plastic sheets were arranged perpendicularly to one another to detect birefringence. Two glass-sealed copper wires (0.16 cm thick) were used as electrodes. A 1 cm length at the end of each wire was exposed outside the glass tube, and the copper wires were separated by 0.8 cm. Platinum or tungsten electrodes were found unsatisfactory because of their poor wetting by oil. The electrical resistance of the mixture was measured by dipping the electrodes, connected to an A.C. conductivity bridge (Beckman model RC 16B2), into the microemulsions. Nuclear magnetic resonance spectra were obtained after the gradual addition of water to the microemulsion in the sample tube of the NMR spectrometer (Varian HA-220 megacycle). Tetramethylsilane was used as an internal standard. All chemicals were of high purity (> 99%), and the water was double-distilled.

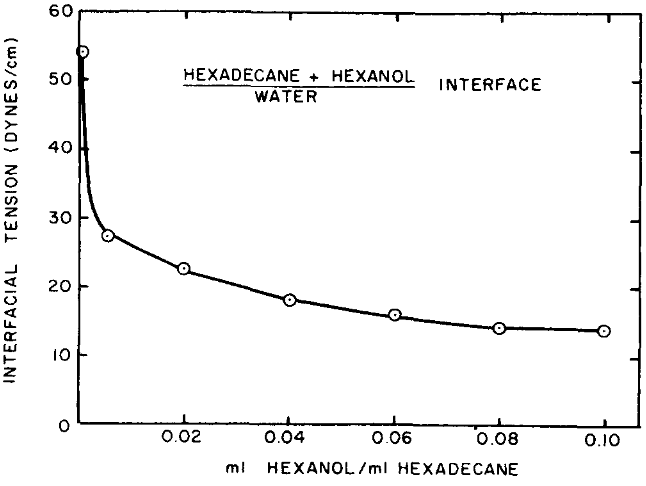

Fig. 1. The effect of hexanol on interfacial tension of hexadecane/water interface.

RESULTS

The interfacial tension of hexadecane/water interface decreased in the presence of hexanol in hexadecane (Figure 1). The most striking reduction in interfacial tension occurred on the addition of the initial amounts of hexanol. At high hexanol concentration the interfacial tension reached a limiting value of 14 dynes/cm. Figure 2 shows the interfacial tension of the hexadecane/water interface in the presence of potassium oleate. Here, also, the most striking reduction occurred on the addition of the initial amounts of potassium oleate. The interfacial tension remained constant at 9.5 dynes/cm with increasing amounts of potassium oleate in water. Attempts to measure interfacial tension of the hexadecane/water interface in the presence of hexanol and potassium oleate in hexadecane and water, respectively, were unsuccessful since a thick viscous layer developed at the interface.

Table 1 shows the effect of hexanol and potassium oleate on the average drop-volume of water in hexadecane. Potassium oleate, even at low concentrations, is more ef-

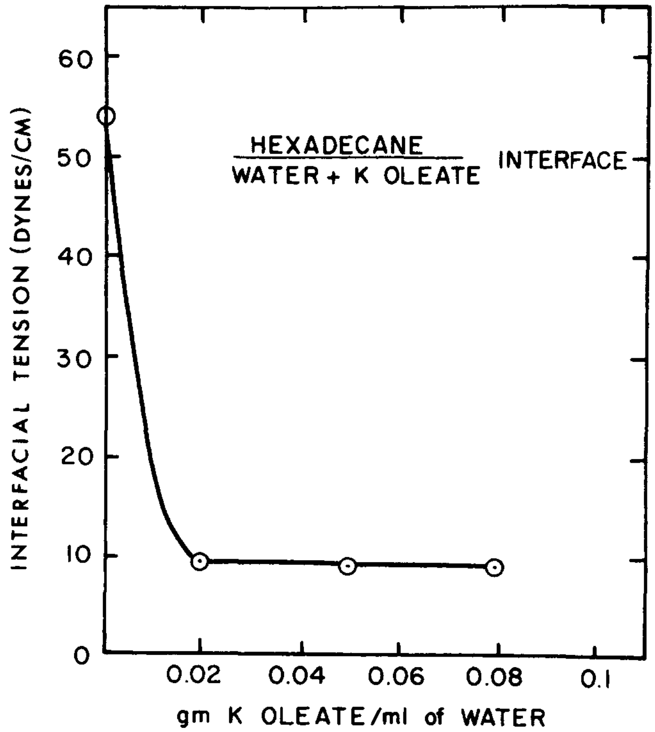

Fig. 2. The effect of potassium oleate on interfacial tension of hexadecane/water interface.

