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Some Structural Aspects of Microemulsions and Co-Solubilized Systems

By

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ABSTRACT

Microemulsions are optically clear, transparent, and stable dispersions of oil, water, surfactant and cosurfactant mixed in specific proportions. Stability and transparency have been used as sufficient criteria for defining microemulsions by several investigators. Using a combination of physical techniques such as electrical resistance, high resolution NMR (220 Mc), spin-lattice relaxation time, and viscosity measurements we have shown that two isotropic clear systems with identical compositions except one containing n-pentanol and the other n-hexanol, are structurally quite dissimilar systems. The isotropic clear system containing pentanol was proposed to be a cosolubilized system (i.e. similar to molecular solution) whereas the hexanol containing system to be a microemulsion. The results suggested that a difference of one carbon atom in the cosurfactant molecule can significantly influence the microstructure as well as the macroscopic properties (e.g. viscosity) of such systems.

Upon increasing the water to oil ratio, these systems undergo a phase transition, namely from an isotropic to a birefringent state. The birefringent liquid crystalline region exhibited unusual rheological properties. Using X-ray scattering and freeze-etching electron microscopy, it was shown that these systems consisted of the lamellar structure and that upon shearing the parallel orientation of the lamellae was transformed into a disordered state. This disordering of the lamellae presumably increases the viscosity of the system.

INTRODUCTION

Microemulsions are optically isotropic, clear, and stable dispersions of oil, water, surfactant and cosurfactant (1,2). Such oil-in-water or water-in-oil microemulsions have been examined by low-angle X-ray measurements (3), light-scattering techniques (4), ultracentrifugation (5), electron microscopy (2), high resolution NMR spectroscopy (6,7) and viscosity (8,9) and have been shown to consist of droplets 100 to 1000 Å in diameter. We have shown previously (10) that upon increasing the water to oil ratio, one can convert a water-in-oil microemulsion to an oil-in-water type. The microemulsions appear transparent because the droplet size is

References and illustrations at end of paper.

smaller than one quarter wave-length of light. Several investigators have considered the transparency and stability as sufficient criteria to define microemulsions. However, in the present study we would like to decribe two stable, isotropic clear systems made with the same oil, water and surfactant but containing n-pentanol or n-hexanol as the cosurfactant and to establish that these two systems have strikingly different microstructure. Therefore, one cannot use transparency and stability as sufficient criteria for defining microemulsions.

We have shown (10) previously that 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 the electrical resistance. Using electrical, birefringence, and nuclear magnetic resonance data we have proposed (10) a mechanism of phase inversion of the microemulsions reported in this paper, which can be described as water spheres in oil → water cylinders in oil → water-oil lamellae → oil spheres in continuous water phase. The birefringent structures exhibit unusual rheological (rheopectic) properties. The present paper reports our results on the structure of the birefringent region as well as the mechanism of rheological changes exhibited by these systems, obtained from X-ray scattering and freeze-etching electron microscopy.

EXPERIMENTAL

Microemulsions were prepared by mixing hexadecane (oil), n-hexanol, and potassium oleate (i.e. oelic acid and equivalent amount of KOH) in a large beaker in the following proportions: For 1ml hexadecane, 0.4 ml n-hexanol, and 0.2 gm potassium oleate. Distilled water was added in small amounts to the mixture which was stirred vigorously to insure homogeneity. For the second system, all the components were the same except n-hexanol was substituted with n-pentanol. Similar systems were also prepared by substituting n-hexanol with 2-hexanol or cyclohexanol. All chemicals were of high purity (greater than 99%), and the water was double-distilled.

Electrical resistance: Two glass-sealed silver wires (diameter=0.16 cm) were used as electrodes. A one centimeter length at the end of each wire was exposed outside the glass tube, and the Ag-AgCl electrodes were separated by 0.8 cm. The electrodes were electro plated in dilute HCl to produce Ag-AgCl electrodes. The electrical resistance of the microemulsions was measured by dipping the electrodes, connected to a conductivity bridge (Beckman model RC 16 B2), into the microemulsions.

High resolution NMR spectroscopy: Nuclear magnetic resonance spectra of microemulsions at various water to oil ratios 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. The chemical shifts of water, methylene and methyl protons were measured as a function of added water to the microemulsion system.

Spin-lattice relaxation time: The spin-lattice relaxation time (T_1) was measured using Praxis pulse NMR spectrometer using 90°-90° pulse program. The long relaxation time component, characteristic of water protons, was plotted as a function of water to oil ratio in microemulsions.

Viscosity measurements: All viscosity measurements were made with a model LVF Brookfield viscometer. For viscosities up to 100 cp, a #1 spindle was used. The viscosity of various microemulsion systems were measured as a function of volume fraction of dispersed water. A plot of relative viscosity against volume fraction of dispersed water was made for systems containing different cosurfactants (e.g., n-pentanol, n-hexanol, 2-hexanol and cyclohexanol).

X-ray scattering measurements: X-ray scattering data were collected using a Phillips copper-anode X-ray tube operated at 40 kilovolts and 20 mA. The spot focus (1.2 mm x 1.2 mm) was used for all experiments. A Bonse-Hart goniometer, with multiple-reflecting crystals removed, served conveniently for mounting components of a block collimation system. Scattered X-rays were detected by means of a NAI (Tl) scintillation detector. Electronic pulses from the detector were passed through a linear pulse amplifier and single channel analyzer was operated in discriminator mode to minimize electrical noise. Output pulses were accumulated by Hewlett-Packard scalar (Model 5243 L) operated in frequency mode. Data were printed on paper tape by Hewlett-Packard digital recorder.

Freeze-etching electron microscopy: Specimens were fractured and replicated in a Balzers freeze-etch apparatus as described elsewhere (11,12). The carbon platinum replica of the fractured surface was photographed through an electron microscope.

