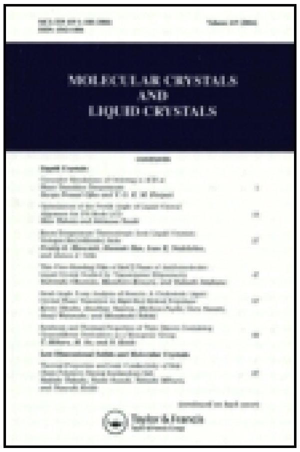

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Solubilization in Non-Aqueous Lyotropic Liquid Crystals

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The solubilization of a hydrocarbon and two alcohols in a non-aqueous lamellar liquid crystal of lecithin and ethylene glycol was investigated determining the phase region of the liquid crystal and the geometrical dimension of the latter by low angle X-ray diffractometry.

The results indicated the solubilized molecules to be located both in the polar solvent between the lecithin layers in the liquid crystal and between the individual molecules. The hydrocarbon was mainly localized between the hydrophobic end surfaces of the amphiphile and the methanol showed a balanced partition. The solubilization of long chain alcohols caused a reduction of the interlayer distance presumably due to enhanced penetration of the ethylene glycol after solubilization of the alcohol.

INTRODUCTION

The interest in amphiphilic association structures based on non-aqueous polar solvents has increased in recent years. Evans and collaborators have investigated the micellar formation in ethylammonium nitrate[1,2] and have been able to relate their results on micellization in hydrazine to the influence of water structure on micellization.[3] Non-aqueous liquid crystals based on amphiphilic substances were early mentioned by Winsor.[4] The compounds contained no solvents and were essentially glasses in which the crystallization of the hydrocarbon chains was prevented by the presence of side chains.

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Non-aqueous lyotropic liquid crystals in which a polar solvent replaced the water were introduced by Moucharafieh.[5] This introduction was followed by a series of articles outlining limitations of structures of the solvent[6,7] and describing the dynamics of the solvent.[8,9] Non-aqueous lyotropic liquid crystals show interesting properties in relation to biological structures as pointed out by McIntosh[10] because glycerol both substitutes for water in biological systems[11] and has been used as a fusogen.[12]

These non-aqueous structures obviously open new possibilities for the study of solubilization phenomena since the interaction with the polar solvent with different properties may influence both the amount of solubilization and the site of the solubilized molecules. With this in mind, we considered an exploratory investigation of the solubilization of a hydrocarbon, decane and two alcohols, methanol and decanol to be of general interest.

EXPERIMENTAL

Materials

The lecithin was vegetable origin from Lucas Meyer, Hamburg, BRD, and purified according to earlier descriptions,[6] giving a product with a single spot on the thin layer chromatogram. The solvents were redistilled and dried to obtain a state of purity described earlier.[6] The solubilizates decane (Eastman Kodak, Gold label) decanol (Eastman Kodak, Gold label) were used without further purification. The methanol (Fisher cert.) was found to contain approximately 0.5% of water and was dried in the following manner. Initial drying was made by dessication over anhydrous sodium sulphate followed by treatment with magnesium methoxide. The resulting product was refluxed over magnesium and iodine for 30 minutes with the condensate passing through a drying tube and finally distilled under reduced pressure. In this manner, the water content was brought to 0.039%.

Sample preparation

The samples were weighed into small glass vials with screw caps under nitrogen atmosphere and repeatedly mixed with a vibromixer followed by centrifugation to remove air bubbles.

The samples were examined, between slide and cover, on a microscope between crossed polarizers, for proper mixing and absence of air to study their optical patterns.

Low Angle X-ray Scattering

A small amount of the equilibrated, well-mixed sample was drawn into a fine, flattened glass capillary and sealed for X-ray diffraction in a Kiessig low-angle camera from Richard Siefert. Ni-filtered Cu radiation was used and the reflections determined by a Tennelec position sensitive detection system (Model PSD-1100).

Optical Microscopy

A microscope (Model PM-10A), attached to an automatic exposure camera was used for photomicrography. A Bailey Instruments Thermoelectric stage (Model Ts-2) with automatic temperature control was also used.