fective in decreasing the average drop-volume than hexanol. However, the presence of both hexanol and potassium oleate in hexadecane and water, respectively, decreases the drop-volume to less than 10^{-6} ml. At concentrations of hexanol higher than 0.075 ml per ml of hexadecane, the aqueous phase did not form a drop. Instead, it flowed continuously downward from the needle as a streak. It is evident from Table 1 that the average drop-volume decreases by a factor of 10^4 in the presence of hexanol and potassium oleate in hexadecane and water, respectively, that is, from 2.8×10^{-2} ml to less than 10^{-6} ml drop-volume.

Figure 3 shows the optical and birefringence characteristics, as well as the measured electrical resistances, as a function of the water/hexadecane ratio. Figure 4 shows the chemical shifts and band width at half-height of the major peaks in the NMR spectra of the microemulsions. As the amount of water increases, the microemulsion passes through a clear to turbid to clear transition. In contrast to the two clear regions, the turbid region exhibits birefringence. After clarity returns for the second time, the dispersion becomes opaque, milky, and nonbirefringent upon further addition of water. The variation of the electrical resistance as a function of water content follows a very unusual pattern (Figure 3). For ratios of water to oil from 0.2 to 0.6, there is no significant change in the resistance. However, in the birefringent region the electrical resistance falls sharply at water/oil ratios close to 0.7 and 1.0; subsequently, it increases and then decreases (Figure 3). The NMR data also indicate that in the birefringent region distinct changes occur in the chemical shifts and in the broadening of the resonance peaks of water and hydrocarbon protons. It is evident that the chemical shift of water protons is markedly influenced in contrast to that of methylene or methyl protons (Figure 4).

TABLE 1. EFFECT OF HEXANOL AND POTASSIUM OLEATE ON THE AVERAGE VOLUME OF WATER DROPS IN HEXADECANE
(Needle: 18 gauge)

Interfacial Composition Hexadecane (Oil)	Water	Average Drop-Volume
No additive	No additive	2.8×10^{-2} ml
Hexanol	No additive	
0.2 ml/ml of oil	No additive	6.0×10^{-3} ml
0.4 ml/ml of oil	No additive	5.0×10^{-3} ml
0.6 ml/ml of oil	No additive	5.0×10^{-3} ml
No additive	Potassium oleate	
No additive	0.02 gm/ml of water	8×10^{-4} ml
No additive	0.06 gm/ml of water	8×10^{-4} ml
No additive	0.1 gm/ml of water	4.4×10^{-4} ml
Hexanol	Potassium oleate	
0.025 ml/ml of oil	0.06 gm/ml of water	1×10^{-4} ml
0.05 ml/ml of oil	0.06 gm/ml of water	6.6×10^{-5} ml
0.075 ml/ml of oil	0.06 gm/ml of water	Volume $< 10^{-6}$ ml

RESISTANCE vs. WATER CONTENT FOR MICROEMULSIONS

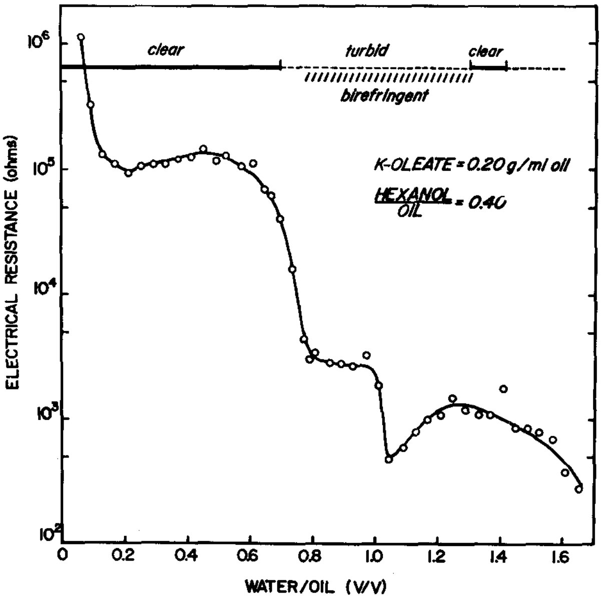

Fig. 3. Variation in electrical resistance, optical clarity, and birefringence of microemulsions as the water to hexadecane ratio increases. The microemulsion contains 0.20 g of potassium oleate/ml of hexadecane; the ratio of hexanol to hexadecane is 0.4 (by volume).

