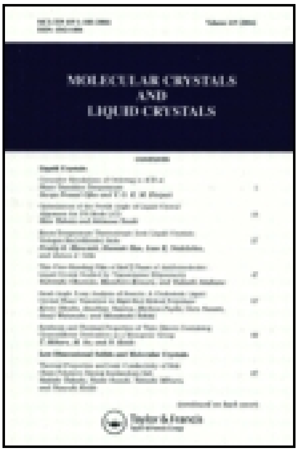

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Mesomorphic Behaviour of Lauric Acid in Dimethyl Sulphoxide

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Mesomorphic Behaviour of Lauric Acid in Dimethyl Sulphoxide

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XRD, DSC and optical texture studies show that mixtures of lauric acid in dimethyl sulphoxide exhibit a lamellar mesophase.

Keywords: lamellar mesophase, lauric acid

INTRODUCTION

Lyotropic liquid crystals are formed by the action of a solvent on an amphiphilic substance since environment around the polar part is changed by the presence of the solvent.[1–2] The early works on such systems[3–8] have focussed entirely on water as solvent. However, non-aqueous lyotropic liquid crystals have been found in polymer/organic solvent combinations.[9–10] The Friberg group has reported the first non aqueous counterpart to the common aqueous systems with surfactants.[11] Somashekar *et al.*[12] have also reported with the existence of lamellar (G) phase in a mixture of non-aqueous systems. Recently, Marthandappa *et al.*[13] have reported the presence of a thermotropic mesophase in a mixture of non-mesogenic compounds.

Since these systems exhibit novel phase behaviour, we found that further investigation into their properties to be of interest. The present paper describes the mesomorphic behaviour observed in the mixture of lauric acid (LA) with dimethyl sulphoxide (DMS) as solvent.

EXPERIMENTAL AND RESULTS

(a) Samples: lauric acid supplied by Sigma (L4250) was used without further purification. The transition temperature was found to be 44.8°C and is in agreement with the standard value.[14] Analar grade DMS supplied by M/S SISCO Research Laboratory was used without purification. The clearing point from mesomorphic phase to isotropic phase of 80% and 90% (by weight) of LA in DMS was determined using the Leitz's polarising microscope in conjunction with a hot stage.

(b) DSC studies: DSC recordings, both in the heating and cooling modes were taken using METTLER TA 3000 SYSTEM for the concentrations 90% and 80% by weight of LA in DMS. For 90% (by wt) concentration of LA in DMS, DSC recordings (in cooling & heating modes) are illustrated in Figure 1. It is evident from Figure 1 that the isotropic to mesomorphic and mesomorphic to solid phase are first order transitions. The transition temperatures in the cooling mode are slightly different compared to the heating mode due to the supercooling property of the mixtures. From the thermographs, the transition temperatures were determined to within ±0.5°C. It is observed that the mesomorphic range increases with increase of concentration of LA in DMS. It must be remarked here that no mesomorphic phase was observed for concentrations below 80% of LA in DMS at room temperature. The transition temperatures obtained from DSC and microscopic studies are in agreement and are given in Table I. We have also obtained the enthalpy from the peak area using the DSC curves and with baseline type 8 integration option, which corrects for the base line curve at the starting and end of the measurements. These values are given in the Table I. The standard deviation

