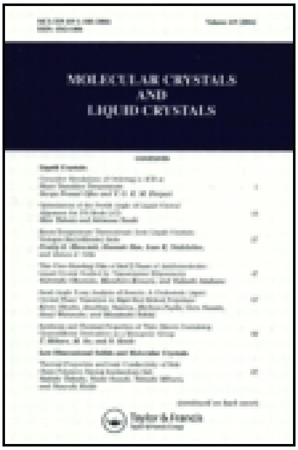

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Lamellar Mesophase(G) in Mixtures of Stearyl Alcohol and Dimethyl Sulfoxide

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Version of record first published: 20 Apr 2011.

To cite this article: R. Somashekar, C. H. Satyanarayana & M. S. Madhava (1985): Lamellar Mesophase(G) in Mixtures of Stearyl Alcohol and Dimethyl Sulfoxide, Molecular Crystals and Liquid Crystals, 131:1-2, 79-90

To link to this article: http://dx.doi.org/10.1080/00268948508084194

Mol. Cryst. Liq. Cryst., 1985, Vol. 131, pp. 79–90
0026-8941/85/1312-0079/$20.00/0

Printed in the United States of America

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(*Received January 16, 1985*)

Using X-ray, DSC and Optical studies, the mixtures of stearyl alcohol and dimethyl sulfoxide were found to exhibit lamellar mesophase(G) with double layer of molecules separated by dimethyl sulfoxide layers. A phase diagram for this binary mixture is also given.

INTRODUCTION

Liquid crystalline behaviour of numerous organic compounds with long chain molecules, has been the subject matter of a number of investigators. Mesomorphic behaviour of mixtures of non-mesogenic and mesogenic and of mixed liquid crystals has been well investigated.[1-4] Liquid crystallinity in binary mixtures of non-mesogenic compounds is also well known.[5-6]

Alcohols have been used extensively in the binary mixtures with a mesogenic as the other component to study the changes in phases, in transition temperatures and also in pitch of the cholesteric compounds.[7-17] Apart from these studies alcohols have been used extensively in ternary mixtures exhibiting lyotropic mesomorphism[18-25] and their structures are well established by investigators like Ekwall, Fontell, Winsor and others.

A first comparison between aqueous and non-aqueous lyotropic liquid crystalline systems of lecithin/ethylene glycol and lecithin/water systems using X-ray and optical microscopy has been carried out by Moucharafieh and Friberg[26] and dynamics of such systems has been investigated by Larsen et al.[27] by observing the NMR quadrupole splitting.

We report here the non-aqueous binary mixtures of stearyl alcohol with dimethyl sulfoxide, the lamellar mesophase(G) which exists over a broad range of temperature and composition. X-ray diffraction[28,29] and optical studies[6] have been employed.

EXPERIMENTAL

a) Transition studies

Stearyl alcohol supplied by M/s Chemical International, Bombay was further purified with benzene and dried. The transition temperature was found to be 59°C and is in agreement with the standard value.[30]Analar grade dimethyl sulfoxide(DMS) supplied by M/s Sisco Research Lab., Bombay, was used without further purification. The sample was taken in a capillary tube and was sealed. In conjunction with a hot stage, the clearing point from mesomorphic phase to isotropic phase was determined. This procedure was repeated for different concentrations of stearyl alcohol in DMS.

DSC studies

For 30 wt percentage of stearyl alcohol in dimethyl sulfoxide, DSC (Perkin-Elmer, Model DSC-2) recording (heating mode) is illustrated in Figure 1. It is evident from the Figure 1 that the solid to mesophase, and mesophase to isotropic transitions are of the first order transition. Similar thermograms were obtained for all other concentrations of stearyl alcohol in dimethyl sulfoxide. From these thermograms, the transition temperatures to within ±0.5°C and all involving endothermic changes on heating are shown in Figure 2 which represents the phase diagram. As can be seen from the phase diagram that the mesomorphic range decreases with increase in concentration of stearyl alcohol. It may be remarked here that the smectic to isotropic transition lies below the melting point of stearyl alchol. The variation in transition temperatures exhibits a minimum as is usual in the case of mixtures.[31-33] The transition temperatures determined from DSC (heating and cooling) and microscopic studies are in agreement. Using the standard procedures,[34] we have obtained the enthalpies from the areas under the corresponding peaks in DSC curve and are given in Figure 3 for various concentrations. The standard deviation in the calculated value of ΔH is ±0.2 cals/gm. The instrument was cali-