NMR DATA vs. WATER CONTENT FOR MICROEMULSIONS

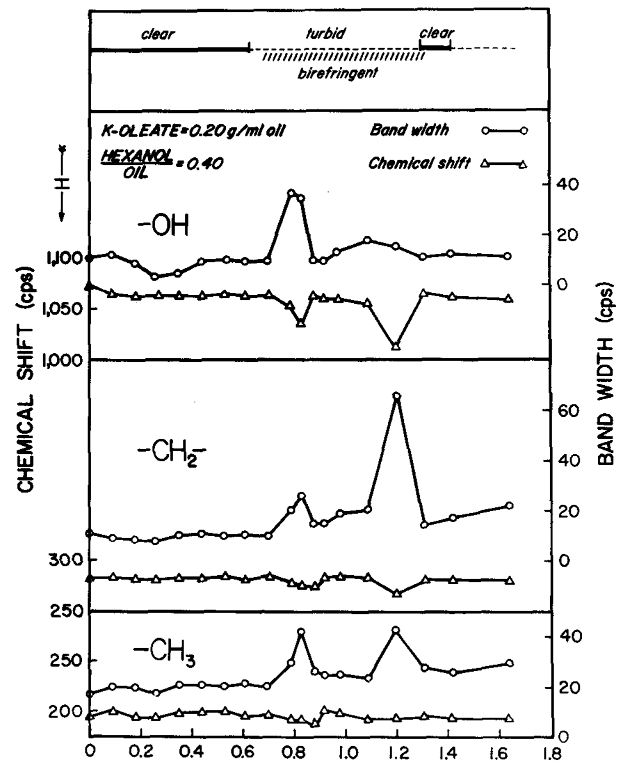

Fig. 4. Variation in the band width at half height and chemical shift of water and hexanol (—OH), methylene (—CH_2—), and methyl (—CH_3) protons in high resolution NMR (220-megacycle) spectra of the same microemulsions as that in Figure 3, as the water content increases. The upper part of the diagram shows corresponding data on optical clarity and birefringence.

Interfacial-tension and Average Drop-volume Measurements

It is evident from Figures 1 and 2 that both hexanol and potassium oleate strikingly decrease the interfacial tension at the hexadecane-water interface. Moreover, Table 1 also shows that the combination of hexanol and potassium oleate strikingly decreases the average drop-volume and, hence, the interfacial tension. For total miscibility of hexadecane and water, the interfacial tension has to be zero. Figure 5 schematically explains the factors influencing the interfacial tension and, hence, interfacial stability. The interfacial tension of hexadecane/water is 53 dynes/cm (Figure 1). The presence of potassium oleate at the interface reduces this interfacial tension to about 10 dynes/cm (Figure 2). Penetration of potassium oleate film at the interface by hexanol molecules results in an expansion of the film with a spreading pressure π (Figure 5). If the spreading pressure π of the penetrated film is greater than the interfacial tension γ_0 in the presence of potassium oleate film at the interface, the resulting interfacial tension γ_f will be less than 0 according to the equation

$$\gamma_f = \gamma_0 - \pi.$$

Since γ_0 is 10 dynes/cm (Figure 2), any value of spreading pressure π in excess of 10 dynes/cm as a result of penetration by hexanol molecules would cause a net negative interfacial tension and, hence, interfacial instability. The hexanol molecules in the interfacial film are in equilibrium with the hexanol molecules in the oil (since they have very poor solubility in water). The number of hexanol molecules in the interface can be altered by changing the amount of hexanol in the hexadecane phase. Therefore, for a given concentration of soap, a minimum amount of hexanol is needed to convert a macroemulsion into a microemulsion (Bowcott-Schulman, 1955). It is generally believed that the interfacial instability develops as a result of penetration of potassium oleate film at the interface by hexanol molecules. The resulting negative interfacial tension breaks down the interface until the curvature of the microemulsion droplet attains equilibrium with its surroundings. Another system, which emulsifies because of the negative interfacial tension, is that of solutions of long chain salts in contact with solutions of cetyl alcohol or cholesterol in oil (Schulman-Cockbain, 1955; Matalon, 1950; Davis-Haydon, 1957). With sodium decyl sulfate in water against cetyl alcohol in toluene, the emulsion can form spontaneously with concentration limits which are quite sharp for both long chain ions and alcohol. These concentration limits agree with those at which the interfacial tension is expected to become negative (Davis-Haydon, 1957). The evidence for the concept that microemulsions are true dispersions of one liquid into another, and not the cosolubilization of components, comes from the electrical measurements as discussed below.