RESULTS AND DISCUSSION

Figure 1 shows the optical appearance

and electrical resistance of dispersions containing n-hexanol or n-pentanol as the cosurfactant. It is evident that both systems remain isotropic, clear and stable up to the water to oil ratio of 0.7. Upon further addition of water both systems became birefringent and transluscent. However, the pentanol containing system was more clear in the birefringent region as compared to the hexanol system. The electrical resistance of these two systems showed a striking difference in the region 0.1 to 0.7 water to oil ratio. As the water to oil ratio is increased from 0.2 to 0.6, the hexanol containing dispersions maintained the electrical resistance at 10^5 ohms. However, the pentanol containing dispersions exhibited a continuous decrease in the electrical resistance from 10^5 to about 50 Ohms upon the addition of water. These results very clearly indicate that although both these systems are isotropic, clear, and stable, their electrical properties are strikingly different, and that the difference of one carbon atom in the chain-length of the cosurfactant molecule can strikingly influence the electrical resistance of these systems.

Figure 2 shows the chemical shift of water and hydroxylic protons' resonance peak in the high resolution NMR (220 megacycles) spectra. As water to oil ratio is increased from 0.1 to 0.7, the chemical shift of these protons remained constant for the hexanol containing system whereas there was a continuous upfield shift of the resonance peak in the pentanol system. This suggests that the environment of water and hydroxylic protons changed continuously as more water was added to the pentanol containing system, whereas in the hexanol containing system the environment of these protons remained the same as shown by the relatively constant chemical shift.

It should be pointed out that this resonance peak is developed jointly by the hydroxylic protons of alcohol and water protons. This single resonance peak for hydroxylic and water protons suggests that the rate of proton exchange must be very rapid between the hydroxyl groups and water molecules. The upfield chemical shift of pentanol containing system upon addition of water can be explained qualitatively as follows. Two factors can contribute towards upfield shift, one the increased separation between pentanol molecules and the other weighted average of chemical shift of protons depending upon the relative number of protons of hydroxyl groups and of water molecules. In the pure alcohol, hydrogen-bonded polymeric structures exist and the chemical shift observed is characteristic of protons with extensive hydrogen bonding. However, upon dilution, monomeric alcohol begins to form and the degree of hydrogen bonding between the hydroxyl groups decreases resulting in an upfield shift. The observed upfield shift of the hydroxylic proton signal is a well-known phenomenon (13). Gillberg et al (14) have shown a 3.5 ppm upfield shift of hydroxylic proton signal upon dilution with benzene. In the present study, the addition of water appears to bring about the separation of pentanol molecules. It is likely that pentanol molecules interact strongly with one another at low water to oil ratio. However, upon addition of water, pentanol molecules appear to disperse in the monomeric form in the system. The addition of water to n-hexanol system does not appear to bring about as much upfield shift as pentanol system.

The average chemical shift of hydroxylic and water protons (δ_{O-H}) can be expressed (14) as

$$\delta_{O-H} = p \cdot \delta_{R-OH} + (1-p)\delta_{H_2O} \quad \ldots\ldots\ldots (1)$$

where $p = n_{OH}/(n_{OH} + 2n_{H_2O})$ and n_{OH} and n_{H_2O} are the number of molecules of alcohol and water respectively. Since the resonance of water occurs upfield compared to that of alcohol, one would expect the resonance signal to move upfield as the amount of water is increased in the system according to equation (1). The two factors discussed above can explain qualitatively the upfield shift of water and hydroxylic protons in the pentanol system. The chemical shifts of methylene and methyl protons showed no significant change upon addition of water for both pentanol or hexanol containing systems.

Figure 3 shows the spin-lattice relaxation time (T_1) of pentanol or hexanol containing dispersions as a function of water to oil ratio. It is evident that at any water to oil ratio the relaxation time of hexanol containing dispersions was greater than that of pentanol containing dispersions. It is also clear that the slope of the relaxation times plot of hexanol containing dispersions is greater than that of pentanol containing dispersions. In view of the observation that the spin-lattice relaxation time is linear with respect to water to oil ratio, the relaxation time can be used to determine the oil/water ratio during several oil recovery processes. It should be pointed out that at water to oil ratio of 0.9 there is a sudden decrease in the spin-lattice relaxation time in hexanol containing system which is presumably due to the formation of liquid crystalline phase within the system.

Using high resolution (100 MC) and pulsed NMR spectroscopy, Hansen (15) investigated potassium oleate-n-hexanol-water-benzene system. It was found that the polar ends of the oleate molecules are relatively immobilized at the aqueous interface, while the terminal methyl end of the molecule is free to reorient in the benzene phase. In contrast, hexanol shows no motional restriction and presumably exchanges rapidly between the interfacial film and the benzene phase. Hansen (15) also measured the spin-lattice relaxation time (T_1) of D_2O containing microemulsions and showed that T_1 increased with droplet size.

The spin-lattice relaxation time T_1 is the half-life required for a perturbed system of nuclei to reach an equilibrium condition (16). A large value of T_1 indicates an inefficient relaxation process. The data presented in Fig. 3 suggest that spin-lattice relaxation process occurs much more efficiently in pentanol containing system as compared to the one containing hexanol.

Devereux (17) used spin-lattice relaxation time measurements of sandstone-water system to characterize pore size distribution within the sandstone. He showed that when sandstone was exposed to various surfactant solutions, the relaxation time increased linearly with the length of the adsorbed surfactant molecules. He also attributed three resolved components of the relaxation time to water in very fine, coarse, and large pores in the sandstone.

Figure 4 shows the relative viscosity plotted against the volume fraction of dispersed water in four isotropic, transparent, stable dispersions containing identical components except different cosurfactants. It is obvious that the relative viscosity of hexanol containing system increases rapidly upon increasing the volume fraction of dispersed water, whereas for pentanol containing dispersions, the relative viscosity increases linearly with volume fraction of dispersed water. It should be pointed out that on the relative viscosity curve for pentanol systems, there is a large peak in viscosity in the birefringent region between volume fraction of water 0.3 to 0.5. If one considers the relative viscosity plot for three hexanols, namely n-hexanol, 2-hexanol, and cyclohexanol, it is obvious that the microstructure of these isotropic, clear systems made by the three hexanols must be different. The relative viscosity of dispersions containing cyclohexanol fall on the plot of Einstein's relationship for relative viscosity and the volume of dispersed phase. The n-hexanol containing dispersions give viscosity that is intermediate to that exhibited by dispersions containing 2-hexanol and cyclohexanol. Figure 4 illustrates very cleary the striking effect of the chain-length and the shape of cosurfactant molecules on rheological properties of such isotropic, clear, and stable dispersions.