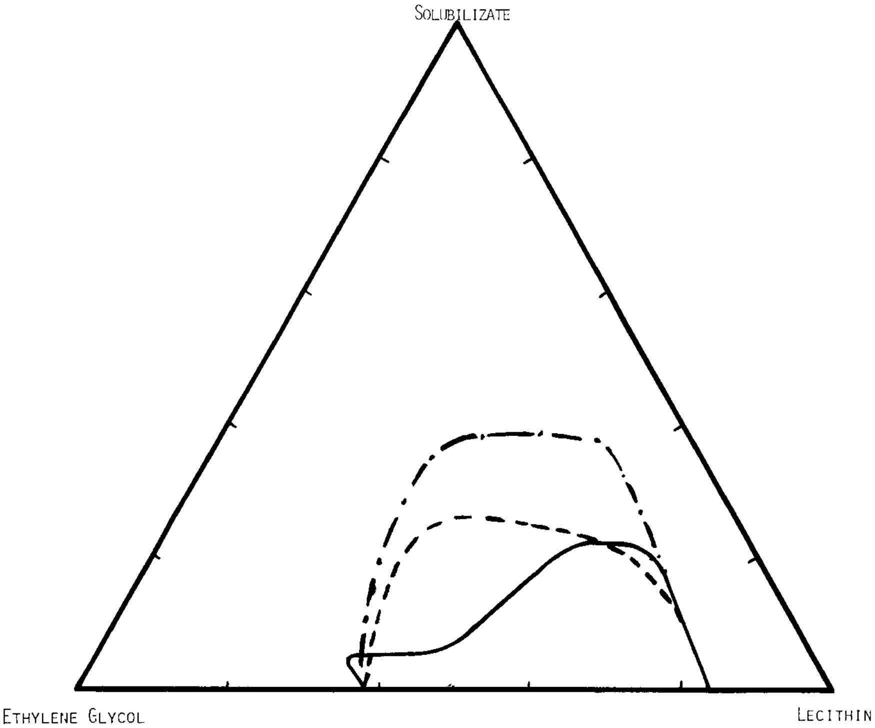

FIGURE 1 The liquid crystalline region in the system ethylene glycol, lecithin and solubilized component.

—Methanol
- - - Decanol
— · —Decane

The samples were removed from the vials and placed on the glass slides. For relaxation and thermal equilibration, these slides were immediately covered and kept for a few minutes at 25 °C level. The samples were then placed on a microscope between crossed polarizers. They were photographed at a magnification of 100x.

RESULTS

Solubilization of Alcohols

The liquid crystalline region in the system ethylene glycol, lecithin and methanol is given in Figure 1. The solubilization of methanol was approximately 20% for higher lecithin content and reduced to less than half that value for lecithin contents less than 60%. The decanol

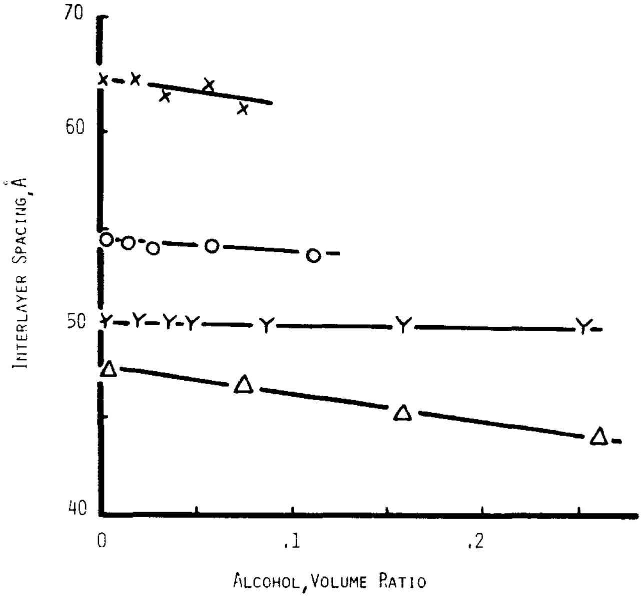

FIGURE 2 Interlayer spacing in the system ethylene glycol, lecithin and methanol.