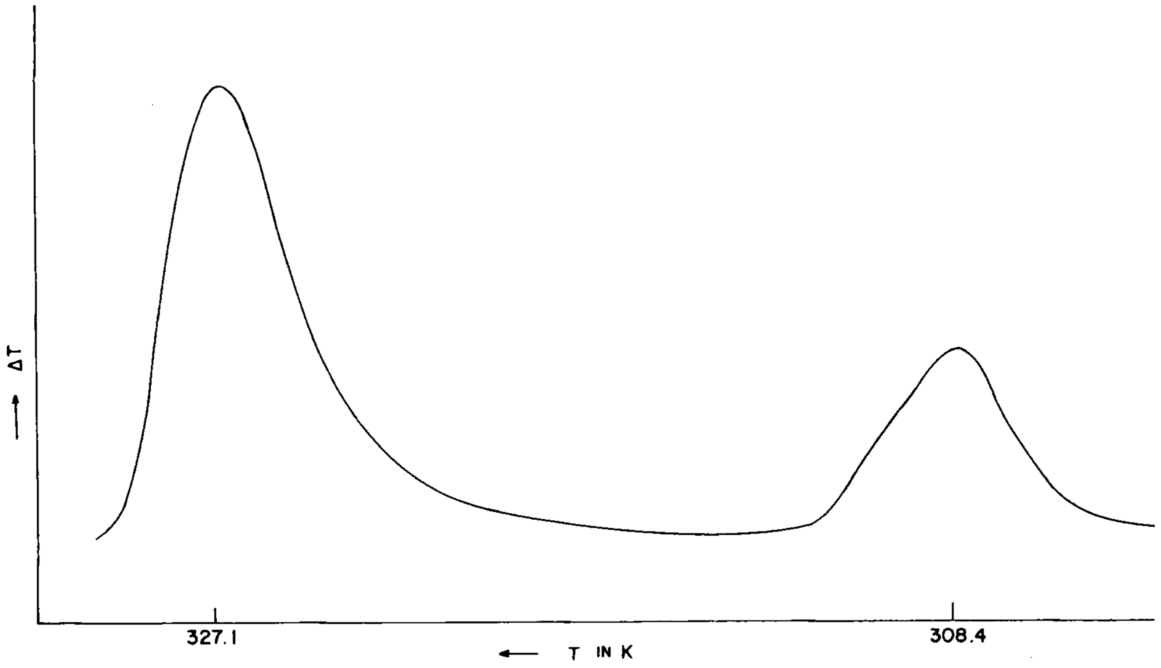

FIGURE 1 DSC thermogram of 30 per cent by weight of stearyl alcohol in dimethyl sulfoxide. X-axis-T and Y axis-ΔT. Heating rate 10°/min, sample size 4.703 mg and 10 m cal/sec.

