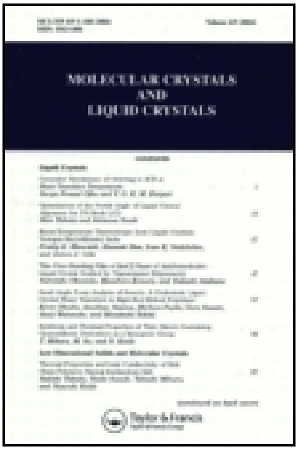

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Studies Around the Second Critical Micelle Concentration in Lecithin

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Abstract—Lipid micelles appear to pass through a transition in the concentration region of 5 to 10%. This has been investigated by measurements of the diffusion coefficient by nuclear magnetic resonance of lecithin in various solvents in the concentration range of 0 to 20% lecithin. Results are also reported for potassium oleate which is shown to behave in a similar manner in this concentration range. The conclusion drawn is that the micelles, which are spherical below 5% pass through a transition region from 5 to 10% and above 10% they appear as cylinders, increasing in length as the concentration increases. Measurements on the increase in permittivity with concentration and also the change in conductivity substantiate the diffusion measurements.

1. Introduction

Micelles of lecithin are reported to form in benzene at a concentration of about 0.00033%.⁽¹⁾ As the concentration of lipid increases, the concentration of the spherical micelles increases. This isotropic solution of spherical micelles then undergoes structural alterations in a broad transition region known as the second critical micelle concentration. In this region Kavenau⁽²⁾ suggests that the micelles lose some of their movement and the X-ray band which is related to the distance between the micelles begins to appear. Vetter⁽³⁾ has reported changes in the viscosity and diffusion coefficient of the sodium salt of sulphonated di (2-hexyl)succinate (commerially known as Aerosol M A) in salt solution. He concludes that up to the second critical concentration the spherical micelles remain the same, except that their concentration increases. Some investigators propose that

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the spherical micelles transform to a cylindrical or quasi-ellipsoidal form when the number of molecules becomes larger than can be accommodated in a sphere.(4,5) Since the difference in energy is not large, it seems likely that both transitions could occur depending on circumstances. The transition to cylindrical micelles in aqueous solution is reported by Luzzati *et al.*(6) They suggest that the cylinders grow longer as the concentration increases. This conclusion is substantiated in the work reported here.

2. Experimental

The lecithin samples used in our experiments were supplied by B.D.H. Ltd., and quoted as being 95 to 100% pure egg yolk lecithin. In order to affirm the water content, and also as an investigation of purity, high resolution nuclear magnetic resonance and infra red spectra of the sample were taken. The high resolution NMR spectrum was run on a Perkin Elmer 60 MHz spectrometer at 30 °C. The lecithin was dissolved in carbon tetrachloride to form a 20% (i.e. 20 gm made up to 100 ml with solvent at 20 °C) solution. No peak appeared corresponding to the presence of free water and due to the presence of other absorptions, it was found impossible to determine whether there was any bound water in the material. The spectrum compared closely with the work of Chapman and Morrison(7) which confirmed that no major impurity was present. The infra red spectrum was run on a Perkin Elmer 225 grating spectrometer, the lecithin being deposited as a thin film between a pair of sodium chloride blanks. An absorption appears between 3600 and 3100 cm^{-1} corresponding to the OH absorption. The intensity of the band is greater than one would expect for free OH, in agreement with the high resolution NMR spectrum. The width of the OH absorption suggests that it is due to hydrogen bonded OH groups. This enables us to estimate that there is in fact between one and two water molecules per lecithin molecule.

The results on lecithin were compared with similar measurements made on the potassium oleate/water system. The potassium oleate was prepared in the laboratory by mixing potassium hydroxide dissolved in ethanol and oleic acid. Phenolphthalein was used as an indicator. The resulting potassium oleate was dried under vacuum.

A high resolution NMR spectrum of the sample was run and the presence of water or any other impurity could not be detected.

The diffusion coefficient was measured by the magnetic resonance method of Carr and Purcell.(8) The pulse spectrometer was basically that described by Jones(9) but with slight modifications to the coil system so that a high r.f. field H_1 could be produced. The frequency of the pulse was 26 MHz and using the single coil system described by Roberts,(10) a field of up to 4×10^{-3} Tesla was obtainable at the sample coil. It is a necessary condition of diffusion measurement that H_1 should be much larger than the applied inhomogeneity G. In our case the applied inhomogeneity was produced by two coils one on either side of the cryostat. These coils were constructed in the form of a " D ", the straight edge being up against the cryostat, the curved section being far enough away from the sample to have a negligible contribution to the gradient. The field gradient produced by these coils was variable up to 0.1 Tesla m^{-1} but for our experiments a gradient of 1.5×10^{-2} Tesla m^{-1} was used.

