

# Effect of Phase-Volume Ratio and Phase-Inversion on Viscosity of Microemulsions and Liquid Crystals

Microemulsions, which are optically transparent oil-water dispersions, were spontaneously produced upon mixing hexadecane, hexanol, potassium oleate, and water in specific proportions. The viscosity of the microemulsions was measured for several water/oil ratios including the phase-inversion region. The striking optical and viscosity changes observed at specific water/oil ratios were in agreement with the proposed mechanism of phase-inversion, namely, water spheres  $\rightarrow$  water cylinders  $\rightarrow$  water lammellae  $\rightarrow$  continuous water phase, for this system. In the phase-inversion region, the dispersion exhibited birefringence and rheopectic properties. An extremely high viscosity ( $> 100,000$  cps) exhibited by the dispersions between water/oil ratios of 2.0 and 3.5 were explained in terms of ion-dipole association between oleate and hexanol molecules on adjacent droplets.

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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 effect of oil/water ratio and phase-inversion phenomenon on the viscosity of these dispersions and to correlate the changes in viscosity with the structural changes in the dispersions.

Since microemulsions form spontaneously and exhibit

low viscosity, they have been considered promising for secondary and tertiary recovery in oil-fields (Gogarty and Tosch, 1968; Hill et al., 1973; Pursley et al., 1973). The phase-inversion region exhibits birefringence indicating structural anisotropy of the system. Previous studies from this laboratory have established that the phase-inversion region consists of liquid-crystalline structures. The rheological properties of microemulsions and liquid-crystalline systems are of considerable interest to investigators in the areas such as microdispersions of drugs, cosmetics, paints, and reactions in which the rate is dependent upon the interfacial area since the microemulsions and liquid-crystalline systems offer the maximal surface/volume ratio in oil-water-surfactant systems.

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## CONCLUSIONS AND SIGNIFICANCE

The following major conclusions were made from viscosity measurements of microemulsions and liquid-crystalline structures (cylindrical and lamellar), prepared by mixing hexadecane, water, hexanol, and potassium oleate in specific proportions.

1. For the water-in-oil microemulsions, that is, water spheres in a continuous oil medium, the relative viscosity ( $\eta_r$ ) followed the expression

$$\eta_r = [1 - 1.35(C - C_0)]^{-2.5}$$

where  $C$  is the volume fraction of the total amount of water and  $C_0$  is that of solubilized water. Any change from the spherical shape caused significant deviation from this expression.

2. Both water-in-oil and oil-in-water microemulsions exhibited low viscosities, whereas the phase-inversion region showed a striking increase in viscosity ( $\approx 46,000$

cps). The changes in viscosity were reproducible and were observed both upon increasing or decreasing water to oil ratios.

3. The optical and birefringence changes observed at specific water/oil ratios were also accompanied by changes in viscosity, which were in agreement with the proposed mechanism of phase inversion, namely, water spheres  $\rightarrow$  water cylinders  $\rightarrow$  water lamellae  $\rightarrow$  continuous water phase for this system.

4. The viscosity in the lamellar liquid-crystalline region increased initially and then leveled off with an increase in shearing time, presumably due to disordering and entanglement of the lamellar structures.

5. Between water to oil ratios of 2.0 and 3.5, the dispersion exhibited extremely high viscosity ( $> 100,000$  cps), which may have been due to ion-dipole association between oleate and hexanol molecules on adjacent droplets.

The structural properties of mixtures containing oil, water, and surface-active agents are important in relation to various biological and industrial applications. In a recent study Shah et al. (1972) have shown, using electrical, birefringence, and high resolution NMR measurements, that upon increasing the amount of water in a microemulsion (of a specific composition), it exhibits a transition from water spheres to water cylinders to water lamellae to a continuous water phase (Fig. 1). These structural changes are due to the alteration in interfacial forces which take place when the ratio of oil to water is varied. Once the water-in-oil microemulsion is formed, addition of water causes an increase in the size and number of dispersed water droplets. Since the total amount of surface-active agent is constant in the dispersion, further addition of water increases the interfacial area, decreases the surface concentration of the surfactant, and hence increases the interfacial tension. At some concentration of water, a critical point is reached at which the intermolecular forces at the oil-water interface will be insufficient to hold the interface together. The result is the collapse of the spherical droplets into cylinders of water and a concomitant decrease in the total interfacial area. It is likely that a large number of spherical water droplets coalesce to form a water cylinder. This same process is repeated during the shift from a cylindrical structure to a lamellar structure upon further addition of water, and again this lamellar structure gives way to a structure of spherical oil droplets dispersed in a continuous water phase upon yet further addition of water.

