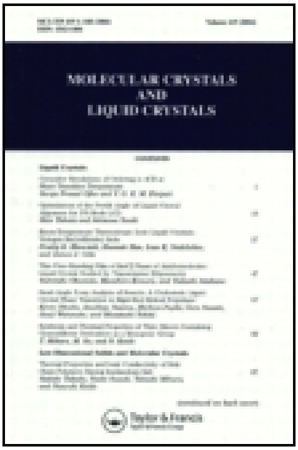

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Mesomorphic Phases in the Mixtures of the Two Non-Mesogenic Compounds

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We report here on the optical and thermal properties of liquid crystalline phases observed in the mixtures of Cetyl pyridinium chloride (CpCl) and Ethylene glycol (EG) at lower concentration of CpCl. The concentration between 10 to 40% of CpCl exhibits I- Sm A - Sm B – Sm E – Cr sequentially, when the specimen is cooled from isotropic phase. The spectroscopic studies like IR and ^{1}H NMR have been carriedout to understand the chemical structure in these mixtures. The phases are identified by the optical, X-ray and DSC studies. Temperature variation of optical anisotropy in these mixtures is also discussed. Helfrich potential and Elastic modulus are estimated in the lamellar Phase using Helfrich model.

Keywords: Mesomarphic phase; Non-Mesogenic; Halfrich potential; Bulk modulus

INTRODUCTION

Mixtures of non-mesogenic compound with polar head and organic solvents exhibit wide variety of liquid crystalline phases depending upon their concentrations and temperatures[1–2]. Lyotropic mesophases are characterized by lamellar, hexagonal and cubic structures. In lameller domain most of the defects are spherulitics i.e packing of spherical bilayers in the form of onions. The Friedels oily steaks[3] are also observed. Frequently mixtures of higher concentrations of amphiphilic compound exhibits classic focal conic domains charecterized by fan shaped textures[4]. The micellar nematic phase has been encountered in the mixture of sodium oleate and glacial acetic acid[5]. It has also been demonstrated that a micellar nematic to cholesteric transition may be induced by addition of optically active compounds[6]. The organic materials which we consider in this investigations are cetyl pyridinium chloride (CpCl) and ethylene glycol (EG). The different phases obtained by the mixture of CpCl and EG are investigated by optical textures, DSC, X-ray studies. The molecular dynamics in mixtures are studies by ^{1}H NMR and IR techniques. Helfrich potential and Bulk modulus of the membranes are calculated[6].

Experimental section

The compound cetyl pyridinium chloride (CpCl) used in this investigation is obtained from Hopkins William Co., UK. It was further purified twice by recrystallisation in benzene. The transition temperature of the CpCl is 130°C and which is in agreement with the reported standard value. Ethylene glycol (EG) supplied by M/s Reechem Research Laboratories, Mumbai, India, and which is used directly without any further purification. Mixtures of about 15 different concentrations of CpCl (by weight percent) in EG were prepared. The phase transition temperatures of the mixtures were measured with the Leitz polarizing microscope provided with hot stage. The X-ray diffractometer traces for different concentrations of CpCl in EG at various temperatures were taken by using Jeol X-ray diffractometer. The density and refractive indices of the mix tures were determined at different temperatures employing the technique as described in our previous paper[4].

Results and discussion

Optical studies

The transition temperatures of the mixtures of different concentrations of CpCl were determined using polarizing microscope and DSC. Various polymorphic smectic modifications and the phase transition temperatures of 40% CpCl in EG are given below.

I 93°C Sm A 57°C Sm B 35°C Sm E 24°C Cr

When the specimen cooled from its isotropic liquid phase it exhibits a focal conic textures of the smectic A (lamellar) phase in which the molecules are arranged in layers, as shown in Fig. 1(a). This phase is appears to be metastable and slowly change over to smectic B phase in which molecules are hexagonally closed packed and this is recognised by the mosaic textures, as shown in Fig. 1(b). At room temperature the fans of focal conics are crossed by a number of arcs which is the characteristic of smectic E phase, see Fig. 1(c).

