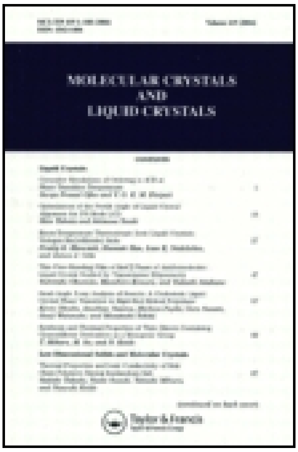

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Thermotropic Liquid Crystalline Phases in Binary Mixture of Nonmesogenic Compounds

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The binary mixture of two nonmesogenic compounds viz., Tetradecyl Trimethyl Ammonium Bromide (TTAB) and Orthophosphoric acid (H_3PO_4) exhibits very interesting liquid crystalline smectic phases at large range of concentrations and temperature. The mixture with lower and higher concentrations of TTAB exhibits Sm A, Sm D, Sm B, and Sm E phases, sequentially when the specimen is cooled from its isotropic phase. Different liquid crystalline phases observed in the mixture were studied using DSC, X-ray, and Optical microscopic techniques. The temperature variation of optical anisotropy has also been discussed. Helfrich potential and elastic moduli have been estimated in the smectic phase using Helfrich model.

Keywords Binary mixture; Helfrich potential; mesomorphic phases; nonmesogenic

Introduction

The binary mixture of some nonmesogenic compounds has created a new era in the field of liquid crystals [1]. It is well known that the molecular ordering in lyotropic mesophase for the majority of amphiphilic systems corresponds to the smectic order [2]. Both thermotropic and lyotropic systems of liquid crystals give rise to several mesophases. They may be classified according to the same space group in spite of their different shapes and chemical structure [3]. Here it is pertinent to mention that, the lyotropic nematic and cholesteric phases are encountered with soaps, water, and long chain alcohol systems [4]. The binary mixtures of nonmesogenic compounds exhibit lyotropic and thermotropic mesophases [5]. Among the earlier investigations on such systems, particular reference must be made to the work of Acimix [6], who used the mixture of l-serine hydrochloride decyl ester and orthophosphoric acid, which are nonmesogenic in character. Nagappa et al. [5] have extensively studied the lyotropic systems of cetyl alcohol and steryl alcohol with orthophosphoric acid. Ethylene glycol has been used as a solvent in forming the micellar phases in lyotropic systems. Generally, the chemical structure is the most salient feature of the molecule forming lyotropic mesophases in the presence of solvent, and therefore, it is quite interesting to investigate the molecular ordering of micellar lyomesophases that are formed by alcohol-solvent system.

In the present study, we have considered the mixture of two nonmesogenic compounds viz., Tetradecyl Trimethyl Ammonium Bromide (TTAB) and Orthophosphoric acid

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(H_3PO_4). The polymorphic smectic modifications of the liquid crystalline phases were observed using microscopic technique and they have been verified from the results of DSC, X-ray, and Optical anisotropic techniques. Helfrich potential and elastic moduli have been estimated in the lamellar smectic phases using Helfrich model with approximation.

Experimental Studies

TTAB used in this investigation was obtained from the Basic Pharma Life Science, P. Ltd., India. They were further purified twice by recrystallization in benzene. The melting point of the purified sample is in good agreement with the reported value. H_3PO_4 was supplied by M/s SISCO Research Laboratory, Mumbai, India. The H_3PO_4 was used after boiling it at 433 K for 6 h. The mixture of 15 different concentrations of TTAB (by wt%) in H_3PO_4 was prepared and kept in a desiccator for a longtime. Phase transition temperatures of the mixtures with different concentrations were measured using Leitz-polarizing microscope and conventional hot stage. The sample was sandwiched between the slide and cover slip, which was sealed for microscopic observation. The DSC thermograms were taken for different concentrations of the mixture using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The phase diagram was obtained by plotting the phase transition temperatures of the mixtures, which were determined by the DSC studies as a function of concentrations of TTAB in H_3PO_4. The phase diagram clearly indicates that the mesomorphism of the mixture is thermodynamically stable for lower and higher concentrations of TTAB. The X-ray diffraction of TTAB in H_3PO_4 at different temperatures was taken by using Laue photograph method as described in an earlier paper [7]. The density and refractive indices of the mixtures were measured at different temperatures employing the technique described in our earlier paper [8].