Figure 5 shows our proposed structures for the isotropic, clear, stable dispersions prepared by using n-pentanol or n-hexanol as cosurfactant. These structures are consistent with the results obtained using electrical resistance, high resolution NMR, spin-lattice relaxation time, and viscosity measurements. We propose that the pentanol containing system is a co-solublilized system in which one can visualize the surfactant and the cosurfactant forming a liquid which can dissolve both oil or water as molecular solution whereas hexanol containing system is a true water-in-oil microemulsion in which water is present as spherical droplets. In the co-solubilized system, as one increases the amount of water the average distance between the water molecules as well as between alcohol molecules would change and this subsequently would influence the hydrogen bonding ability of water and alcohol molecules which subsequently would influence the chemical shift of the resonance peak. Also in the co-solubilized system as one adds more water it becomes more and more electrically conducting and hence exhibits a continuous decrease in the electrical resistance. However, in the hexanol containing system since it contains water spheres in a continuous oil medium, the addition of water creates more spheres and/or larger spheres. However, the continuous medium is still an oil phase and hence the electrical resistance is maintained at a high value (10^5 ohms).

The relative viscosity increases much more rapidly in the hexanol containing system as compared to pentanol system which does not contain spherical droplets of water. It has been shown by Einstein (18) that at extreme dilution, the relative viscosity (η_r) for a suspension of spheres in a liquid should be given by the relation

$$\eta_r = 1 + 2.5\ C \quad \text{.....(2)}$$

where C is the volume fraction of the dispersed phase. However, Ward and Whitmore (19) 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 funciton of the size distribution. For the relative viscosity (η_r) of a suspension containing a high concentration of uniform (monodispersed) spheres, Roscoe (20) has given the following expression

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

where C is the volume fraction of spheres (dispersed phase). However, Matsumoto and Sherman (21) subtracted the term C_o from C, where C_o is the volume fraction of the dispersed phase which is molecularly solubilized by the excess surfactant molecules and C is the total volume fraction of the dispersed phase. Therefore, $C-C_o$ is the volume fraction of water present in the form of microemulsion. In our previously reported study (9) on the rheology of microemulsions and liquid crystals, we have used the following expression for the best fit of experimental data.

$$\eta_r = [1-1.35\ (C-C_o)]^{-2.5} \quad \ldots\ldots\ldots\ldots (4)$$

Recently, Attwood et al (22) have used the following expression to describe the relative viscosity of micellar solutions in the presence of solubilized oil,

$$\eta_r = \exp\left[\frac{aC}{(1-kC)}\right] \quad \ldots\ldots\ldots\ldots\ldots (5)$$

where a is a constant and k is the hydrodynamic interaction coefficient. In support of our conclusion that cosolubilization leads to a lower relative viscosity than microemulsification, we have studied (unpublished) the relative viscosity of molecular solutions of water containing different volume fractions of ethanol, propanol or butanol. The plot of relative viscosity vs volume fraction of dissolved alcohol of these systems exhibited a slope of 2.5 to 3.3, but always less than the slopes for microemulsions.

In summary, we would like to emphasize that isotropic, clear, stable systems composed of identical components except a small change in the chain-length or the shape of cosurfactant molecules can have strikingly different microstructure and that it is desirable to use a combination of physical techniques to elucidate their microstructures.

Very extensive studies on the phase-equilibria as well as electrical, birefringence, and viscosity characteristics of microemulsions of interest in tertiary oil recovery have been reported by Healy and Reed (23, 24). It is likely that some of the microemulsion systems reported in the literature which exhibit low electrical resistance at a relatively small water to oil ratio may be cosolubilized systems rather than true microemulsions.

The formation of liquid-crystalline phases has been observed often during the phase-inversion of several micro- and macroemulsions (7,10). A birefringent liquid-crystalline phase also formed after the initial isotropic, clear region in the systems reported in this paper. This liquid- crystalline phase had very unusual rheological properties. If the sample was kept on a shelf for a day or so the viscosity decreased strikingly and the sample became very fluid. However, if such a sample was vigorously shaken for 30 seconds, it became gel. Figure 6 shows the liquid-crystalline phase of the n-hexanol containing system at the water to oil ratio of 1.4 before and after shaking the sample tube. We were interested in determining the mechanism of this striking change in the rheology of the liquid-crystalline phase.

Figures 7 and 8 show the X-ray scattering intensity of the birefringent phase before and after shaking the sample tube. The intensity of scattered X-rays is plotted as a function of scattering parameter S (i.e. $S = 2\sin\theta/\lambda$, where θ is the scattering angle and λ the wave-length of the X-rays). The first-order diffraction maxima at $S = 0.0053$ and the birefringent properties as well as previously reported high resolution NMR (220 MC) characteristics of the sample indicated that this system is probably in the form of parallel lamellae. The increased width of the first order maximum for the shaken sample (Figure 8) can be due to variation in the separation or orientational disorder of the lamellae. It is evident from Figures 7 and 8 that the maximum intensity of scattered X-rays at $S = 0.0053$ sharply decreases after shaking as well as the deconvoluted band-width increases. The X-ray scattering data suggest that after shaking the sample tube, the degree of order decreased in the birefringent sample.

Figures 9 and 10 are the electronmicrographs of the lamellar liquid-crystalline structures before and after shaking the sample tube, obtained using the freeze-etching technique. It is obvious that before shaking the tube, the lamellae orientate parallel to one another as seen in Figure 9 whereas upon shaking the sample tube, the disordering takes place in the arrangement of the lamellae as well as significant breakdown of the lamellae occurs. It should be pointed out that each leaflet seen in Figure 9 is about 62 Å thick, which corresponds to the thickness of a bi-layer of surfactant and cosurfactant molecules swollen with oil. Therefore, it appears that upon standing on the shelf the lamellae orientate parallel to one another. They slide past one another during the flow and exhibit the characteristics of low viscosity fluid. However, upon agitation or shaking, the lamellae are disordered and are entangled with one another resulting in a gel-like state.

In summary, using X-ray scattering and freeze-etching electronmicroscopy, we have

been able to elucidate the structure as well as the mechanism of rheological changes that are induced in such birefringent systems upon shearing. Although the studies presented here were carried out on well defined systems, work is in progress on similar systems and phenomena in petroleum sulfonate and crude oil containing systems.