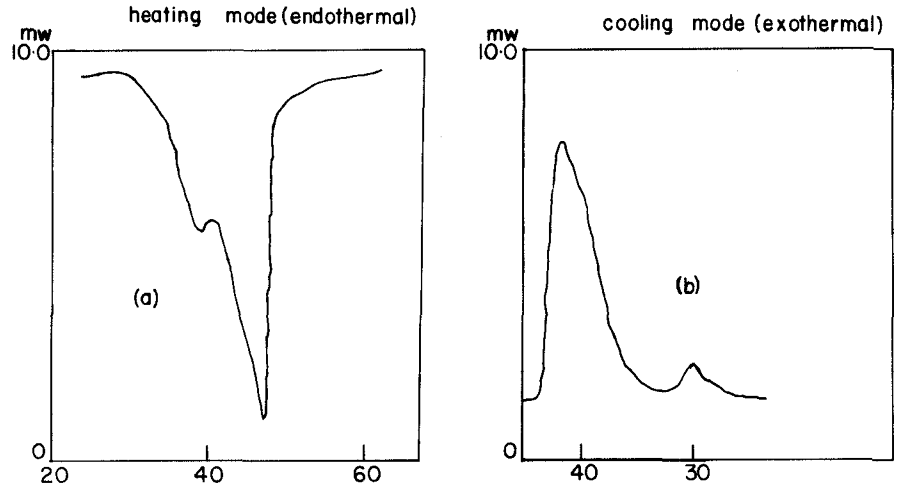

FIGURE 1 DSC recording of 90% (by wt) of LA in DMS.

TABLE I

Transition temperatures obtained by DSC and change in enthalpy (exothermal) (values obained from microscopic studies are given in brackets)

Concentration of LA in DMS (wt%)	Transition temp in °C		Change in enthalpy Δ in cal/gm	
	Iso-Meso	Meso-Solid	Iso-Meso	Meso-Solid
80	32.7 (32.5)	24.0	10.27	4.39
90	41.2 (41.0)	30.5	15.05	6.44

in the calculated values of enthalpy is ±1.2 cal/gm. It can be seen that the mesomorphic-isotropic transition involves a greater enthalpy change than the mesomorphic-solid transition with alteration in ordering.

(c) X-ray studies: X-ray diffraction patterns with 80% and 90% of LA in DMS taken on a glass slide without cover slip and without any definite orientation were recorded using JEOL (Japan) X-ray Diffractometer (XRD) by varying the scanning angle from 1° to 30° (in 2θ), with a scanning speed of 1°/min, and chart speed of 40 mm/min. Two sets of samples for each concentration were used to detect the consistency of the recordings. Manganese filtered Fe radiation (λ = 1.934 Å) was used for both the concentrations. The recordings were taken at room temperature. The X-ray diffractometer records taken for LA (90% wt) in DMS is shown in Figure 2. The geometry of XRD is such that the diverging beam is incident on the sample and scattered beam is focussed on to the detector. For the calculation, we have used the formula $2d \sin \theta = \lambda$, as the diffraction rings are sharp. There is a sharp inner ring as shown in the X-ray recordings. This ring corresponds to the first order diffraction from the set of layer like planes and along with the reflections 2 and 5, the '*d*' spacings are in the ratio 1:1/2:1/5. The effective spacing determined using the above equation, denoted by '*d*' is 26.1 Å. The third and fourth reflections correspond to the planes with '*d*' spacings 8.4 Å and 5.4 Å, and the corresponding relation to the earlier reflections is not clear to us. These are given in Table II. From the skeletal structure of LA, the molecular length turns out to be 17.1 Å and the ratio of the effective spacing determined from the inner ring to the estimated

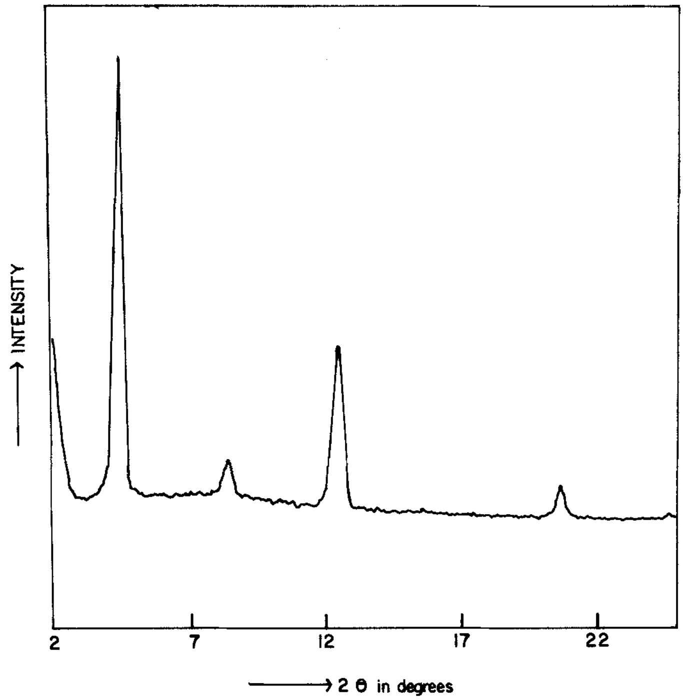

FIGURE 2 X-ray diffraction recording of 90% (by wt) of LA in DMS, at room temperature.