From X-ray diffraction studies, the water spheres in microemulsions have been shown to be 100 to 500 Å in diameter (Schulman et al., 1948) whereas the water cylinders and lamellae have been found to be respectively 10 to 35 Å in diameter and 5 to 30 Å in thickness in many surfactant-water systems (Ekwall et al., 1968).

The present paper reports the effect of these interfacial forces and consequent structural changes (shown in Fig. 1) on the bulk rheological properties of oil-water dispersions. Since microemulsions are considered to be monodispersed systems (Cooke and Schulman, 1965), we have used a comparison between experimentally observed relative viscosity and theoretical relative viscosity proposed by Roscoe (1952) and Brinkman (1952) for the dispersion of identical spheres in a liquid to determine the phase volume ratio beyond which spherical droplets do not exist. In the present paper, we have also investigated

the time and shear-dependent properties of these systems since the formation of cylindrical and lamellar structures in the phase-inversion region involves considerable rearrangement of molecules.

## EXPERIMENTAL METHODS

Microemulsions were prepared in two ways. In the first method hexadecane (oil), hexanol, and potassium oleate (that is, oleic acid and equivalent amount of KOH) were mixed in a large beaker in the following proportions: for 1 ml hexadecane, 0.4 ml hexanol, and 0.2 g potassium oleate. Distilled water was added in small amounts to the mixture which was stirred vigorously after each addition to insure homogeneity. In the second method, a mixture of hexadecane, hexanol, and potassium oleate was prepared as before. Then, this solution was added in small amounts to distilled water. Hence, the soap to hexanol ratio was kept constant and only the water to oil ratio was varied in both cases. It should be emphasized that if KOH was present in a small excess of oleic acid, the microemulsions did not form.

In the first series of experiments, viscosity and optical properties were measured after each addition of water or oil. In the second series of experiments, four solutions with water to oil volume ratio of 1.4 were prepared by the first method. These solutions were allowed to stand for 0, 8, 16, and 32 hours before making viscosity measurements. All viscosity measurements were made with a Model LVF Brookfield viscometer. For viscosities up to  $10^2$  centipoises, a #1 spindle was used with shear rates of 6.29, 12.58, 31.46, and 62.91  $\text{sec}^{-1}$ . For viscosities between  $10^2$  and  $10^5$  centipoises, a #4 spindle was used. The shear rate for all non-Newtonian fluid (lamellar and cylindrical liquid-crystalline phases) was 1.69  $\text{sec}^{-1}$ . Upon increasing the shearing-time, the final constant value of viscosity was recorded as the steady-state viscosity. The vis-

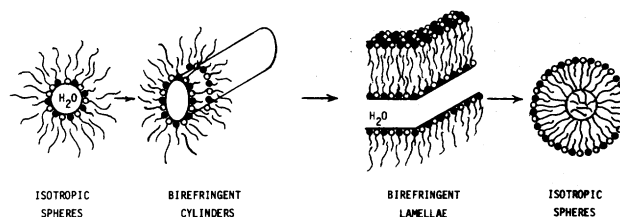
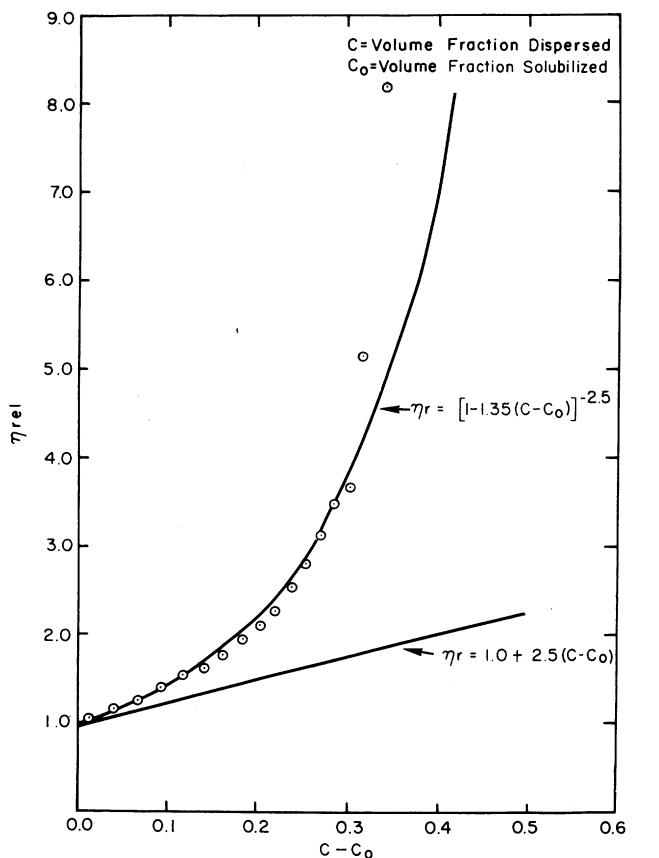