CONCLUSIONS

The isotropic, clear, and stable systems can be either true microemulsions or co-solubilized systems. By using a combination of physical techniques such as electrical conductivity, high resolution NMR, pulse NMR, and viscosity measurements one can distinguish between them. Therefore, transparency and stability are not sufficient criteria to define microemulsions.

The spin-lattice relaxation time of microemulsions or co-solubilized systems increases linearly with the water to oil ratio. The slope of such a plot can be considered a characteristic of the microstructure of the surfactant formulation.

The unusual rheological properties of the lamellar liquid-crystalline phase are related to disorientation of lamallae upon shearing. Physical techniques such as X-ray scattering and freeze-etching electron-microscopy can elucidate the mechanism of such rheological changes.

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REFERENCES

1. Schulman, J.H., Stoeckenius, W., and Prince, L.M.: "Mechanism of Formation and Structure of Microemulsions by Electron Microscopy",J. Phys. Chem., (1959) Vol. 63, 1677- 1680.

2. Stoeckenius, W., Schulman, J.H., and Prince, L.M.: "The Structure of Myelin Figures and Microemulsions as Observed with the Electron Microscope", Kolloid Zeitschrift (1960) Band 169, Heft 1-2, 170-180.

3. Schulman, J.H. and Riley, D.P.: "X-ray Investigation of the Structure of Transparent Oil-Water Disperse Systems.I", J. Colloid Sci. (1948) Vol.3, 383-405.

4. Schulman, J.H. and Friend, J.A.: "Light Scattering Investigation of the Structure of Transparent Oil-Water Disperse Systems II", J. Colloid Sci. (1949) Vol. 4, 497-509.

5. Bowcott, J.E. and Schulman, J. H.: "Emulsions", Zeitschrift fur Elektrochemie (1955) Band 59, Heft 4, 283-290.

6. Shah, D.O. and Hamlin, M.Jr.: "Structure of Water in Microemulsions: Electrical, Birefringence and Nuclear Magnetic Resonance Studies", Science (1971) Vol. 1 483-485.

7. Zlochower, I.A. and Schulman, J.H.: "A Study of Molecular Interactions and Mobility at Liquid/Liquid Interfaces by NMR Spectroscopy", J. Colloid and Interface Science (1967) Vol. 24, 115-124.

8. Cooke, C. E. and Schulman, J.H.: "The Effect of Different Hydrocarbons on the Formation of Microemulsions", Surface Chemistry, ed. Ekwall, P., Groth, K., and Runnstrom, V.,Academic Press,1965, 231-25

9. Falco, J.W., Walker, R.D. and Shah, D.O.: "Effect of Phase-Volume Ratio and Phase-Inversion on Viscosity of Microemulsions and Liquid Crystals", AIChE J. (1974) Vol. 20 No.3,510 - 514.

10. Shah, D.O., Tamjeedi,A., Falco, J.W., and Walker, R.D.: "Interfacial Instability and Spontaneous Formation of Microemulsions", AIChE J. (1972) Vol. 18 No. 6,1116-1120.

11. Deamer, D.W., Leonard, R., Tardieu, A., and Branton, D.: "Lamellar and Hexagonal Lipid Phases Visualized by Freeze-Etching" Biochim. Biophys. Acta. (1970) Vol. 219, 47-60.

12. Branton, D.: "Fracture Faces of Frozen Membranes", Proc. Natl. Acad. Sci. U.S. (1966) Vol. 55 pp. 1048- 1056.

13. Davis, J.C.,Jr., Pitzer, K.S. and Rao, C.N.R.: "Nuclear Magnetic Resonance Studies of Hydrogen Bonding.II Alcohols", J. Phys. Chem. (1960) Vol. 64, 1744-1747.

14. Gillberg, G., Lehtinen, H. and Friberg, S.: "NMR and IR Investigation of the Conditions Determining the Stability of Microemulsions", J. Colloid and Interface Sci. (1970) Vol. 33, 40-53.

15. Hansen, J.R.: "High-Resolution and Pulsed NMR Studies of Microemulsions", J. Phys. Chem. (1974) Vol. 78, 256-261.

16. Chapman, D. and Magnus, P.D.: "Introduction to Practical High Resolution Nuclear Magnetic Resonance Spectroscopy", Academic Press, London and N.Y. p. 21 1966.

17. Devereux, O.F.: "Effect of Crude Oil On the Nuclear Magnetic Relaxation of Water Protons in Sandstone", Nature (1967) Vol. 215, 614- 615.

18. Einstein, A.: Ann. Phys., Lpz., 19 p. 289 (1906) 34 p. 59 (1911).

19. Ward, S.G., Whitmore, R.L.: "Studies of the Viscosity and Sedimentation of Suspension, I", British J. Applied Phys. (1950) Vol. 1,286- 290.

20. Roscoe, R.: "The Viscosity of Suspensions of Rigid Spheres", British J. Applied Phys. (1952) Vol. 3,267-269.

21. Matsumoto, S. and Sherman, P.: "The Viscosity of Microemulsions", J. Colloid and Interface Sci. (1969) Vol. 30 No. 4, 525-536.

22. Attwood, D., Currie, L.R. and Elworthy, P.H.: "Studies of Solubilized Micellar Solutions, III", J. Colloid and Interface Sci. (1974) Vol. 46 No. 2, 261-275.

23. Healy, R.N. and Reed, R.L.: " Physicochemical Aspects of Microemulsion Flooding", Soc. Pet. Engn. J. (1974).

24. Healy, R.N., Reed, R.L. and Stenmark, D.G.: "Multiphase Microemulsion Systems", SPE 5565 paper presented at 50th Annual Fall Meeting in Dallas, Sept. 28, 1975.