Ethylene glycol/lecithin weight ratio	Sign
0.19	Δ
0.45	Y
0.67	○
1.00	×

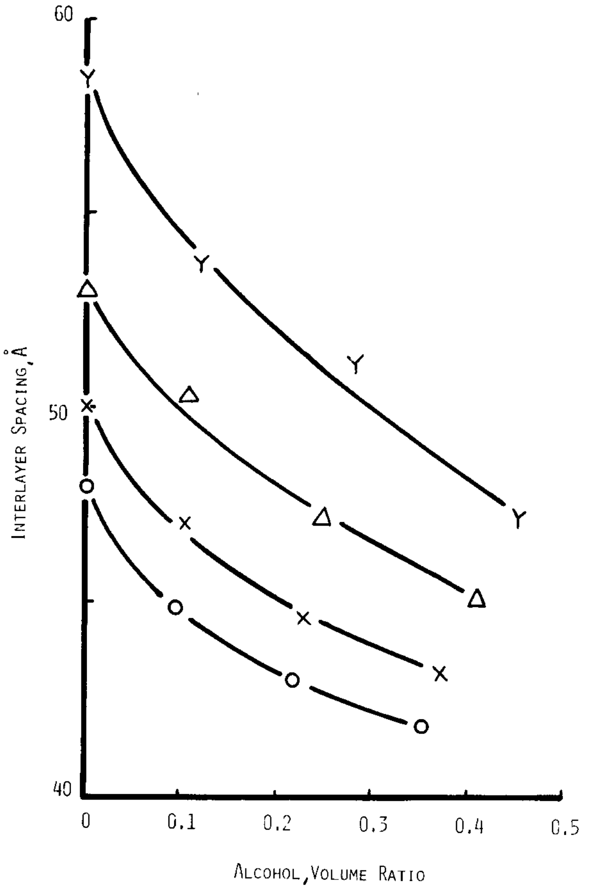

FIGURE 3 Interlayer spacing in the system ethylene glycol, lecithin and decanol.

Ethylene glycol/lecithin weight ratio	Sign
0.54	O
0.67	X
0.82	Δ
1.00	*Y*

and decane did not show such changes with the ethylene glycol/lecithin ratio. The decanol gave a solubilization of about 20% by weight for the entire region and decane gave a similar solubilization at 40%.

The interlayer spacings with methanol added are shown in Figure 2. Addition of alcohol gave no change in interlayer spacing.

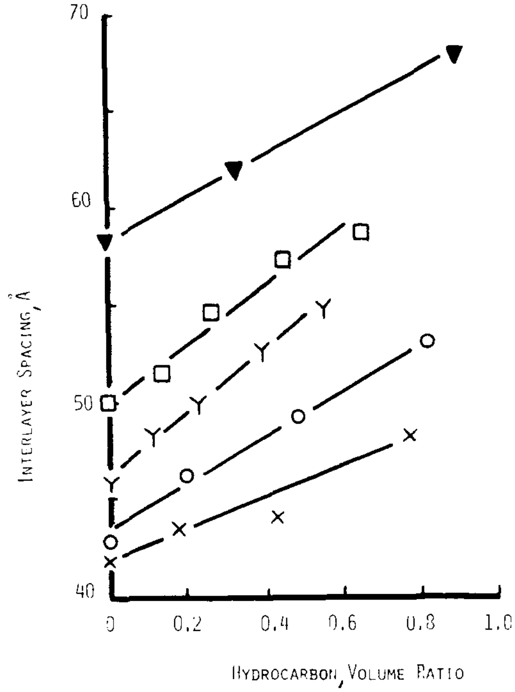

FIGURE 4 Interlayer spacing in the system ethylene glycol, lecithin and decane.

Ethylene glycol/lecithin weight ratio	Sign
0.11	×
0.25	○
0.43	Y
0.67	□
1.00	▼

The interlayer spacings with decanol solubilized are shown in Figure 3. The interlayer spacing was reduced on addition of alcohol with the reduction being larger for higher ethylene glycol content.

Solubilized hydrocarbon gave a strong increase of interlayer spacing as shown by Figure 4. The increase was similar for different fractions of ethylene glycol present.