Fig. 1. A schematic presentation of the phase inversion of a microemulsion upon addition of water: From left to right, water spheres in oil, water cylinders in oil, oil/water lamellar structure, and oil spheres in water.



EFFECT OF PHASE VOLUME RATIO ON RELATIVE VISCOSITY

Fig. 2. The effect of volume fraction of emulsified water on relative viscosity ( $\eta_r$ ) of the microemulsions. Straight line indicates the Einstein relation for relative viscosity and the volume fraction of dispersed spheres. Circles represent the experimental values of relative viscosity, and the curved line shows the relation  $\eta_r = [1 - 1.35(C - C_0)]^{-2.5}$ , where  $C$  is the volume fraction of total water added, and  $C_0$  is the volume fraction of molecularly dispersed water.

cosities reported in the first series of experiments (Figures 2 to 4) are the steady state values. The clarity and birefringence of the dispersions were noted after each addition of water to oil or oil to water. The samples were placed between two polarizing plastic sheets to detect birefringence.

## RESULTS

The viscosity was independent of shear rate in the initial isotropic clear region (water/oil ratio 0.0 to 0.7) whereas the phase-inversion region exhibited time and shear-dependent viscosity. Figure 2 is a plot of relative viscosity and volume fraction of water dispersed in the form of microemulsions. The relative viscosity was calculated by dividing the viscosity of microemulsions by that of hexadecane containing hexanol and potassium oleate. The term  $C - C_0$  in Figures 2 and 3 represents the volume fraction of water dispersed in the form of microemulsion, where  $C$  is the volume fraction of total amount of water added and  $C_0$  is the volume fraction of molecularly solubilized water. Water added initially dissolves by the process of molecular solubilization, that is, in the form of water of hydration around potassium ions and carboxyl groups. For the best fit of experimental data to a theoretical curve, the value of  $C_0$  was found to be 0.028. It is evident from Figure 2 that the experimental values of the relative viscosity for mixtures having a volume fraction of dispersed water above 0.3 are much higher than those expected from theory. At very low values of volume fraction of dispersed water, the relative viscosity values are close to those predicted from

Einstein's equation  $\eta_r = 1 + 2.5 C$ . The volume fraction 0.3 of dispersed water corresponds to a water to hexadecane ratio of 0.75, suggesting that the microemulsions exist only up to this point; beyond this ratio there is a transition from spherical to cylindrical structure of water (Figure 1).

Figure 3 shows the viscosity of these dispersions plotted against the ratio of water to hexadecane. It is evident that the water-in-oil microemulsions exhibit low viscosity (< 80 cps); however, above a water to hexadecane ratio of 0.8, there is an abrupt increase in the viscosity which begins to increase very rapidly above the ratio of 1.0.