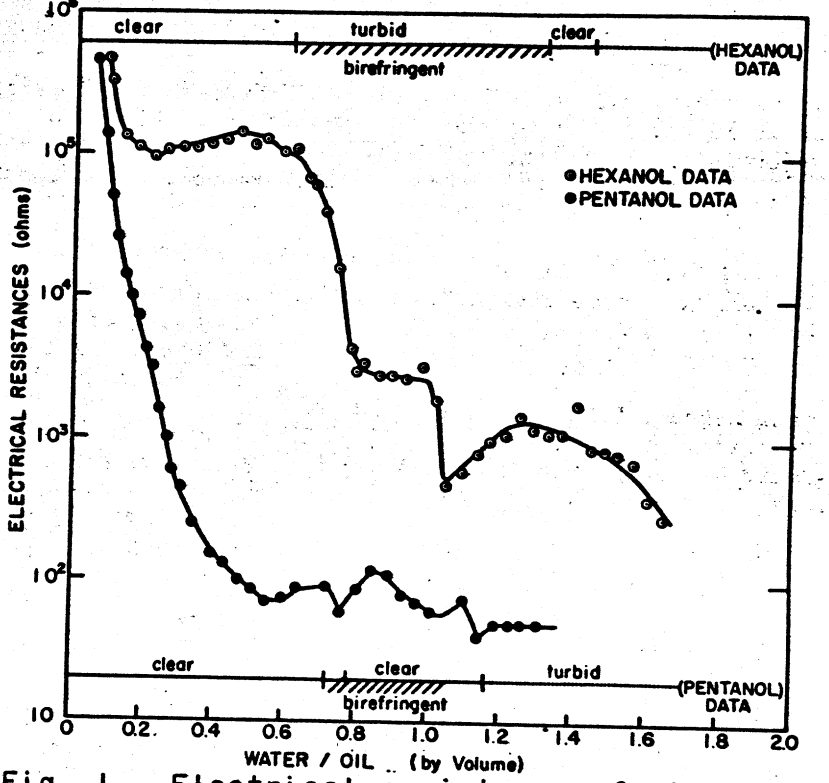

Fig. 1 - Electrical resistance of microemulsions containing hexanol or pentanol as the cosurfactant. (Microemulsion system: hexadecane + potassium oleate+cosurfactant + water).

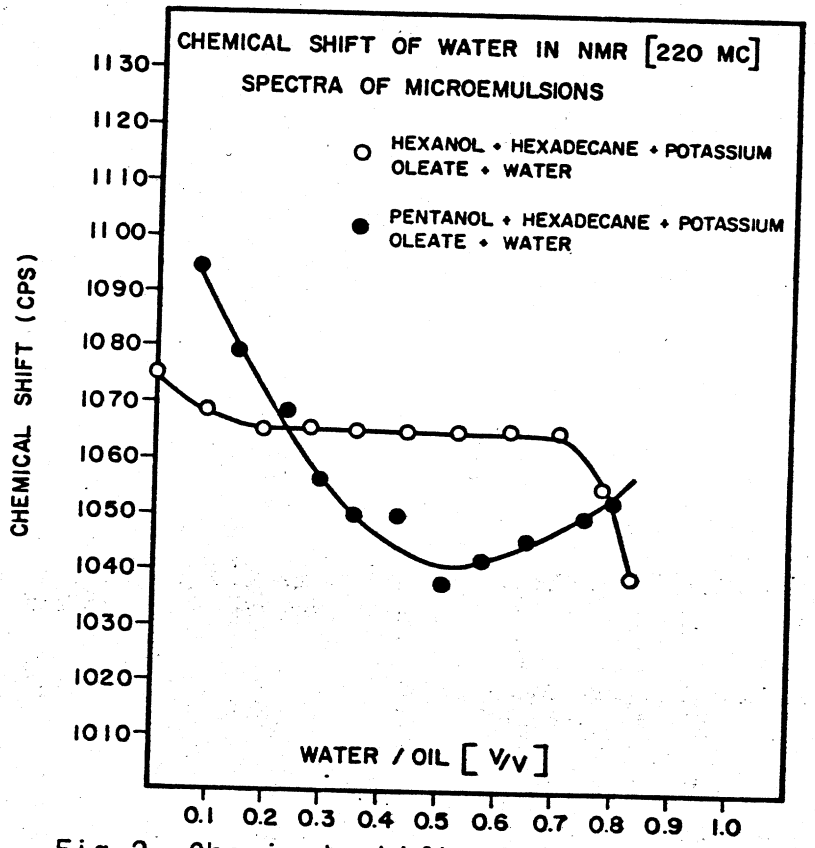

Fig 2 -Chemical shift of water and hydroxylic protons resonance peak in high resolution (220MC) NMR as a function of water to oil (Hexadecane) ratio in microemulsion containing hexanol (o) or pentanol (●).

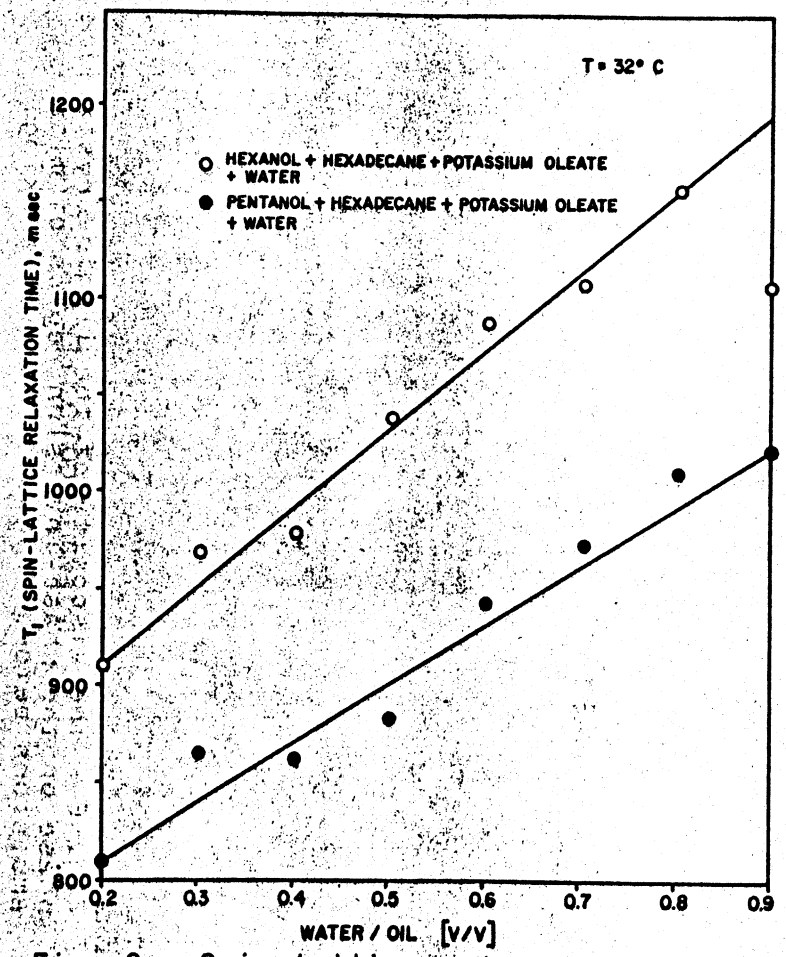

Fig. 3 - Spin-lattice relaxation time (T_1) of microemulsions containing hexanol or pentanol as a function of water to oil (hexadecane) ratio.