DISCUSSION

The results clearly indicate the difference in the effect of the three classes of solubilizate on the structure of the lecithin/ethylene glycol lamellar liquid crystalline phase. Addition of hydrocarbon caused an increase in the interlayer spacing. This increase indicates a preferential location of the added hydrocarbon molecules between the lecithin hydrocarbon chain *layers* with little penetration occurring between the lecithin hydrocarbon chains. This result is in good agreement with investigations on lecithin/water systems.[13] McIntosh and collaborators found short chain alkanes to form a liquid alkane region between the amphiphile layers. Moucharafieh[14] gave a similar interpretation of his results of solubilized alkane in a water/polyethylene glycol dodecyl ether liquid crystal. Gruen[15-17] has made extensive statistical-mechanical calculations on amphiphilic bilayers with solubilized alkane chains. His results emphasize the fact that the hydrocarbon shows only a small degree of intercalation with the hydrocarbon chains of the amphiphile. Recent investigations by Ward[18] on the order parameter of solubilized hydrocarbons in the Moucharafieh system showed extremely small values of the order parameters indicating a liquid alkane layer in the structure.

The present experimental results showed the long chain alcohol, on the other hand, to cause a reduction of the interlayer distances. This reduction may be due to several factors of which an increased tilt of the amphiphile chains, an enhanced disorder of them due to difference in chain length between the alcohol and the lecithin and an augmented penetration of solvent molecules are immediately evident possibilities. Their potential for reducing the interlayer distance may be evaluated with simple geometric estimations.

A reduction of the interlayer spacing by 10 Å (Figure 3) would correspond to a tilt change of at least 38° if Tanford's values for chain length[19] are used. This change in tilt is too large to be reasonable and the enhanced disorder due to the difference in chain length of the alcohol and the lecithin must play a role. The reduction in interlayer spacing due to insertion of shorter alcohol molecules may be estimated in the following manner. Assume the alcohol to be inserted between the lecithin molecules. The alcohol is shorter by eight carbon units than the hydrocarbon chain of the lecithin. This difference represents a volume of 215 Å^3[19] for each chain.

Using this value the following expression is obtained for the reduction of interlayer spacing

$$\Delta = 14.1 - 990.5 f_L^M / (f_A A_A + f_L A_L)$$

in which

Δ = reduction of interlayer spacing
f_A = molecular fraction of alcohol
f_L = molecular fraction of lecithin
A_A = molecular area of alcohol
A_L = molecular area of lecithin

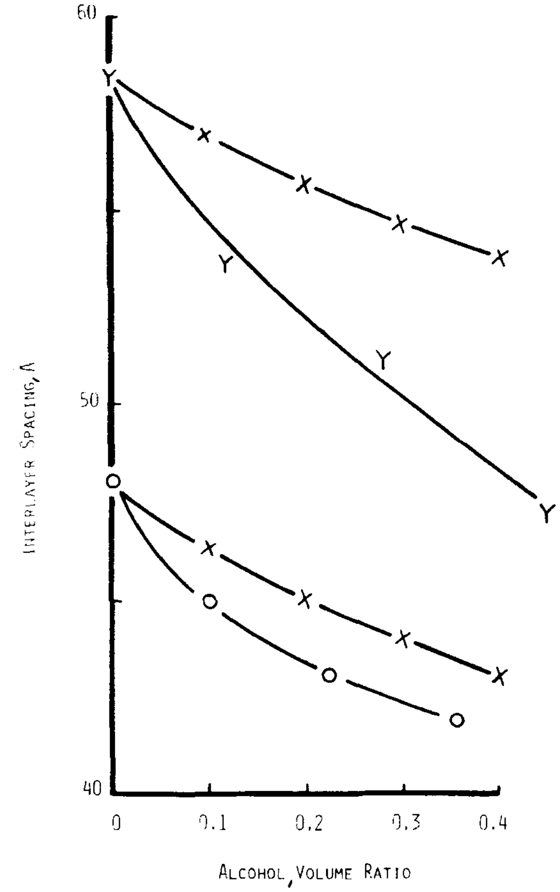

FIGURE 5 A comparison between calculated (×) (See text) interlayer spacings and experimental ones for ethylene glycol/lecithin weight ratios of 0.54 (○) and 1.0 (*Y*).