The Structure and Mechanism of Phase Inversion of Microemulsions

As shown in Figure 3 the dispersions up to a water to oil ratio of 0.7 are optically clear and isotropic. These dispersions can be either microemulsions or simple mixtures resulting from cosolubilization of components. The constancy of electrical resistance (10^5 ohms) of dispersions between the ratios 0.1 to 0.7 of water to hexadecane supports the conclusion that this region consists of discrete droplets of water dispersed in a continuous oil phase. If this were the region of cosolubilization then electrical resistance would have decreased continuously with increasing amounts of water. The variation in electrical resistance can be explained as follows. The resistance drops from 10^6 to 10^5 ohms as the ratio of water to hexadecane approaches 0.1; this effect is presumably due to the molecular solubilization of water in the hexadecane-hexanol-potassium oleate mixture. This interpretation is supported by the observation that the hydroxylic protons of hexanol show an up-field shift from 1075 to 1065 cycles/sec with the initial addition of water (Figure 4). The occurrence of a single peak for hydroxylic and water protons suggests that there is a rapid rate of exchange between these protons. The constancy of resistance between the ratios 0.1 to 0.65 suggests that further addition of water results in the formation of microemulsions consisting of water spheres in the continuous oil medium, in which the interface between the oil and water is the main barrier controlling ion transport between the electrodes. It is expected that microemulsions having such water spheres would be optically isotropic.

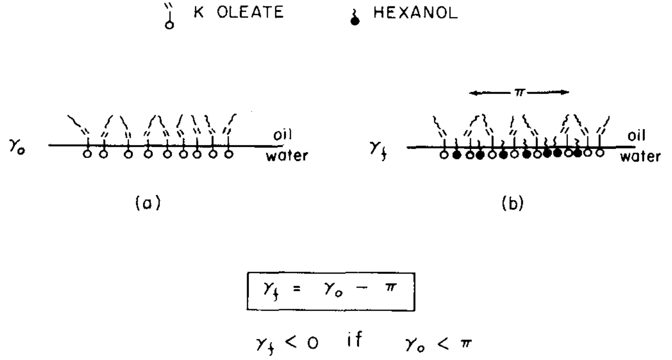

Fig. 5. A schematic presentation of the spontaneous development of negative interfacial tension as a result of penetration of interfacial film of potassium oleate by hexanol at the hexadecane/water interface.

With further addition of water, the isotropic clear region changes to a turbid and birefringent one, which subsequently becomes clear and isotropic. In the birefringent region the electrical resistance falls sharply at the ratios close to 0.7 and 1.0 and subsequently increases and then decreases (Figure 3). The NMR data also indicate that, in the birefringent region, distinct changes occur in the chemical shifts and in the broadening of the resonance peaks of water and hydrocarbon protons. We propose that the sharp drop in resistance and the development of birefringence are due to a transition in the structure of water from water spheres to water cylinders to water lamellae in the system. The NMR data, which indicate that water exists in two distinct molecular environments in the birefringent region, support this mechanism. In the first environment in the birefringent region, the chemical shift of water protons moves upfield by 25 cycles/sec, and in the second environment by 50 cycles/sec as compared to that of water spheres (Figure 4). However, the band width at half-height of water protons is considerably greater in the first as compared with the second environment. The band width is related to molecular mobility or motion. In general, the greater the band width, the smaller the molecular mobility. The measurements of the band width at half-height suggest that water molecules are less mobile in the first environment than in the second. In contrast to water protons, the band width of methyl protons suggests that hydrocarbon chains are less mobile in the second environment than in the first. These are the expected characteristics if the first environment consists of water cylinders dispersed in a continuous oil medium, and the second environment consists of water and oil lamellae. Water molecules would be less mobile in the cylinders because of the restriction imposed by the cylinder diameter than in the lamellae. Moreover, the formation of these structures would also decrease electrical resistance since the ions could migrate within water cylinders or lamellae without passing through the oil/water interface. The formation of these structures can also account for the development of birefringence. The ratios of water to oil characterizing the two distinct molecular environments on the basis of NMR data are slightly higher than those showing one abrupt decrease in electrical resistance. This effect is presumably due to the high spinning rate (6,500 rev./min) of the NMR sample tube which may provide enough mechanical energy to shift the transition of water spheres to water cylinders to a higher ratio of water to oil. The most interesting finding is the observation that the chemical shift of water, when it is distributed as spheres, is different from that of water distributed as cylinders or lamel-