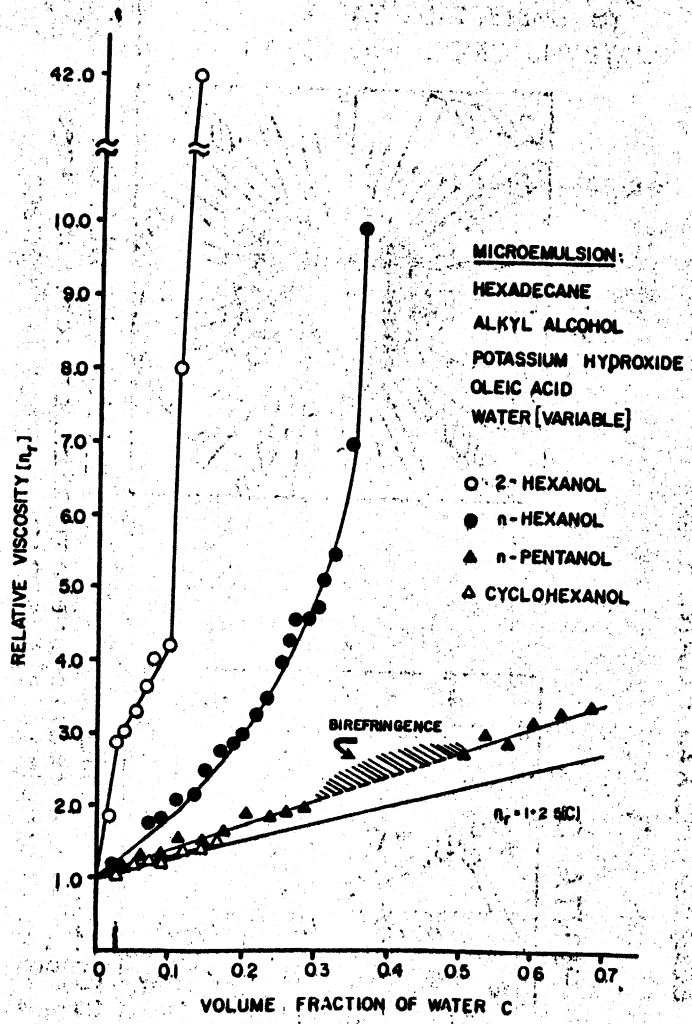

Fig. 4 - Relative viscosity of microemulsions containing various cosurfactants as a function of volume fraction of water.

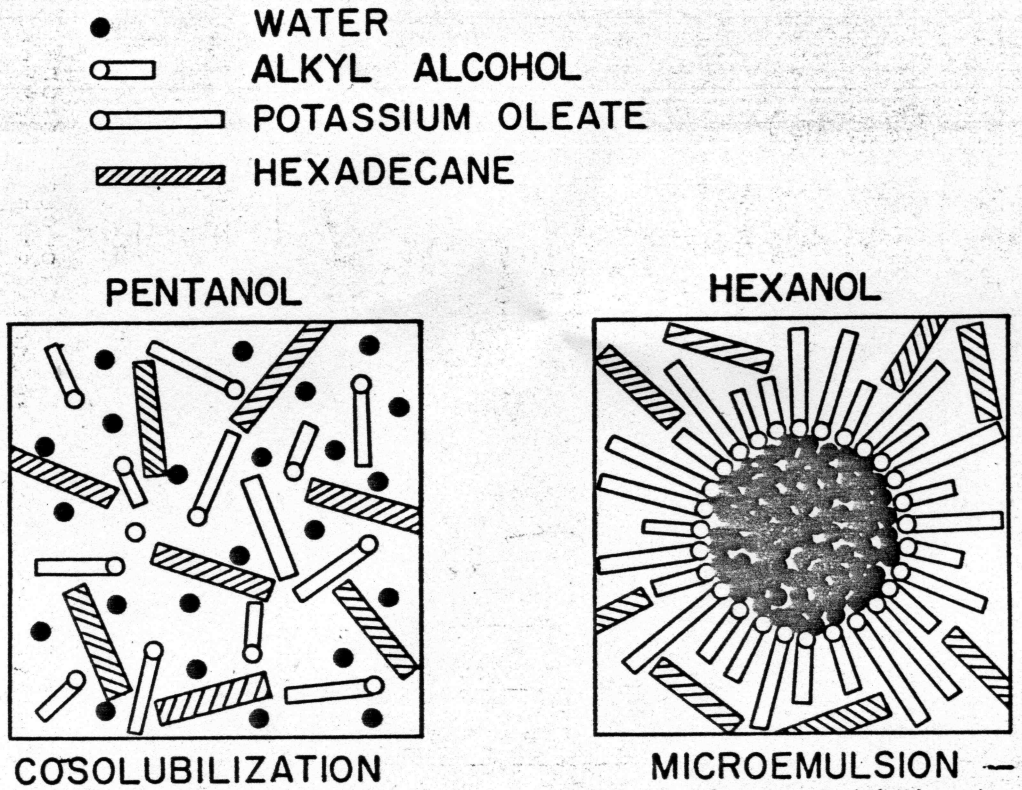

Fig. 5 - Schematic presentation of cosolubilized and microemulsions systems.