The permittivity and conductivity measurements were made with a Wayne Kerr B.331 autobalance precision bridge. The solution was contained in a stainless steel three-terminal cell. The empty capacity of the cell was 11.5 pF and the plate separation 0.25 mm.

3. Results

Pulse measurements were first carried out on a solution of lecithin in carbon tetrachloride. In this system only the lecithin gives a nuclear signal. The decay of the spin echo was found to be exponential and independent of concentration. This meant that the relaxation time T_2 was too short to enable us to measure the diffusion coefficient itself. Measurements of the relaxation time T_1 in the same system at 20 °C gave a value of 58 m sec compared with 40 m sec for T_2 obtained from the echo decay.

Although we could not measure the diffusion coefficient of lecithin itself we could see what effect lecithin had on the diffusion coefficient of some protonic solvent whose diffusion coefficient could be easily measured. Lipids dissolve readily in hydrocarbons. Micelles are formed in which the polar head groups are innermost whilst the fatty acid tails are in contact with the hydrocarbon solvent.(2) Figure 1 shows the effect of various concentrations of lecithin on the diffusion coefficient of *n*-hexane. *n*-hexane is a relatively small molecule compared with the lecithin, and the pure hydrocarbon has quite a high diffusion coefficient of 4.2×10^{-9} m^2 sec^{-1}. It is seen that on adding lecithin, initially the diffusion coefficient starts to fall rapidly. This is what one might expect if spherical micelles exist in the solution in the region 2 to 4%. Considering that the relaxation times of the lecithin are comparatively short, what we are in fact observing is the change in diffusion coefficient of the solvent. However, at about 6% a turning point is encountered and the diffusion coefficient from then on rises to a maximum of about 10%. This indicates that for some reason the lecithin offers less resistance to the motion of the hexane in this region. After 10% the diffusion coefficient falls at a rate comparable to the initial fall, reaching a plateau in the region 14 to 20%. At this concentration the solution has taken the appearance of a gel.

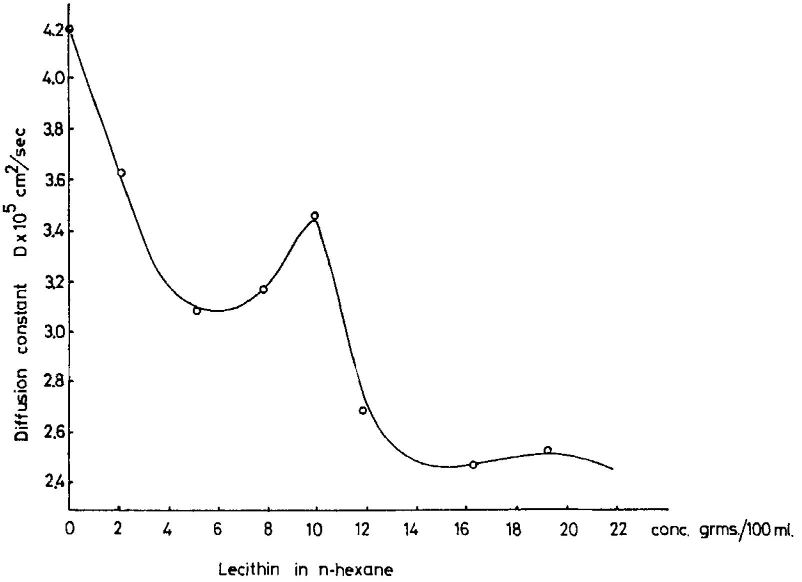

Figure 1. Plot of diffusion coefficient against concentration of lecithin dissolved in *n*-hexane.

The experiment was repeated with lecithin dissolved in *n*-decane and gave an identical result. There is first a fall in the diffusion coefficient to a minimum at 5% and then a rise to a maximum at 10% before falling and levelling off again. The change in diffusion coefficient is not quite as large as in *n*-hexane but since decane is a larger molecule this can be expected.

Lecithin dissolved in methanol will form micelles in which the polar head groups are on the outside.(2) The hydrocarbon tails forming what might be described as an oil droplet inside. The experiment was repeated for lecithin in methanol in order to ascertain that the effect we were observing was in fact a physical property of the micelles and not a solvent effect associated with the hydrocarbons. The results are shown in Fig. 2. As can be seen, the behaviour of the diffusion coefficient between 5 and 10% is not so pronounced but the behaviour is similar enough for us to conclude that the effect is in fact a physical property of the micelle and not a solvent effect.