Results and Discussions

Optical Studies

The polymorphic smectic modifications and the corresponding isotropic to liquid crystalline phase transition temperatures for the mixture with 40% of TTAB in H_3PO_4 are given below.

I-77.20°C, Sm A-63°C, Sm D-53.03°C, Sm B-41.23°C, Sm E-33.07°C.

On cooling the specimen from its isotropic melt, the setting point is marked by the genesis of nucleation at several points which appear as minute bubbles initially, but which progressively grow radially and form a focal conic fan texture of smectic-A phase in which the molecules are arranged in layers and the texture is shown in Fig. 1(a). This phase

Figure 1. Microphotographs obtained in between the crossed polars: (a) focal conic fan-shaped texture of smectic-A (Lamellar) phase (250X) (b) focal conic fans with radial striation of smectic-E phase (250X).

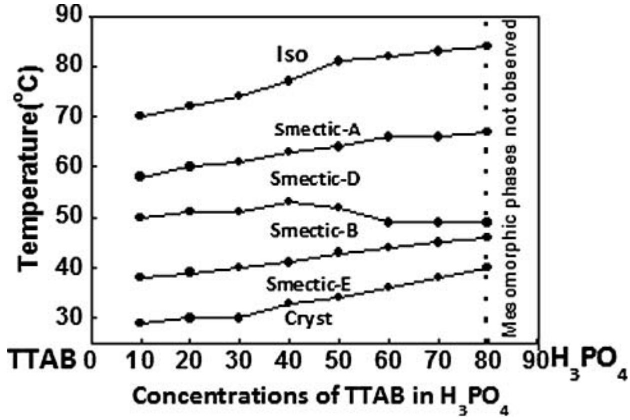

Figure 2. Partial phase diagram for the mixture of TTAB in H_3PO_4.

appears to be metastable and undergoes slow transformations to give a viscous smectic-D phase [9]. When the optically extinct smectic-D phase is submitted to the external pressure or stress by touching the cover slip over the sample, no flash or change in the birefringence was observed. This is one of the basic tests to identify the smectic-D phase. The isotropic viscous smectic-D phase is also metastable and transforms to focal conic fan-shaped texture on cooling the specimen. This texture corresponds to the paramorphotic [10] focal conic fan-shaped texture of ordered smectic-B phase in which the molecules are arranged in hexagonal close-packed structure. On further cooling, focal conic fan texture with radial striation on the fans, which is the characteristics of smectic-E phase, is observed and it is shown in Fig. 1(b). At this phase transition, i.e, from smectic-B phase to smectic-E phase, it is observed that there is a drastic change in the values of density, refractive index, and electroconductivity of the sample. This anomalous behavior is presumably associated with high degree of order of the molecular arrangement in smectic-E phase.

The phase diagram is shown in Fig. 2. It illustrates that, the lower and higher concentrations of TTAB exhibit wide variety of liquid crystalline phases. Here it is pertinent to remark that, the smectic-E phase exists at room temperature for the concentrations from 10% to 80% of TTAB. But above 80% of TTAB, the mixture exhibits only a birefringent region and it is difficult to associate the texture with any of liquid mesophases. The most remarkable feature of these TTAB molecules is the tendency of their constituent parts to segregate in space with the creation of interfaces. Evidently, the polymorphism seems to be entirely depending on the interfacial behavior and this behavior ultimately leads to the limiting of the polymorphism for homogeneous interfaces for higher concentrations of TTAB.

It can be noticed that the phase transition temperatures observed in the present study are different from the values observed in a similar type of study by Nagappa et al. [5] in which the mixture of a different compound with H_3PO_4 has been studied. Hence, the interaction of H_3PO_4 looks to be different with different compounds.