Figure 4 shows the effect of water to hexadecane ratio

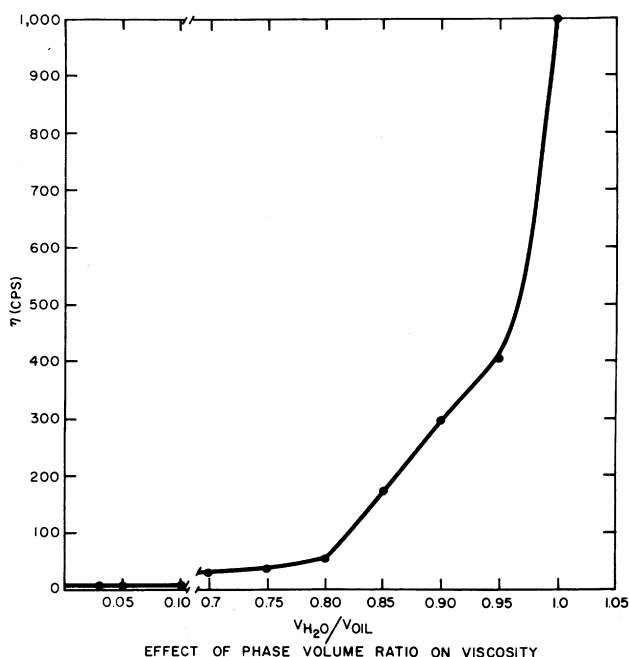


Fig. 3. Changes in the viscosity of microemulsions due to the formation of cylindrical and lamellar structures upon increasing the water/hexadecane ratio above 0.8.

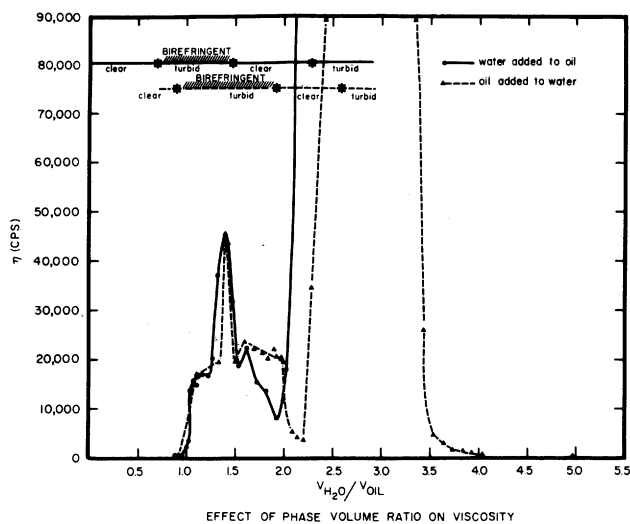


Fig. 4. Changes in the viscosity of microemulsions and liquid crystals (cylindrical and lamellar structures) upon increasing the water/hexadecane ratio. Solid line represents the viscosity changes when water was added to hexadecane containing potassium oleate and hexanol; broken line represents the changes when hexadecane containing potassium oleate and hexanol was added to water.

on the viscosity of these dispersions. The maximum in the viscosity at a ratio of 1.4 corresponds to the lamellar structures occurring at this ratio (Figure 1). However, the viscosity peak between the ratios 2.0 and 3.5 was beyond the measuring limit of our instrument ( $> 90,000$  cps), and this larger value was quite unexpected. Both these viscosity peaks were observed upon increasing or decreasing the water to hexadecane ratio. The viscosity maximum at the 1.4 ratio occurred in the birefringent region, whereas the other occurred in the turbid region.

Figure 5 shows the viscosity of four samples having lamellar structures, at a water to hexadecane ratio of 1.4, which were left standing for 0, 8, 16, and 32 hours after their formation. Each sample showed an increase in viscosity with shearing time (0 to 25 min.). It is evident that the viscosity increased initially with shearing time and then leveled off to a steady state value. It was observed that the longer the time after the formation of these structures, the smaller was the steady state value of the viscosity. It should be mentioned that the lamellar liquid-crystalline system at the water/oil ratio of 1.4 exhibits low viscosity when placed on a shelf for a few days. However, upon vigorous shaking, the dispersion immediately becomes gel and does not flow.

## DISCUSSION

It has been shown by Einstein (1911) that at extreme dilution, the relative viscosity ( $\eta_r$ ) for a suspension of spheres in a liquid should be given by the relation

$$\eta_r = 1 + 2.5C \quad (1)$$

However, Ward and Whitmore (1950) have found that, while the relative viscosity is independent of the viscosity of the suspending liquid and the absolute size of the spheres at a given concentration, it is a function of the size distribution. For the relative viscosity ( $\eta_r$ ) of a suspension containing a high concentration of uniform spheres, Roscoe (1952) and Brinkman (1952) have given the following expression

