Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Mesomorphic phases in mixtures of two non-mesogenic Compounds

Nagappa [a], S. K. Naveen Kumar [a], J. Mahadeva [a] & P. Nagaraj [b]

[a] Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, India

[b] Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore, India

Version of record first published: 18 Oct 2010

To cite this article: Nagappa, S. K. Naveen Kumar, J. Mahadeva & P. Nagaraj (2004): Mesomorphic phases in mixtures of two non-mesogenic Compounds, Molecular Crystals and Liquid Crystals, 409:1, 1-8

To link to this article: http://dx.doi.org/10.1080/15421400490435459

*Mol. Cryst. Liq. Cryst.*, Vol. 409, pp. 1–8, 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490435459



# MESOMORPHIC PHASES IN MIXTURES OF TWO NON-MESOGENIC COMPOUNDS

*Nagappa, S. K. Naveen Kumar, and J. Mahadeva*
*Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570 006, India*

*P. Nagaraj*
*Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India*

*The binary mixture of non-mesogenic compounds a sodium lauryl sulphate (SLS) and ethylene glycol (EG) exhibits a liquid crystalline phase over a large range of concentrations and temperatures. The concentration of 40% of SLS exhibit I–Sm A–Sm E–Cry sequentially when the sample is cooled from the isotropic phase. Spectroscopic studies like UV, IR, and $^1H$ NMR, have been carried out to understand the molecular dynamics of the mixtures. The phases were identified by optical, X-ray and DSC studies. Temperature variation of the optical anisotropy of these mixtures is also discussed. The free energy per unit area and Helfrich potentials are estimated in the lamellar phase using the Helfrich model.*

*Keywords*: bulk modulus; halfrich potential; mesomorphicphase; non-mesogenic

## INTRODUCTION

Binary mixtures of two non-mesogenic compounds exhibit both lyotropic and thermotropic mesophases [1]. Molecular ordering in lyotropic mesophases for the majority of amphiphilic systems correspond to the smecticlike phase, however frequently some mixtures encounter lyotropic nematic and chiral nematic phases in which micellar aggregate in the medium [2]. Thermotropic and lyotropic substances which are exhibiting several mesophases may be classified according to the same space group. From the microscopic point of view, the thermotropic and lyotropic mesogenic molecules are quite different owing to their shape and chemical

Address correspondence to S. K. Naveen Kumar, University of Mysore, Manasagangotri, Mysore 570 006, India.

structure. Among the other earlier investigators Nagappa *et al.* reported the lyomesophase behaviour for a mixture of cetyl alcohol and $H_3PO_4$ [3], sodium oliate and glacial acetic acid [4] such mixtures exhibit several mesophases over a wide range of concentrations and temperatures.

In the present investigation, we consider two non-mesogenic compounds viz sodium lauryl sulphate(SLS) and ethylene glycol(EG). To investigate the chemical nature and mesophase behaviour we have studied the optical and thermal properties of the mixtures. Optical texture, X-ray, NMR, and IR studies were carried out to investigate the molecular ordering in these mixtures.



## EXPERIMENTAL

The mixtures of ten different concentrations of sodium lauryl sulphate (SLS) and ethylene glycol (EG) were prepared by purifying the SLS twice using benzene as solvent by evaporation technique. The transition temperatures of the different concentrations were determined using the optical microscopy. These transition temperatures of the mixtures obtained from texturual studies are in good agreement with the transition temperatures obtained from DSC thermograms. The transition temperatures are drawn against concentrations to obtain the phase diagram which is as shown in Figure 1.

The phase diagram illustrates that the lower concentrations of SLS shows only smectic A phase (Sm A) at higher temperature and crystalline phase at lower concentration but the concentrations from 40% to 90% of SLS shows Sm A phase at higher temperatures and Sm E phase at lower temperatures. It is observed that the biphase region are obtained i.e. (crystalline and Sm E phase) at lower and higher concentrations of SLS. In the case of 10% of SLS and below we observe only the Sm A phase from temperature 40°C to 60°C.