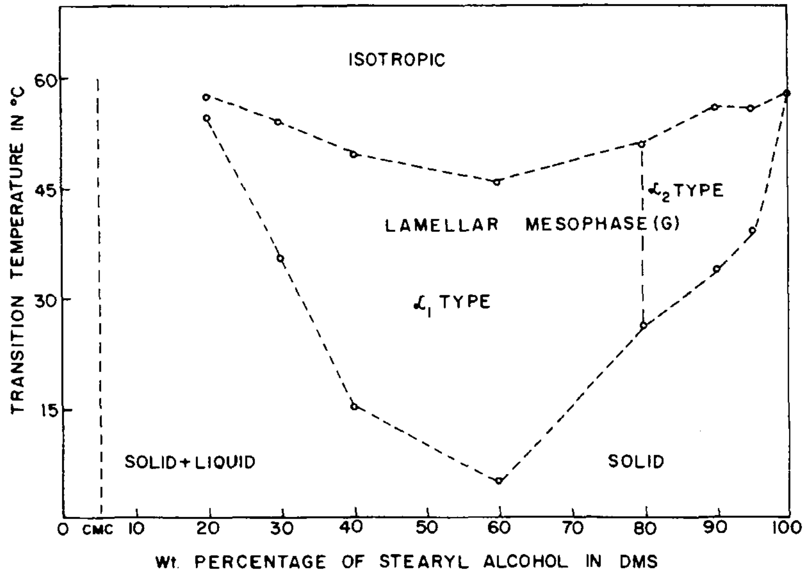

FIGURE 2 Phase diagram of stearyl Alcohol in dimethyl sulfoxide obtained by DSC studies.

brated using semiconductor grade Indium. It can be seen that the lamellar mesophase to isotropic transition involves the greater enthalpic change than the solid to lamellar mesophase, consistent with the greater alteration in ordering.

b) X-ray studies

X-ray diffraction pattern from samples of different concentrations of stearyl alcohol in dimethyl sulfoxide taken on a glass slide, without coverslips and without any definite orientations, were recorded using JEOL (Japan) X-ray diffractometer by varying scanning angle from 1 to 40°, with following specifications: 30 kv, 35 ma, scanning speed of 1 degree per minute, and chart speed of 20 mm/min. Two sets of samples were used to check the consistency of the recording. Manganese filtered Fe radiation was used. For all the samples, the recordings were taken at room temperature. X-ray diffractometer recording taken for a mixture of stearyl alcohol (30 wt per cent) in dimethyl sulfoxide is shown in Figure 4. The geometry of the XRD is such that a diverging beam is incident on the sample and the scattered beam is focussed on to the detector.

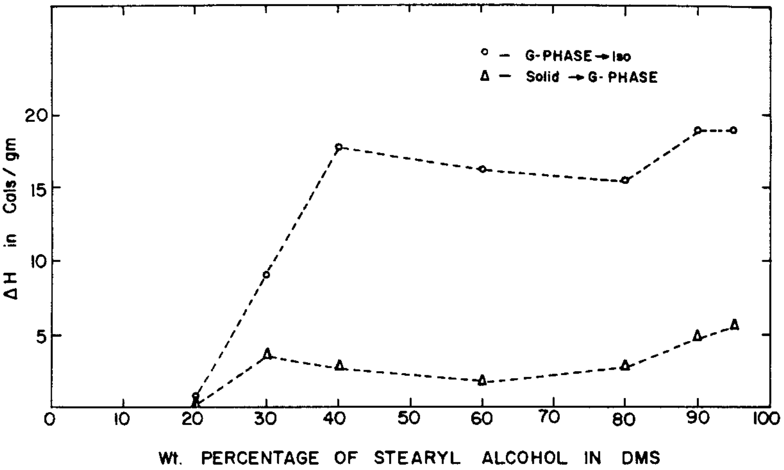

FIGURE 3 Variation of enthalpy (cals/gm) with concentration of stearyl Alcohol in DMS.