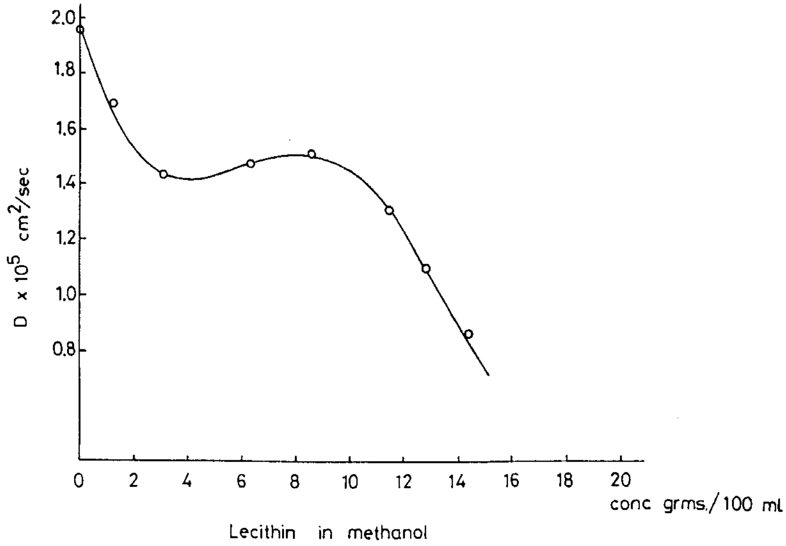

Figure 2. Plot of diffusion coefficient against concentration of lecithin in methanol.

With these results in mind, the potassium oleate/water system was then investigated. Potassium oleate is ionic as opposed to the zwitterionic structure of lecithin, and it was hoped that by looking at this system we could ascertain whether the electrical properties of the lipid molecules played an important role in determining the size and structure of the micelles. A measurement of the T_1 and T_2 relaxation times in the potassium oleate–carbon tetrachloride system showed that again the T_2 relaxation time of potassium oleate was too short (16 m sec) to enable diffusion measurements to be carried out. But as before it did enable us to observe the effect of potassium oleate on the diffusion coefficient of some solvent. This time water was chosen as the solvent and the results are shown in Fig. 3. A similarity is at once noticed with the previous results on lecithin, the turning points of the curve are at approximately the same concentration. Thus the effect observed must be a physical property of micelles and to a first approximation appears independent of solvent and electrical properties of the lipid molecule.

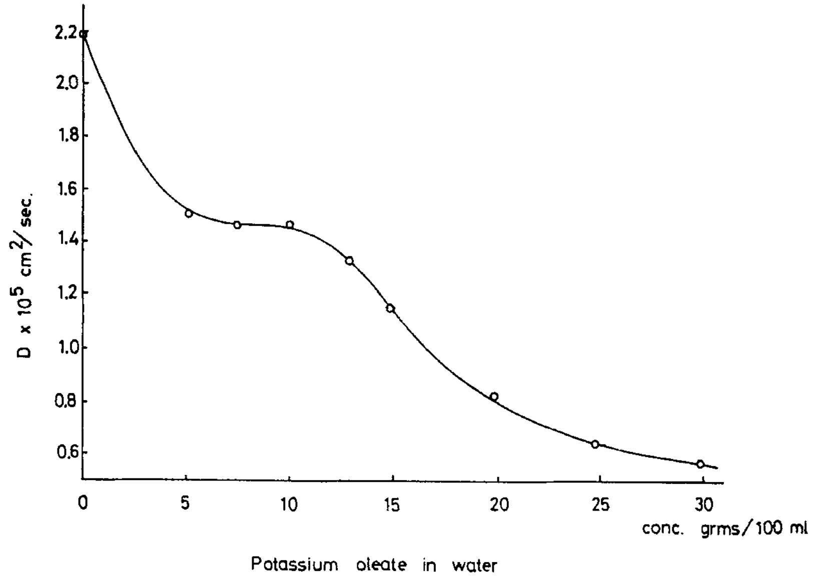

Figure 3. Plot of diffusion coefficient against concentration of potassium oleate in water.

4. Discussion

As was mentioned previously, Vetter,(3) from the viscosity and the diffusion measurements on Aerosol MA concludes that initially the micelles are spherical, increasing in number with increasing concentration. This is substantiated by our work, for up to 5% the diffusion coefficient falls, as one might expect if there is a regular increase in the concentration of micelles offering resistance to the translational motion of the solvent. From 5 to 10% is a transition region in which the X-ray band which is related to the distance between the micelles, begins to appear. After 10% the micelles have established themselves in a new structure and the diffusion coefficient again falls.