Ethylene glycol/lecithin weight ratio	Sign
0.54	○
1.00	*Y*

Putting $A_A = 21$ Å^2 and $A_L = 70$ Å^2,[6] the reduction of interlayer spacing is

$$\Delta = 14.1 - 1/\left(0.0707 + 0.0212 R^M_{A/L}\right)$$

in which $R^M_{A/L}$ is the alcohol/lecithin molecular ratio or approximately

$$\Delta = 14.1 - 1/\left(0.099 R^V_{A/L} + 0.0707\right)$$

in which $R^V_{A/L}$ is the alcohol/lecithin volume ratio.

A comparison between the calculated curve and the experimental one for the series with lowest ethylene glycol content is given in Figure 5. The reduction in interlayer spacing due to disordering caused by decanol voids in the structure covers most of the experimental reduction for the series with lowest ethylene glycol content. For the series with highest ethylene glycol content, on the other hand, only a minor fraction of the reduction is covered and it appears reasonable to conclude the presence of decanol to cause enhanced penetration of the solvent into the amphiphilic layer of lecithin.

The methanol gave no change in the interlayer spacing. It is a compound soluble both in the polar and the hydrocarbon parts of the structure. The invariance of interlayer spacing with its concentration is most probably a fortuitous consequence of alcohol partition between ethylene glycol and amphiphile to compensate the increase in interlayer spacing from the solubility in the solvent layer with the interlayer distance reduction from the partition between the lecithin molecules.

Acknowledgment

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References

1. D. F. Evans, S. H. Chen, G. W. Schriver and E. M. Arnett, *J. Am. Chem. Soc.*, **103**, 481 (1981).
2. D. F. Evans, A. Yamauchi, R. Roman and E. Z. Casassa, *J. Colloid Interface Sci.*, **88**, 89 (1982).
3. M. S. Ramadan, D. F. Evans and R. Lumry (In press).

4. P. A. Winsor, *Chem. Rev.*, **68**, 1 (1968).
5. N. Moucharafieh and S. E. Friberg, *Mol. Cryst. Liq. Cryst.*, **49**, 231 (1979).
6. M. A. El Nokaly, L. D. Ford, S. E. Friberg and D. W. Larsen, *J. Colloid Interface Sci.*, **84**, 228 (1981).
7. L. Ganzuo, M. El Nokaly and S. E. Friberg, *Mol. Cryst. Liq. Cryst.*, **72**, 183 (1982).
8. D. W. Larsen, S. E. Friberg and H. Christenson, *J. Amer. Chem. Soc.*, **102**, 6565 (1980).
9. D. W. Larsen, S. B. Rananavare, M. El Nokaly and S. E. Friberg, Finnish Chemical Letters (Festschrift for Ingvar Danielsson) (1982) pages 96–104.
10. R. C. McDaniel, T. J. McIntosh and S. A. Simon, *Biochemical et Biophysica Acta*, **731**, 97 (1983).
11. B. Schobert, *J. Naturforsch.*, **34c**, 699 (1979).
12. Q. F. Ahkong, D. Fisher, W. Tampion and J. A. Lucy, *Nature*, **253**, 194 (1975).
13. T. J. McIntosh, S. A. Simon and R. C. MacDonald, *Biochimica et Biophysica Acta*, **597**, 445 (1980).
14. N. Moucharafieh, S. E. Friberg and D. W. Larsen, *Mol. Cryst. Liq. Cryst.*, **53**, 189 (1979).
15. D. W. R. Gruen and D. A. Haydon, *Biophys J.*, **33**, 167 (1980).
16. D. W. R. Gruen, *Biochim. Biophys. Acta*, **595**, 161 (1980).
17. Idem, *Chemistry and Physics of Lipids*, **30**, 105 (1982).
18. A. J. I. Ward, S. E. Friberg and D. W. Larsen, ACS Symposium Proceedings (Washington, DC August 1983) (In press).
19. C. Tanford, *J. Phys. Chem.*, **78**, 2469 (1974).