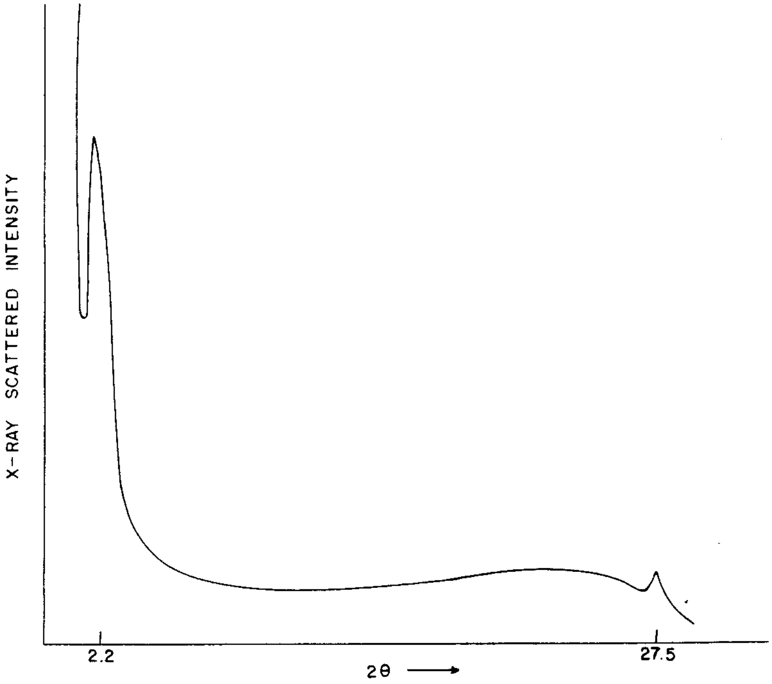

FIGURE 4 X-ray diffractometer recording for 30 per cent by weight of stearyl Alcohol in dimethyl sulfoxide.

For the calculation of the intermolecular distances, i.e., the average distance between the long axes of neighboring parallel molecules, from the diffraction angle of the outer diffraction ring, we have used the formula $2D \sin\theta = \lambda$, as the diffraction rings are sharp. The measured spacing turns out to be 4.1Å. Apart from this ring there is a sharp inner ring as shown in X-ray recording. This ring corresponds to the first order diffraction from the set of smectic layer like planes. The effective spacing determined using the above equation, denoted by 'd' is 50Å. This corresponds to the smectic layer spacing. The values obtained for different concentrations of stearyl alcohol in DMS are tabulated in Table I.

TABLE I

Spacings determined using XRD recordings calculated values of S, the interfacial area per polar group and d_{hc} the average thickness of the hydrocarbon layers obtained for different concentrations of stearyl alcohol in DMS

wt.percent of stearyl alcohol	d in Å	D in Å	S in Å^2	d_{hc}
20	-	-	-	-
30	50.4	4.1	66.7	44.85
40	53.3	4.1	50.2	44.69
50	58.6	4.1	39.5	45.47
60	59.9	4.1	35.9	41.66
70	59.6	4.1	36.0	35.61
	56.8			
80	27.7	4.1	42.6	26.36
	17.1			
90	-	-	-	-

d_s = 5.5 Å, minimum thickness of DMS.

From the skeletal structure of stearyl alcohol, the molecular length turns out to be 24Å (fully extended). The effective spacing determined using XRD is 53Å and hence corresponds to twice the molecular length of stearyl alcohol. Here the stearyl alcohol molecules are arranged alternatively in planar double layers with a constant repeat distance between the double layers, separated by dimethyl sulfoxide layers (see Figure 5.2(a) p.202, Ref.24, Vol.I). X-ray spacings are in the ratio 1:1/2:1/3 (Table I) for higher concentrations of stearyl alcohol. X-ray diffraction recordings show only one low angle ring and one outer ring for concentrations below 80% indicating that there is a gradual change of phase with concentration from lamellar mesophase G (type α_1) to lamellar mesophase G(type α_2).[35] In fact from the variation of the interfacial area per polar group(S) on the lamellar face with bulk concentration, which is given in Table I clearly indicates the two phase region. The area (S) per polar group was calculated using the X-ray layer spacings, densities of the solutions, molecular weight and wt concentration of the constituents.[36] We have compared the variation of S per polar group with wt per cent of stearyl alcohol in DMS[6]. The above results are in agreement with the enthalpy studies, wherein the enthalpy associated with lamellar mesophase to isotropic transition increases with concentration of stearyl alcohol, consistent with the greater alteration in ordering for the lamellar mesophase G (type α_2). Because of experimental difficulties, we were unable to study the temperature variation of S, the interfacial area per polar group.