$$\eta_r = (1 - 1.35C)^{-2.5} \quad (2)$$

where  $C$  is the volume fraction of spheres (dispersed

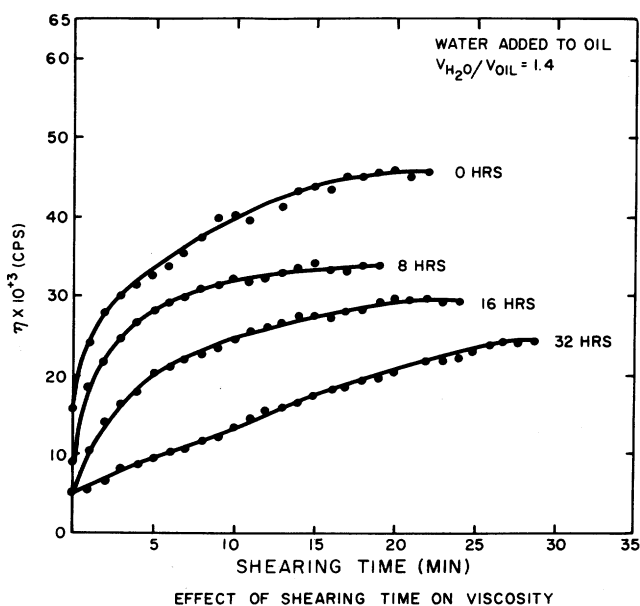


Fig. 5. The effect of shearing time on the viscosity of the lamellar liquid crystalline structures at 0, 8, 16, and 32 hours after their formation. Each curve represents a different sample.

phase). However, Matsumoto and Sherman (1969) subtracted the term  $C_0$  from  $C$ , where  $C_0$  is the volume fraction of the dispersed phase which is molecularly solubilized by the excess surfactant molecules and  $C$  is total volume fraction of the dispersed phase. Therefore,  $C - C_0$  is the volume fraction of water present in the form of microemulsion. Hence, for the best fit of experimental data to the theoretical equation

$$\eta_r = [1 - 1.35(C - C_0)]^{-2.5} \quad (3)$$

the volume fraction of solubilized water ( $C_0$ ) was found to be 0.028. This value yields a molecular ratio of 2.5 between water and potassium oleate. Since Ekwall and Mandell (1968) have shown that the minimum molar ratio of water to soap for formation of reversed micelles in oil is between 2.0 and 3.0, our value of  $C_0$  seems reasonable. Figure 2 shows a comparison between theoretical and experimentally measured relative viscosities as a function of the volume fraction of water emulsified in the microemulsion. As might be expected, both theoretical and experimental relative viscosities obey Einstein's equation for dilute dispersions. It should be noted that, in the region in which the microemulsion gives way to a cylindrical structure ( $C - C_0 = 0.3$ ), the experimental relative viscosity deviated significantly from the viscosity predicted by Equation (3). Before the dispersion became birefringent, the maximum number of water molecules per molecule of soap in the isotropic region was 62. The soap to hexanol ratio for this mixture was 1:5. The fact that a far greater number of molecules of water per molecule of soap were present than could be accounted for by solubilization or hydration strongly indicated that the mixture was a true microemulsion rather than a molecular solubilization.

The observation that the viscosity was independent of the shear rate in the initial isotropic clear region (water to oil ratio of 0.0 to 0.7) suggested that the microemulsions were Newtonian dispersions. When the microemulsion undergoes a transition from water spheres to water cylinders to water lamellae to a continuous water phase, the viscosity changes abruptly (Figures 3 and 4). The change in viscosity observed at the ratio 0.8 corresponded to the formation of water cylinders, and the viscosity peak observed at the ratio 1.4 corresponded to the formation of lamellae structures. The minimum in viscosity at the ratio 2.0 is that of isotropic, clear, water continuous microemulsion. The occurrence of the lamellar structure at a higher water to oil ratio (1.4), as indicated by the viscosity measurements, compared to that obtained by NMR technique (Shah et al, 1972) (ratio 1.2) can be explained as follows. Since there is an inherent breakdown of the lamellar structure due to shearing, a higher water-to-oil ratio is required for the formation and stabilization of the lamellar structure. It was observed that the dispersions having lamellar structure at the ratio 1.4 were very viscous upon their formation. However, they exhibited a decrease in viscosity with time. In order to understand the mechanism of the decrease in viscosity, four dispersions of identical chemical composition consisting of the lamellar structure at the ratio 1.4 were prepared and left unstirred for 0, 8, 16, and 32 hours after their formation. As shown in Figure 5 each sample exhibited an increase in viscosity with the shearing time. The viscosity increased initially with shearing time and then leveled off to a steady state value. Both the initial and final (steady state) values of viscosity decreased with increase in the time after the formation of these structures. The initial increase in the viscosity with shearing time can be attributed to disordering and entanglement of the lamellar structures upon shearing (Figure 6). A similar explanation has been of-