## RESULTS AND DISCUSSION

### Optical Studies

For the observations of the optical textures, the sample is sandwiched between the slide and a cover glass and melted by keeping it in a hot stage. The temperature of the sample can be controlled by voltage stabilizer. The textures were observed under a polarizing microscope and hot stage. Various polymorphic smectic modifications and the phase transition temperatures of 40% of SLS in EG are shown sequentially.

I 128°C Sm A 88°C Sm E 60°C Cr

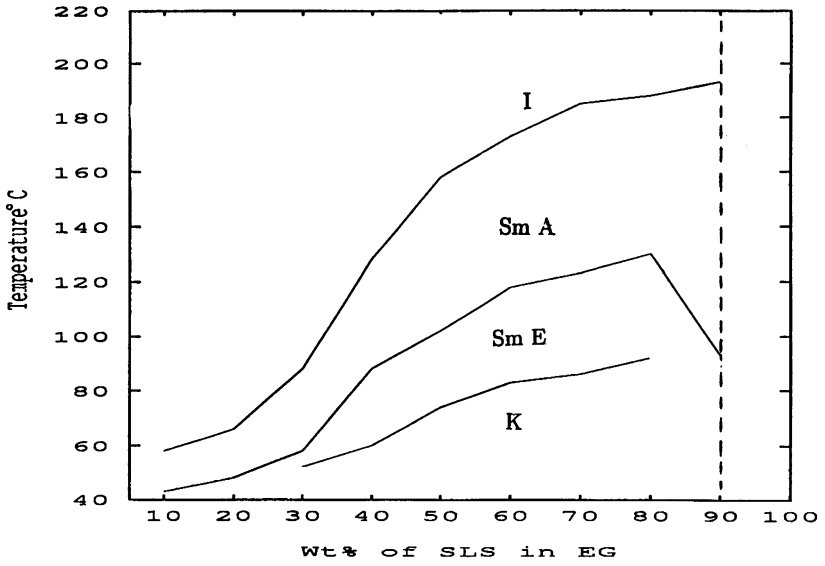



**FIGURE 1** Partial phase diagram of wt% SLS in EG.

When the specimen is cooled form its isotropic liquid phase, the setting point is marked by the genesis of nucleation at several points which appears as minute bubble initially, but which progressively grow radially and form a focal conic texture of the smectic A (lamellar) phase in which the molecules are arranged in layers, as shown in Figure 2(a). This phase is appears to be metastable and slowly changes over to smectic E phase in which molecules are arranged in herringbone pattern, see Figure 2(b).

## X-ray Studies

X-ray diffractometer traces were obtained at different temperature for the Sm A and Sm E phases of the 40%, 60%, and 80% of the SLS sample. The X-ray diffractometer trace is taken for 40% of SLS in EG at 120°C and 105°C, and the trace consists of two sharp peaks at $2\theta = 3.5^\circ$ and $6.5^\circ$, and it is characteristics of Sm A phase. The peak at $3.5^\circ$ is sharp owing to the fact that within each layer there is an exactly regular arrangement of molecules in the lateral direction laying in the plane of each layer. The X-ray diffractogram of the 40% of SLS which is taken at 120°C is shown in Figure 3. The diffractograms obtained at different temperatures for different concentrations exhibit a sharp peak at the same low angle.