c) Optical studies

Optical textures: Stearyl alcohol solution in DMS (30 wt per cent, isotropic phase) is allowed to flow into the cross between four 1 cm square coverslips (0.2 mm thick) arranged on a slide and covered with a 2 cms square coverslip and the sample is allowed to undergo peripheral cooling to room temperature, a band of the G phase appears at the edge of the slide and extends slowly inwards. With 80 wt% of stearyl alcohol in DMS, the G phase succession from type α_1 to type α_2 could not be detected at room temperature with addition of DMS, using polarizing microscope. The texture photographs reproduced here correspond to the separated lamellar mesophase using centrifuge technique (swinging type). When this sample was allowed to cool from isotropic phase, there occurred the growth of the batonnets (Figure 5(a)) which could be observed between cross polars. Using interference technique described in an earlier paper,[37] it was found that the long axes of the molecules are parallel to the length of the batonnet, indicating that they are G batonnets. In some regions rounded G droplets were also observed. The displacement of the coverslip gave 'Oily streaks' pattern and it is shown in Figure 5(b). The 'oily streaks' are formed in the wake of air bubbles present in the medium and here also the molecules are parallel to the length of the streaks. When the substance was cooled to room temperature, the typical focal conics are observed and are shown in Figure 5(c).

Optical anisotropy: For the different mixtures prepared by us, the densities and refractive indices were determined using the techniques described earlier.[38] These are tabulated in Table II. Here n_e and n_o in Table II are respectively the extraordinary and ordinary refractive indices, indicating that the material is uniaxial positive, as is the

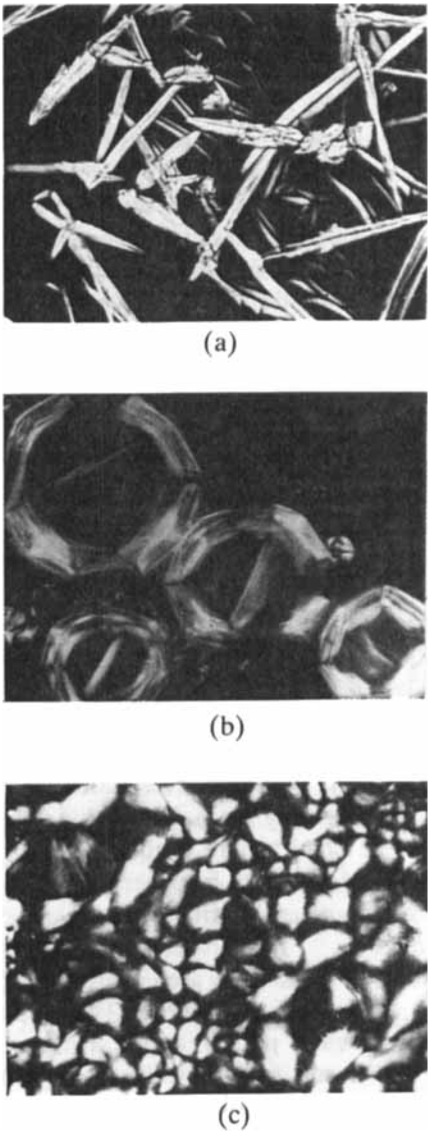

FIGURE 5 Microphotographs of—a) Batonnets (63 ×), b) Oily streaks (270 ×), and c) Focal conics (270 ×) observed in a mixture of stearly alcohol and DMS.

TABLE II

Refractive indices and densities of the mixtures of stearyl alcohol and DMS for λ5893 at different temperatures (when cooled from the Isotropic phase)

wt percentage of stearyl alcohol	Temp. in °C	30	34	38	42	46	50	54	58
	n_e	-	-	-	-	-	-	1.502	-
20%	n_o	-	-	-	-	-	-	1.472	1.453(iso)
		-	-	-	-	-	-	0.964	0.933
	n_e	-	-	1.500	1.495	1.490	1.468	-	-
30%	n_o	-	-	1.476	1.471	1.469	1.458	1.453	-
		-	-	1.114	1.081	1.052	1.031	(iso)	-
								1.007	
	n_e	-	-	1.504	1.500	1.497	-	-	-
40%	n_o	-	-	1.477	1.474	1.470	1.452	-	-
		-	-	1.124	1.096	1.077	(iso)	-	-
							1.028		
	n_e	1.504	1.500	1.497	1.477	-	-	-	-
60%	n_o	1.477	1.473	1.468	1.457	1.448	-	-	-
		1.113	1.088	1.066	1.011	(iso)	-	-	-
						1.001			
	n_e	-	1.504	1.501	1.497	1.489	-	-	-
80%	n_o	-	1.474	1.468	1.465	1.462	-	1.453	-
		-	1.002	0.972	0.952	0.932	-	(iso)	-
								0.908	
	n_e	-	-	-	1.503	1.495	1.490	-	-
90%	n_o	-	-	-	1.478	1.467	1.462	-	1.447(iso)
		-	-	-	1.043	1.004	0.988	-	0.909