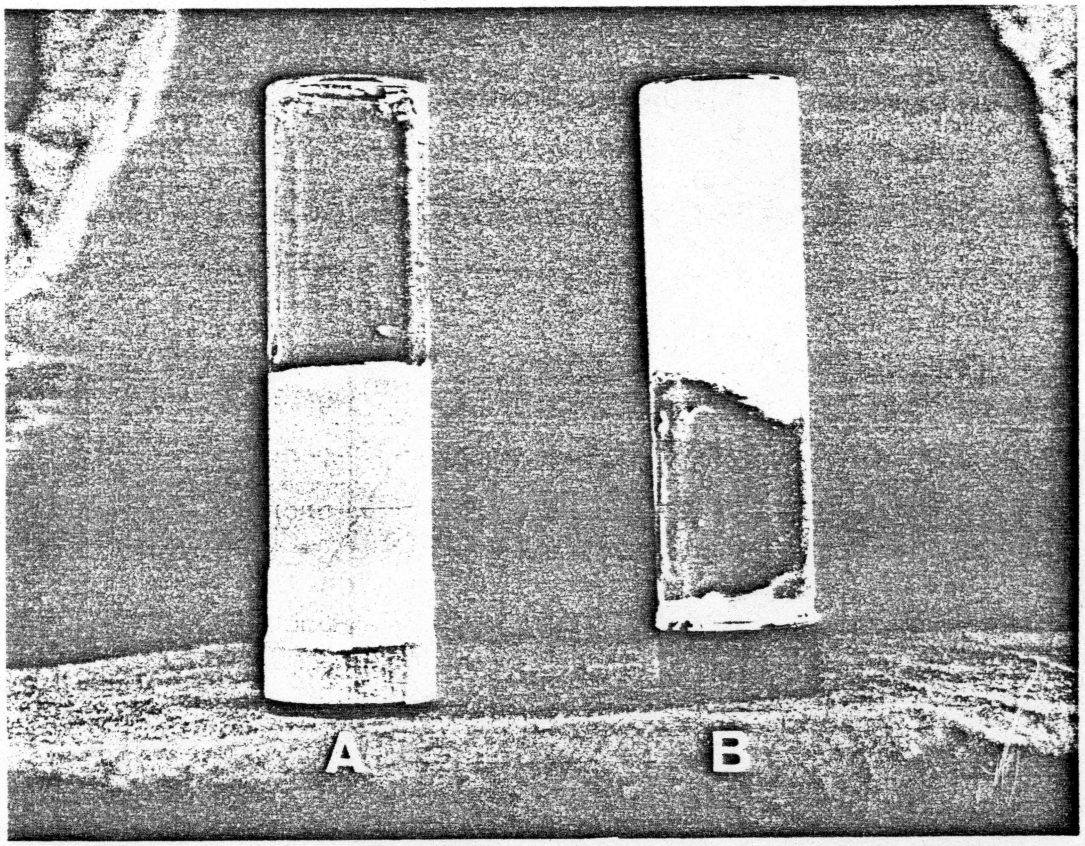

Fig. 6 - The viscosity of the liquid-crystalline phase on the phase-inversion region of micro-emulsions before (A) and after (B) shaking.

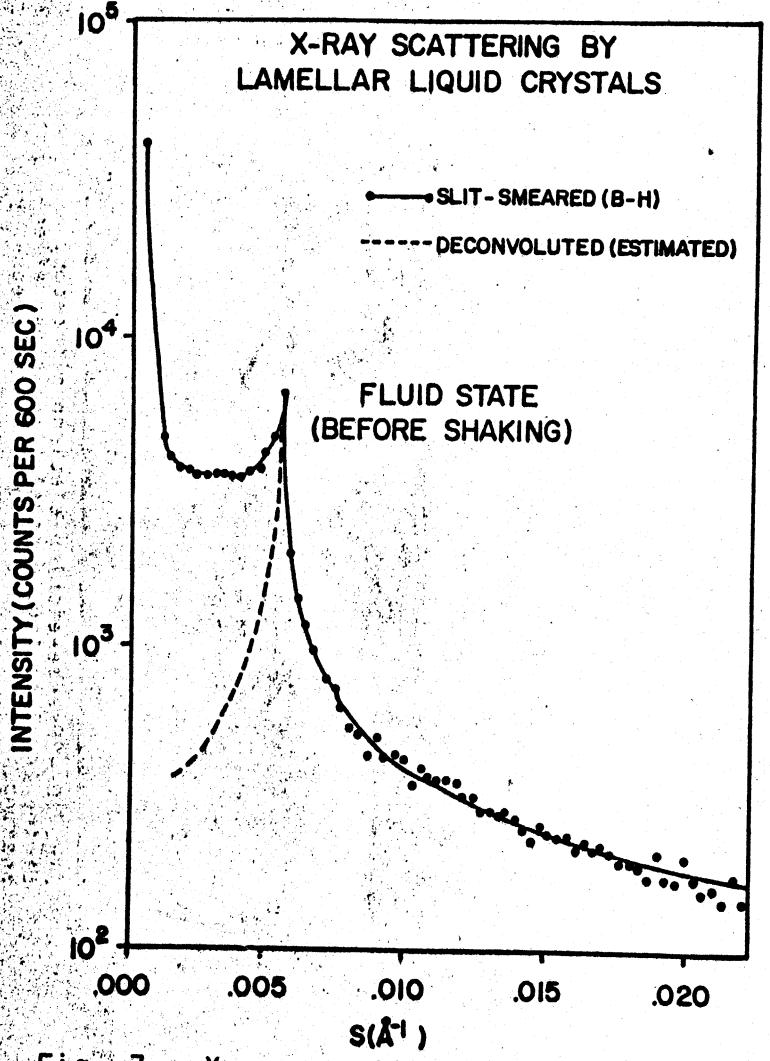

Fig. 7 - X-ray scattering by the liquid-crystalline phase before shaking.