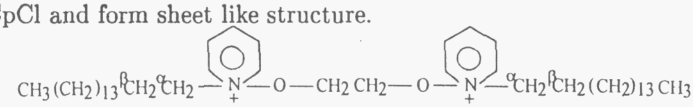
The partial phase diagram shown in Fig.2 is obtained by drawing the phase transition temperatures against concentration of CpCl in EG. It is found from the phase diagram that the mesomorphism is thermodynamically stable for lower concentrations of CpCl in the mixtures. As the concentration of CpCl is increase from 5% the smectic polymorphism is found to increases up to 50% of CpCl and then decreases gradually. Above 50% of CpCl only some birefringent regions are observed and it is difficult to associate them with any of the mesophases. The most remarkable feature of the CpCl molecule is the tendency of their constituent parts to segregate in space with creation of interfaces. The polymorphism seems to be entirely dependent on the interfacial behaviour. This behaviour ultimately leads to the limiting of polymorphism for homogeneous interfaces for higher concentration of CpCl.

X-ray studies

The x-ray traces presented in Fig. 3(a,b) is taken for 40% of CpCl in EG at 35°C and 24°C, displays two sharp peaks at 2θ=4° and 5° which are characteristics of smectic A phase at respective temperature. The peaks at angle 27° is sharp owing to the fact that within each layer there is an exactly regular arrangement of molecules in the lateral direction lying in the plane of each layers. The effective d spacings are calculated by $2d \sin\theta = n\lambda$. In light of the above results it is confirmed that the non-aqueous binary mixture of CpCl in EG exhibits lamellar mesophase at different temperatures. At higher temperature CpCl molecules are arranged alternatively in planar double layer separated by EG layers leading to Sm A phase. From the skeletal structures of CpCl the molecular length turns out to be 22.78Åwhich is approximately half of the effective d spacing obtained from x-ray diffraction recording.

^{1}H NMR studies

The 40% of CpCl in EG mixture shows signals at δ 1.3 (bs, 58H)due to hydrophobic methylene and methyl protons, δ 2.0 (bs, 4H) due to β-methylene protons, δ 2.95 (bs, 4H) due to α-methylene protons, δ 4.9 (bt, 4H) due to -O-CH_2-CH_2-O- protons and the aromaticprotons appear at δ 8.2, 8.5 and 9.3 respectively. Peaks due to the hydroxyl groups of EG is missing in the NMR spectrum. This clearly indicates that the EG gets associated with two molecules of CpCl and form sheet like structure.



IR studies

The IR spectrum of 40% CpCl in EG mixture shows the IR frequency at 1633 cm^{-1}, 1583 cm^{-1} due to the prasence of pyridinium salts and 1250-1195 cm^{-1} due to the prasence of O-CH_2- linkage which was absent in the spectrum of pure CpCl. This clearly shows that CpCl is associated with EG and helps to form the lamellar phase.

Birefringence studies

The refractive indices n_e and n_o for extraordinary and ordinary ray respectively were measured at different temperature using abbe refractometer. The electric susceptibility χ is related to Nα where N is the number of molecules per unit volume and α is the polarizability. χ_e = Nα_e, χ_0 = Nα_0 and χ_e - χ_0 = $\Delta\chi$ which is corresponds to polarizability anisotropy. Here α_e and α_o are effective polarizabilities of extraordinary and ordinary rays respectively. The temperature variation of n_e, n_o and $\Delta\chi$ are shown in fig. 4(a,b). The values of χ_e and χ_o at various temperatures are calculated by using Neugebauer's relation[7]. For higher concentration of CpCl the values of $\Delta\chi$ decreases because the effective optical anisotropy associated with the molecules of CpCl decreases.

Helfrich potential and Elastic modulus

The free energy of steric interaction between the undulating membranes when they are side by side in multilayer systems[8]. The undulation modes in multilayer systems can be treated in terms of de Gennes theory[9] of fluctuations in smectic phase which invokes curvature elasticity and smectic compressibility. To estimate the Helfrich potential (V(ξ)), we consider the Free energy per unit area,

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

where $\beta = \frac{3\pi^2}{128}$, $k_0/k_B T = 0.75$ (The repulsive force between the membrane), k_0 = bare bending constant, k_B is Boltzman constant.