Figure 4 shows a plot of the permittivity increment $\Delta\epsilon_0$ against concentration for a solution of lecithin in hexane. Up to 5% $\Delta\epsilon_0$ can be considered linear indicating that the dipole moment of the micelles remains constant. This again suggests that the micelles

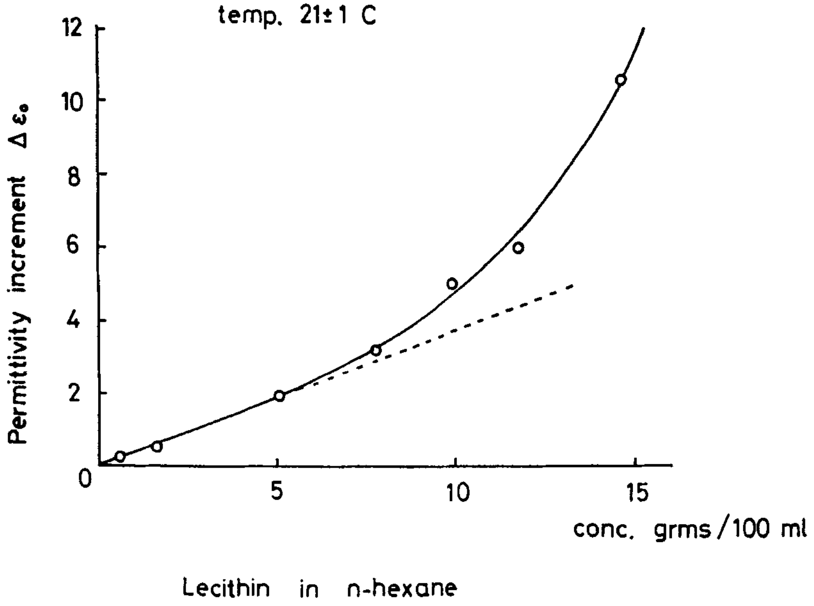

Figure 4. Plot of permittivity increment $\Delta\epsilon_0$ against concentration of lecithin in n-hexane.

do not change in structure in this region. Above this concentration the permittivity increment departs from linearity, suggesting that the effective dipole moment of the micelles is increasing. This could be accounted for by the micelles taking a cylindrical structure in which the effective dipole moment lies along the axis of the cylinder so the net dipole moment would increase as the cylinders increase in length. Figure 5 shows a plot of conductivity against concentration for the same system. A maximum is observed at about 10% concentration. This could be accounted for by the water

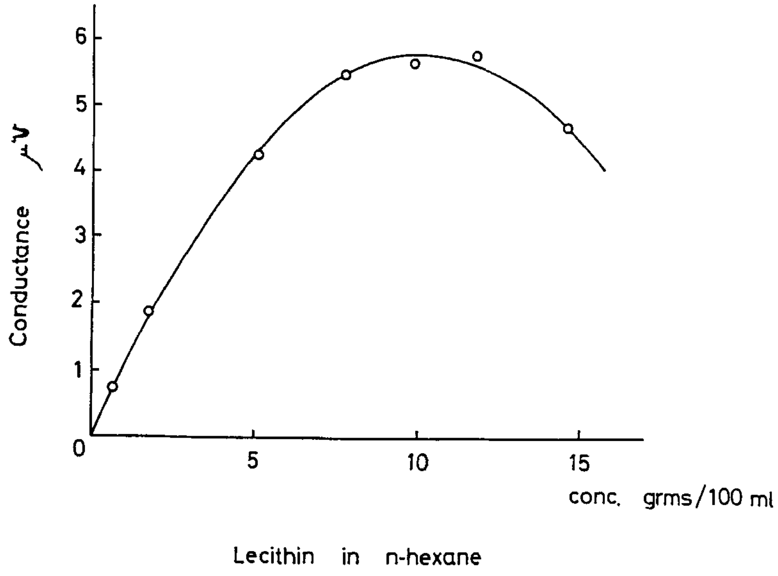

Figure 5. Plot of observed conductivity against concentration of lecithin in *n*-hexane (1μ℧ (measured) = 8n℧/cm specific conductivity).

which is present around the lecithin becoming immobilized at this concentration due to the high electric fields produced at the centre of the cylinders. Up to this point the water has been free to exchange and thus give a conductance which increases almost linearly with concentration. At concentrations higher than 10% the conductivity falls due to the high electric fields preventing the water from exchanging.

In conclusion we say that micelles of lipid molecules in solution are originally spherical, and up to about 5% concentration it is simply the number of spherical micelles that increases. From 5 to 10% there exists a transition region. After this, the micelles have assumed a new structure, probably cylindrical, as proposed in Refs. 4, 5 and 6, and as the concentration increases these cylinders are observed to grow in length.

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