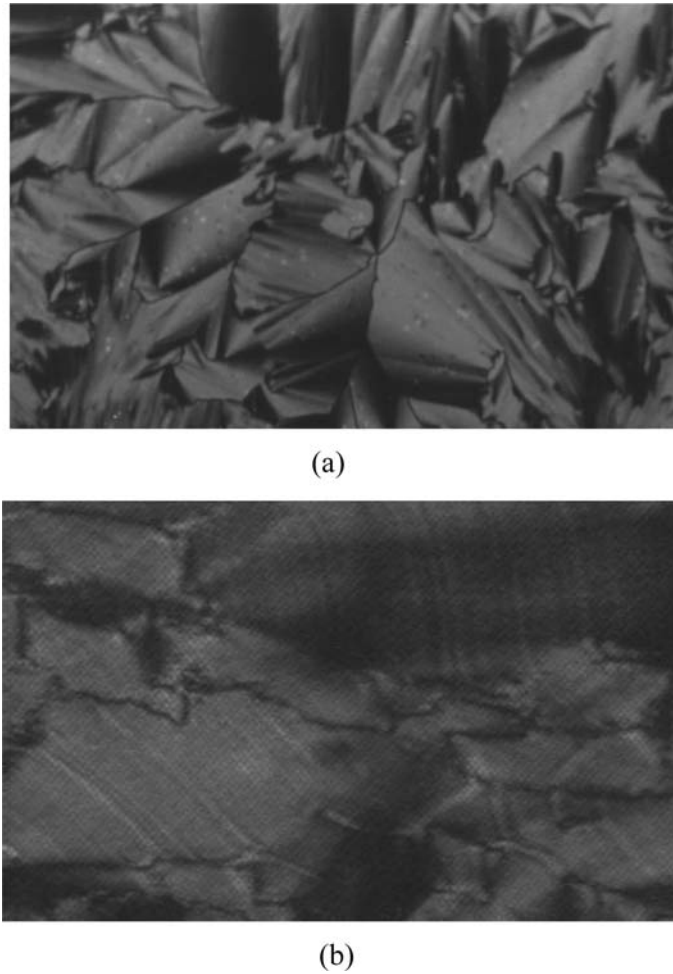



**FIGURE 2** (a) Microphotographs of Sm A (180X) (b) Microphotographs of Sm E (220X).

This is indicative of the fact that the d spacing in the smectic phase is almost constant. At low angle there is not much change in the bilayer swelling at different temperatures. The effective d spacings were calculated using $2d\ Sin\theta = n\lambda$. In light of these results it is confirmed that the non-aqueous binary mixture of SLS in EG exhibits lamellar mesophase at higher temperature. The X-ray traces exhibit a sharp peak at lower angle and broad peak at higher angle. For smectic phases there is always a sharp peak at low angle from which layer spacings are calculated.

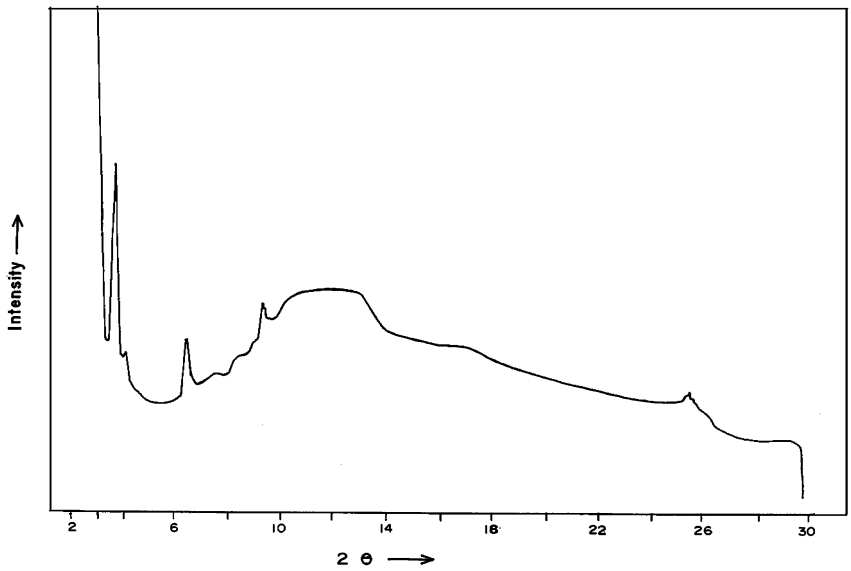



**FIGURE 3** XRD pattern for 40% SLS in EG at 120°.

## Birefringence studies

The refractive indices $n_e$ and $n_o$ of different concentrations were measured at various temperatures using abbe-refractometer and precession goneometer spectrometer, $n_e$ and $n_o$ are the refractive indices of extraordinary ray and ordinary ray respectively. The polarizabilities $\chi_e$ and $\chi_o$ are calculated using Negubour relation [5] for all concentration.