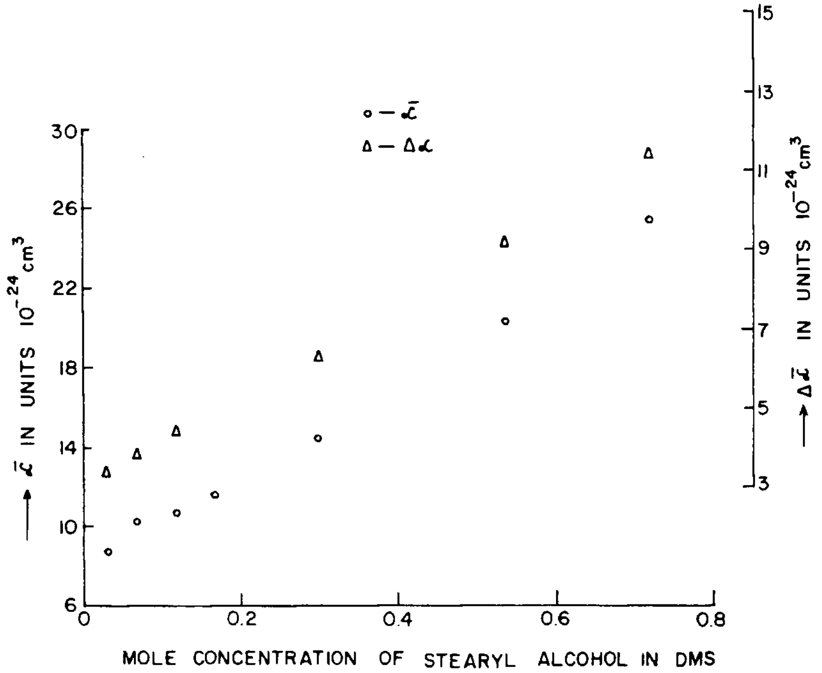

FIGURE 6 Variation of $\bar{\alpha}$ and $(\alpha_e - \alpha_o)$ with the concentration of stearyl alcohol in DMS.

characteristic of the smectic phase. A detailed discussion of the determination of the indices using the Abbe refractometer and the method of identification of n_e and n_o was given in an earlier paper.[38] The effective polarizabilities are calculated from the Lorenz-Lorentz formula.[37] For example for the extraordinary index n_e

$$\frac{n_e^2 - 1}{n_e^2 + 2} = \frac{4\pi N\alpha_e}{3} (mix) \tag{1}$$

By using a correspondingly similar equation for n_o, it is possible to calculate the effective polarizability for the ordinary ray. For all the concentrations the birefringence is relatively low. Hence, any anisotropy in the Lorentz field factors may be neglected and the use of Lorenz-Lorentz relation is justifiable. The following conclusions emerge from our calculations. For a given concentration of mixtures, the values of $(\alpha_e - \alpha_o)$ decrease with increase of temperature very slowly indicating that there is no major change in molecular ordering with temperature. Further, the values of ($\alpha_e - \alpha_o$) and $\bar{\alpha}$ increase with increase of concentration because the effective optical anisotropy associated with the molecules of stearyl alcohol is far greater than that associated with DMS and this is clearly indicated in Figure 6.

DSC, XRD, Optical textures and interference studies clearly indicate that the mixtures of stearyl alcohol in DMS (a non-aqueous), exhibits lamellar mesophase(G) (α_1 and α_2 types) in which the molecules are arranged alternately in planar double layers separated by dimethyl sulfoxide layers.

Acknowledgment:

Authors thank the University Grants Commission, New Delhi (India) for financial assistance. We are thankful to Professor S. Chandrasekhar, Raman Research Institute, Bangalore, for permitting us to use the DSC equipment and Dr. U. D. Prahllad, CISL, University of Mysore, for his assistance in taking the XRD recordings.

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