TABLE II

'*d*' Spacings, surface area per polar groups (*S*) obtained from XRD readings and density (ρ) and refractive index (*n*) at 300°K

Concentration of LA in DMS (wt%)	'd' spacings in Å				S Å^2	ρ gm/cc	n
	d_0	d_1	d_2	d_3			
80	26.1	13.5	8.4	5.4	32.49	0.846	1.448
90	26.1	13.9	9.0	5.4	31.47	0.939	1.444

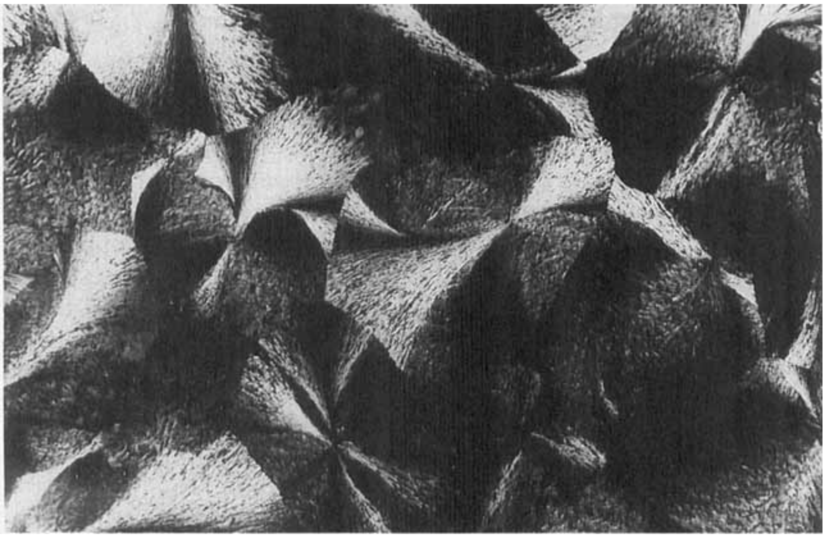

FIGURE 3 Microphotograph of focal conic texture observed between crossed polars. Magnification 160×.

length of LA, including correction for thermal expansions,[15] turns out to be 1.5. A number of examples and explanations are now known where '*d*' is greater than the estimated length (1).[16–17] It is possible to explain the difference (*d* − 1) in terms of an interdigitated dimer model with room filling by dimethyl sulphoxide molecules. The area per polar group (*S*) was calculated using the layer spacing, densities of the solutions, molecular weight and wt% of the solutions and this value is given in Table II.[18] With increase in concentration of LA in DMS, we find that there is slight decrease in the value of *S*. But significantly, we also find that the intensity of all reflections observed decreases with concentrations of LA in DMS and these results are in agreement with enthalpy studies.

(e) Optical studies: A sample of 80% of LA in DMS taken between a microscopic slide and cover slip shows characteristic focal conical texture (Figure 3) when observed between crossed polarisers using the Leitz microscope at room temperature. This is characteristic of a lamellar phase. Apart from this, we could not observe any other texture either by cooling or heating in either concentration.

Optical birefringence: We have measured for both concentrations, the density and refractive index at room temperature using the technique described earlier.[19] With this technique, we could measure only one refractive index. Under these circumstances, we have determined Δn for a sample prepared, using the Leitz microscope, on a microscope slide in conjunction with a Brace-Köhler compensator and the estimated value is 0.005 (λ = 5893 Å). We have also used the interference technique employed by Krishnamurthi *et al.*[20] to determine the birefringence of the sample taken on a microscope slide. This value is 0.0048 (λ = 5893 Å) and is in very good agreement with the earlier result. Using these value and Vuk's relation,[21] we have estimated the optical anisotropy ($\Delta\alpha$) to be less than 1×10^{-24} cm^3.

CONCLUSION

DSC, XRD and optical studies clearly indicate that the mixtures of LA in DMS above 80% exhibit a lamellar mesophase in which the molecules are arranged in an interdigitated model with room filling by DMS.

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