The V(ξ) of membrane varies with the inversquare of membrane spacing assuming that the local tilt of the membrane induced by undulations remain in effect well below $\frac{\pi}{2}$. ξ is mean membrane separation. Here it has been consider ξ is equal to d [10], and its value is 27.78 $\AA$

The V(ξ) of layers at different concentration of CpCl at different temperature in smectic phase is calculated and shown in Table 1. It is interesting to note that as concentration of CpCl increases the V(ξ) value also increases. This result invokes that in dilute region of the mixture V(ξ) value decreases.

The elastic modulus (K) [10] of smectic compressibility is calculated using the relation,

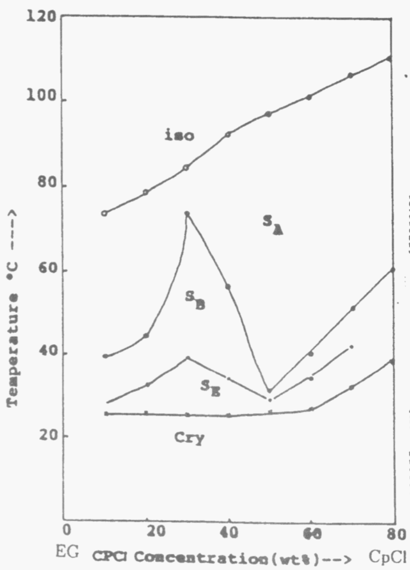
$$K = \frac{3\pi^2}{64} \frac{(k_B T)^2}{k_c d}$$

Where k_c is curvature elastic modulus.

The elastic modulus for different concentration at various temperature has been estimated and are shown in Table 1. It is observed that as concentration of CpCl decreses the value of the bulk modulus also decreses, because of the fact that the smectic layers have no interaction with the neighbouring layers in the dilute regions. The Helfrich steric contribution is small, for a perticular forms of dislocations and also loss in entropy with respect to the dilute region.

Table 1: Helfrich potential and elastic modulus at lamellar space at different temperature and concentration.

Conc. of CpCl	T^0C at S_A	$V(\xi)$ in erg/cm^2	$Kx10^7$ dyne
80 %	106	0.0583	0.00177
70 %	102	0.0561	0.00164
60 %	97	0.0533	0.00149
50 %	93	0.0511	0.00137
40 %	88	0.0484	0.00122
30 %	80	0.0440	0.00101
20 %	74	0.0407	0.00086
10 %	69	0.0379	0.00075