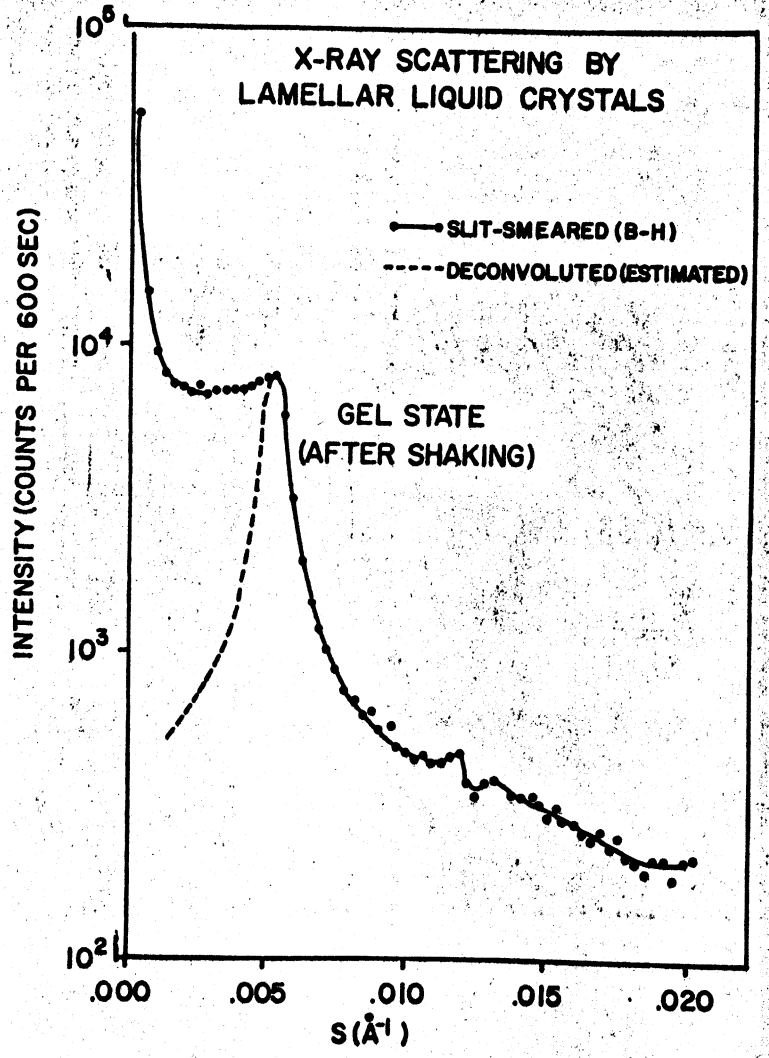

Fig. 8 - X-ray scattering by the liquid-crystalline phase after shaking.

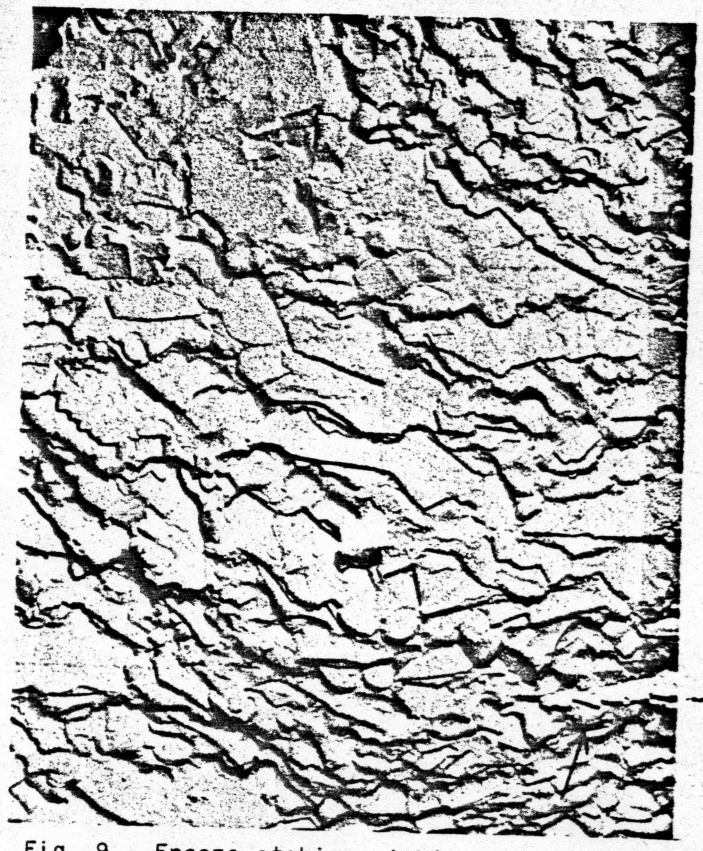

Fig. 9 - Freeze etching electron microscopy of the lamellar liquid-crystalline phase before shaking. Note the parallel orientation of lamellae before shaking.

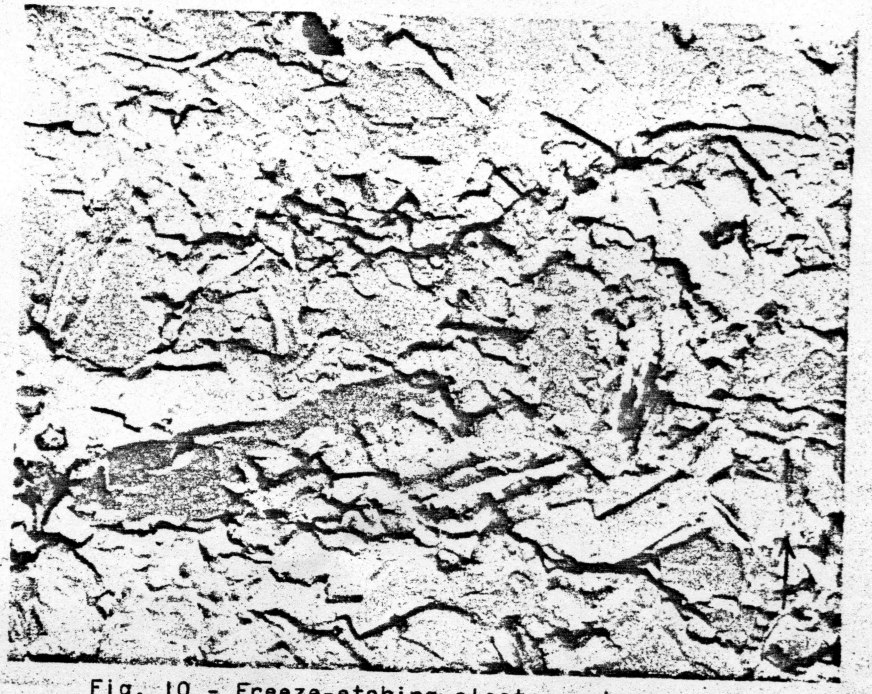

Fig. 10 - Freeze-etching electron microscopy of the lamellar liquid-crystalline phase after shaking. Note the disorientation and breakage of the lamellae upon shaking.