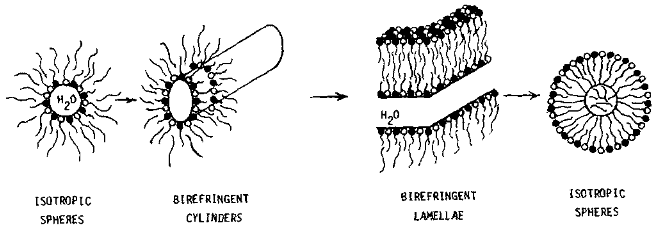

Fig. 6. A schematic presentation of the mechanism of phase-inversion of microemulsions based on electrical, optical, and NMR measurements. From left to right, water spheres in the continuous oil, water cylinders in the oil, lamellar structure of the surfactants *and water where the oil is solubilized within the surfactant bilayer,* and the water continuous microemulsions, where the oil droplets are stabilized by the surfactant film.

lae, indicating a distinct molecular environment of water in each of these structures. This is of considerable interest in relation to water in membranes and other biological systems.

The existence of such water cylinders of diameter 10 to 35 Å and lamellae 5 to 30 Å thick has been established in various lipid water systems (Luzzati-Husson, 1962; Mandell et al., 1967; Ekwall et al., 1968). Zlocchower and Schulman (1967) have shown that tight packing of hydrocarbon chains in the lamellar structure causes extreme broadening of the methylene peak in the NMR spectra.

From electrical and birefringence data we suggest that the two clear isotropic regions represent a water-in-oil and an oil-in-water type of microemulsion, respectively. It is expected that, as the amount of water increases, the lamellar structure will break down and the water will form a continuous phase containing micro-droplets of oil stabilized by potassium oleate and hexanol. The increase in electrical resistance above the ratio of water to hexadecane of 1.0 is due mainly to the disruption of the lamellar structures, and the subsequent decrease above a ratio of 1.3 can be attributed to the formation of a continuous water phase (clear isotropic region). Therefore, the transition from water spheres to water cylinders to water lamellae to a continuous water phase represents the mechanism of phase-inversion in microemulsions (Figure 6). However, it should be emphasized that the formation of such structures depends upon the concentration of emulsifiers, which, in turn, determines the area available for surface active molecules at the oil/water interface (Shah). Phase inversion may result in a macro- or micro-system, and the birefringent region may be transparent or turbid, with the degree of turbidity dependent upon the chemical constitution of the system. It should be mentioned that the viscosity of the microemulsions changes abruptly when water cylinders and lamellae are formed, and that the birefringent region is viscoelastic (Falco et al). The formation of such structures by simply changing the ratio of water to hexadecane also accounts for the formation of the thick, very viscous region at the interface of hexadecane-water containing hexanol and potassium oleate during interfacial tension measurements. Here, the diffusion of water into hexadecane phase and vice versa would cause a gradient in the water to oil ratio across the interface and, hence, lead to the formation of cylinders and lamellae at the interface.

It should be mentioned that the soaps of fatty acids and long chain alcohols are known to form complexes in the molecular ratios of 1:2 and 1:3 (Shah, 1969, 1970, 1971) which strikingly alters the packing of molecules both at the air-water and oil-water interfaces. This, in turn, influences the characteristics of mixed monolayers, foams, micro- and macroemulsions. The transition from lipid spheres to lipid cylinders to lipid lamellae is known for soaps (McBain-Lee, 1943). However, in this report we describe such transitions for water. The chemical shift of water, when it forms the continuous phase, is the same as that of water when it is dispersed in spherical form (Figure 4). This result implies that the molecular environment of water in spherical droplets in a microemulsion is the same as that of normal water, and that the polar groups of surface active molecules do not significantly alter the molecular environment. Since Gratin and Robertson (1965) and Frank and Zografi (1968) have reported that the chemical shift of solubilized water is different from that of emulsified water, it is likely that water in microemulsions represents only one type of water. Using NMR and infrared spectroscopic measurements, Gillbert et al. (1970) have investigated the conditions determining the stability of microemulsions. We have considered other possible phases of lipid-water systems, but the proposed structures are the only ones that are supported by electrical, birefringence, and NMR data. In summary, the present paper reports the mechanism of formation of microemulsions as a result of interfacial instability and the mechanism of phase-inversion of microemulsions by changing water/oil ratio.

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