Here we use $\chi_e = N\alpha_e$, and $\chi_0 = N\alpha_0$

Where N is number of molecules per unit volume. The polarizability anisotropy $\chi_e - \chi_0 = \Delta\chi$ at different temperatures were calculated and the variation of $\Delta\chi$ against temperature are shown in Figure 4 for concentrations 40%, 60% and 80% of SLS.

The temperature variation of $\Delta\chi$ shown in Figure 4 for different temperature shows a discontinuity at each phase transitions. The optical textural change is also obvious in each phase transitions.

## NMR Studies

The $^1H$ NMR spectra for the mixture of 40% of SLS were recorded using a Jeol 60 MHz spectrometer. The singlet peak obtained at 0.9 and 1.25 ppm shown in NMR spectra correspond to $CH_3$ and 10 $CH_2$ protons respectively.

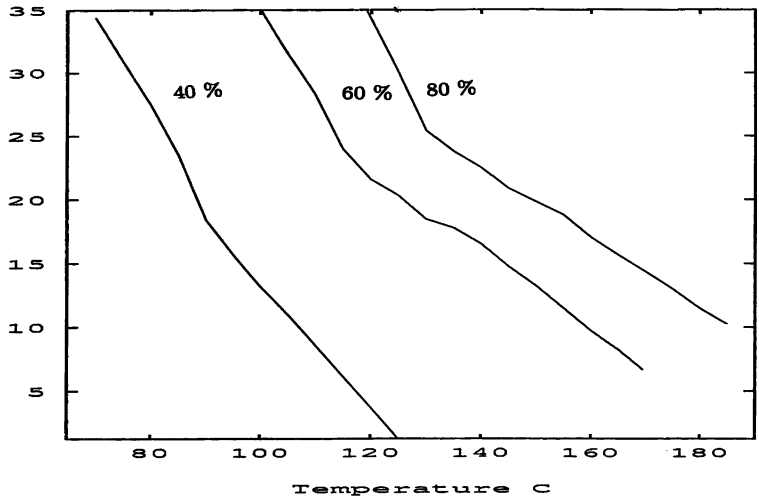
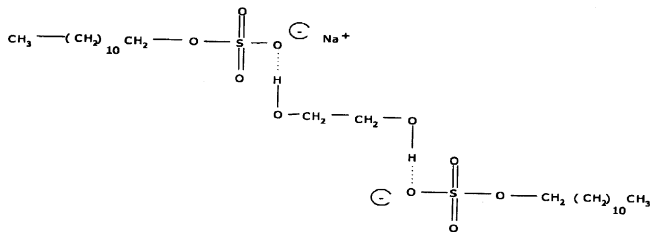



**FIGURE 4** Variation of $\Delta\chi \times 10^{-3}$ with temp for the conc. of 40%, 60%, and 80% of SLS in EG.

The broad singlet at 3.62 PPM is due to $CH_2$ group while the broad singlet at 4.4 ppm is due to $OCH_2CH_2$ (glycol protons). $^1$H NMR spectra of pure SLS shows broad singlets at $\delta$ 0.9 ppm corresponding to 10 $CH_2$ protons and a broad singlet peak at 4.0 ppm due to $OCH_2$ group. From this it is evident that SLS does not form any ester with glycol but it is associated with glycol and forms a sheet like structure. This was further confirmed by IR studies.