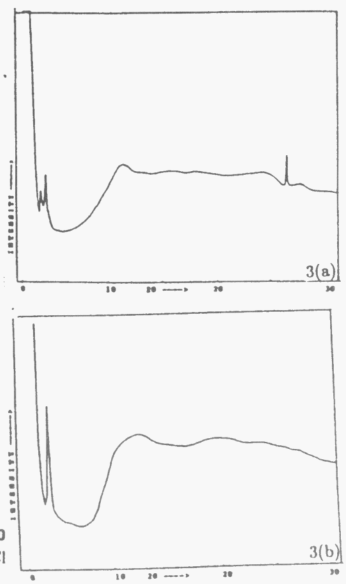
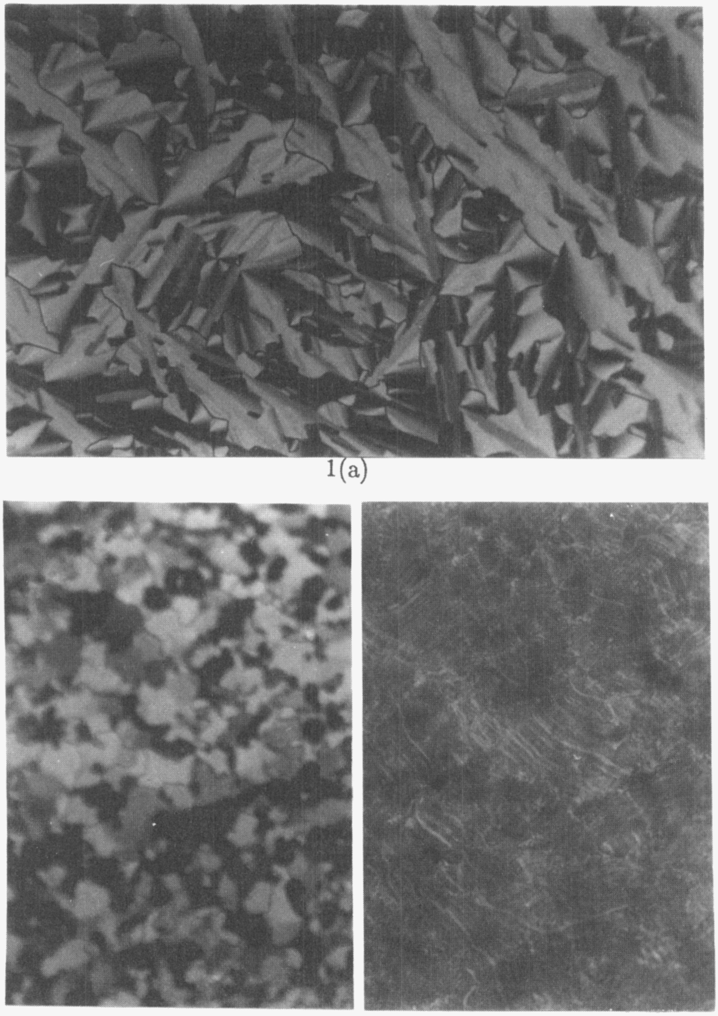


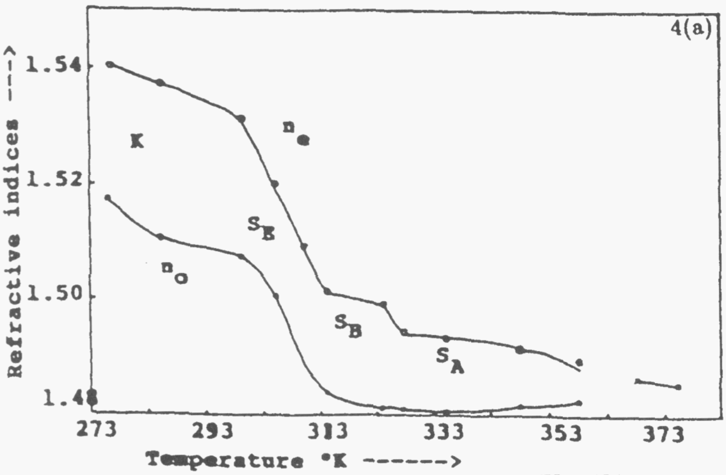
Fig.2. Partial phase diagram (Wt % of CpCl in EG)

Fig.3. XRD-Recording for 40% of CpCl in EG a) at 35^0C in S_A b) at 24^0C in crystalline



1(a) 1(b) 1(c)

Fig.1. Microphotographs of a) S_A (180X), b) S_B (200X), c) S_E (220X). See Color Plate IX at the back of this issue.



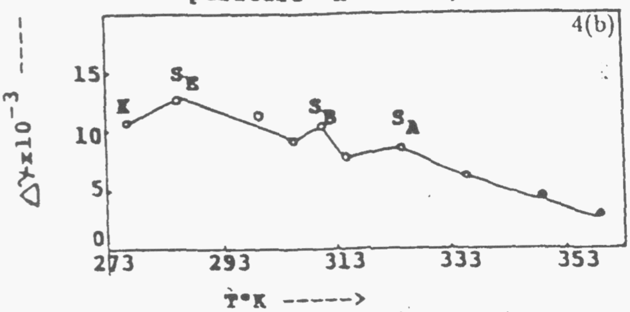


Fig.4(a) Variation of n_e and n_0 with temperature

Fig.4(b) Variation of $\Delta\chi$ with temperature

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