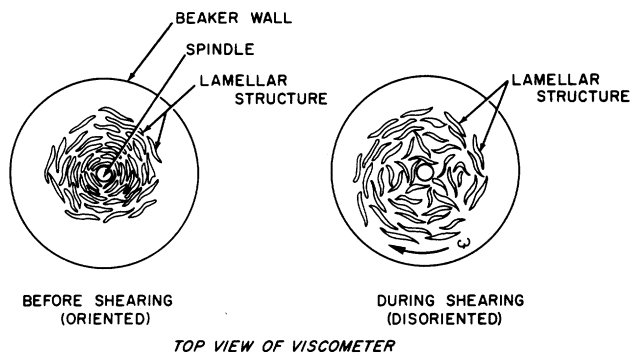


Fig. 6. A schematic representation of the effect of shearing on the orientation of lamellar liquid crystalline structures. Disorientation and mutual entanglement results in higher viscosity than that of the initially well oriented structures.

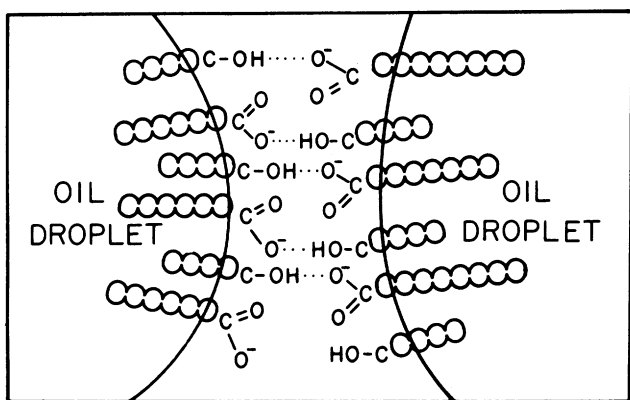


Fig. 7. A schematic representation of the ion-dipole association between carboxyl and hydroxyl groups from adjacent droplets causing an abrupt increase in viscosity between water/hexadecane ratio of 2.0 to 3.5 shown in Figure 4.

ferred to account for the initial increase in the viscosity of polymer solutions (Peterlin, 1968; Bianchi and Peterlin, 1969).

An unexpected increase in the viscosity also was observed between the ratios of 2.0 and 3.5 (Figure 4). The shift in viscosity observed around the ratio 2.0 upon the addition of oil to water compared to water to oil is presumably due to molecular relaxation processes in this extremely viscous oil-water dispersion. A similar shift in the appearance of birefringence agrees with this explanation. The viscosity peak occurring between the ratios 2.0 and 3.5 cannot be due to either cylindrical or lamellar structures because it occurs in the nonbirefringent and turbid region. Since the high viscosity region occurs upon addition of water to the oil-in-water microemulsion at a ratio of 2.0, the increase in ionization of soap molecules upon increasing the water content, may cause interdroplet cross-linking by ion-dipole association between the hydroxyl groups of hexanol and the ionized carboxyl groups of oleate from the adjacent droplets, resulting in a gel-like high viscosity structure (Figure 7). We have also observed that the addition of salts such as NaCl, KCl, strikingly decreases the viscosity of the dispersions in this region (water/oil ratio 2.0 to 3.5), which also supports the above interpretation. Such ion-dipole association between fatty acids and alcohols is known to influence the average molecular area in the mixed monolayers, foam stability, rate of evaporation through mixed monolayers, interfacial tension, and emulsion characteristics (Shah and Dysieski, 1969; Shah, 1970; Shah, 1971).

In summary, the results indicate that the microemulsions reported here are low viscosity dispersions, whereas the phase-inversion region exhibits very high viscosity and rheopexy. The microemulsions are optically isotropic whereas phase-inversion region is anisotropic consisting of liquid-crystalline structures. The ion-dipole association between surfactant molecules on the adjacent droplets can increase strikingly the viscosity of the oil-water dispersions.

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