## IR Studies:

The IR spectrum of 40% SLS in EG mixture exhibit the peak at 1651 cm$^{-1}$ which is absence in the IR spectrum of pure lauryl sulphate. From this we can assume that the sodium lauryl sulphate may associate with the ethylene glycol via intermolecular hydrogen bonding. This leads to the formation of lauryl sulpuric acid and sodium ethylene glycolate.

## Helfrich Potential and Elastic Modulus

We consider the free energy of steric interaction between the undulating membranes in multilayer systems [6]. The method used here is a phenomenological theory of smectic elasticity with which to calculate the curvature elasticity. The undulation modes in multilayer systems can be treated in terms of the de Gennes theory [7] of fluctuations in smectic phase, which invokes curvature elasticity and smectic compressibility. To estimate the Helfrich potential ($V(\xi)$), we consider the free energy per unit area,

$$V(\xi) = \beta \frac{(k_B T)^2}{k_o \xi^2}$$

where $\beta = \frac{3\pi^2}{128}$ (constant of free energy of steric interaction), $k_B$ is the Boltzmann constant and $k_o$ is the bare bending constant.

The V($\xi$) for membrane varies with the inverse square of the membrane spacing assuming that the local tilt of the membrane induced by undulations remains in effect well below $\frac{\pi}{2}$. $\xi$ is mean membrane separation. Here it has been considered that $\xi$ is equal to d obtained from X-ray to compute the potential.

The V($\xi$) of layers at different concentration of SLS at different temperatures in the smectic phase is calculated and shown in Table 1. It is interesting to observe that as the concentration of SLS increases the V($\xi$) value also increases. This result invokes that in dilute region of the mixture V($\xi$) value decreases.

The bulk modulus (K) [8] of smectic compressibility can be also calculated using the relation,

$$K = \frac{3\pi^2}{64} \frac{(k_B T)^2}{k_c d}$$

where $k_c$ is the curvature elastic modulus $= 2 \times 10^{-12}$ erg/cm$^{-3}$.

The bulk modulus for different concentrations at various temperatures has been estimated and is shown in Table 1. It is observed that as the concentration of SLS decreases the value of the bulk modulus also decreases,

**TABLE 1** Helfrich potential (V($\xi$)) and Bulk modulus (K) at Lamellar Phase at Different Temperature and Concentration

| Concen. of SLS | T/°C at Sm A | $\xi$ | V($\xi$)erg/cm$^{-3}$ | K/10$^7$dyne |
|---|---|---|---|---|
| 30% | 65 | 31.59 | 0.093 | 0.00058 |
| 40% | 105 | 31.59 | 0.0252 | 0.00153 |
| 50% | 125 | 31.59 | 0.0344 | 0.00217 |
| 60% | 165 | 31.59 | 0.0463 | 0.00292 |

because the smectic layers have no interaction with the neighbouring layers in the dilute regions. The Helfrich steric contribution is small, for particular forms of dislocations and also loss in entropy with respect to the dilute region.

## REFERENCE

[1] Skoulios, A. & Guillon, D. (1988). *Mol. Cryst. Liq. Cryst.*, *165*, 317.
[2] Ekwall, P. (1975). *Adv. Liquid Crystals 1*, 1.
[3] Lawrence, A. S. E. (1970). *Liquid Crystals and ordered Fluids*, Johnson, J. F. & Porter, R. S. (ed.) Plenum Press: New York 289.
[4] Nagappa, S. K., Nataraju, & Krishnamurthi, D. (1988). *Mol. Cryst. Liq. Cryst.*, *165*, 317.
[5] Neugebauer, H. E. J. (1954). *Canad. J. Phys.*, *32*, 1.
[6] Helfrich, W. (1978). *Z. Naturfersch*, *33a*, 305.
[7] de Gennes, P. G. (1969). *J. Phys. Paris, colloque 4*, 64.
[8] de Gennes, P. G. & Prost, j. (1998). *The physics of liquid crystal*, Clarendon press Oxford, UK, 103.