X-Ray Studies

X-ray studies are very useful for the identification of various types of arrangement of molecules in the liquid crystalline mesophases. Using XRD data, an attempt has been made

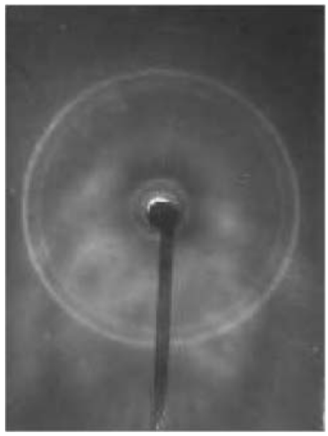

Figure 3. Laue X-ray photograph for the mixture of 40% TTAB in H_3PO_4.

to understand the molecular arrangement in the mixture of TTAB in H_3PO_4. The X-ray diffraction photograph of 40% TTAB in H_3PO_4 is shown in Fig. 3, which exhibits two sharp outer and inner rings, these are the characteristics of smectic-E phase [11]. The outer rings are sharp owing to the fact that within each smectic layer, there is an exactly regular arrangement of molecules in the lateral directions lying in the plane of the layers. The sharp inner ring corresponds to the first order diffraction from the set of smectic layers. The effective 'd' spacing in smectic-E phase comes out to be 38.66 Å and this corresponds to the smectic layer spacing. The molecular length of TTAB is 27.44 Å, which is calculated from the skeletal structure of TTAB using the bond lengths. The effective 'd' spacing is 1.4 times the molecular length of TTAB and, hence, it forms an imbricated layer-like structure [12]. This study along with the optical observations clearly indicates that the nonaqueous binary mixture of TTAB in H_3PO_4 shows a lamellar mesophase, which exists over a broad range of compositions and temperatures.

Optical Anisotropy

Results of this investigation are further supported by the optical studies. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the mixture were measured at different temperatures for the different concentrations using Abbe Refractometer and Precission Goniometer Spectrometer. The variations of refractive indices as a function of temperature for 40% of TTAB in H_3PO_4 are shown in Fig. 4. The value of n_e is greater than n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for 40% of TTAB in H_3PO_4 have been calculated using Neugebauer relation [13] at different temperatures. The variation of electrical susceptibility as a function of temperature for the mixture is shown in Fig. 5. From the figure, it can be observed that wherever there is an isotropic-liquid crystalline phase transition, the value of electrical susceptibility changes appreciably, which indicates that the changes correspond to various smectic modifications. Further, with increase in the concentration of TTAB, the value of electrical susceptibility decreases with temperature because the effective optical anisotropy associated with the molecules of TTAB also decreases.

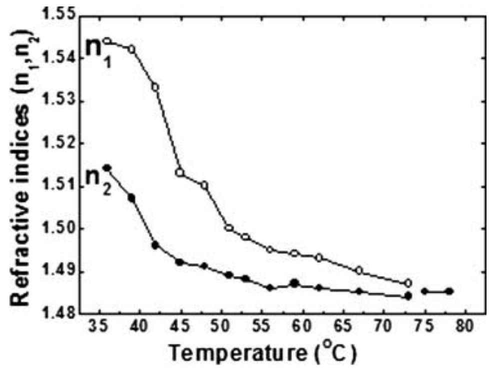

Figure 4. Variation of refractive indices as a function of temperature for the mixture of 40% TTAB in H_3PO_4.

Helfrich Potential and Elastic Modulus

The free energy of steric intermembrane interactions exists between undulating neighboring membranes, when they are side by side in the multilayer systems [14]. The undulation modes in multilayer systems can be treated in terms of the de Gennes theory [15] 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

$$V(\xi) = \beta \frac{(k_B T)^2}{k_0 \xi^2} \tag{1}$$

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

The $V(\xi)$ of membrane varies with inverse square of the membrane spacing assumed that the local tilt of the membrane induced by undulations remains in effect well below $\pi/2$. ξ is the mean membrane separation. Here, it has been considered that the value of 'ξ' is equal to the value of 'd' [16].

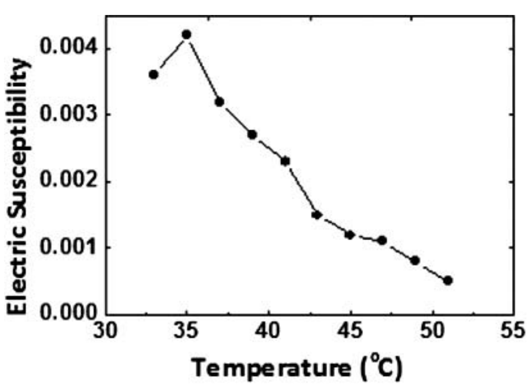

Figure 5. Variation of electric susceptibility as a function of temperature for the mixture of 40% TTAB in H_3PO_4.

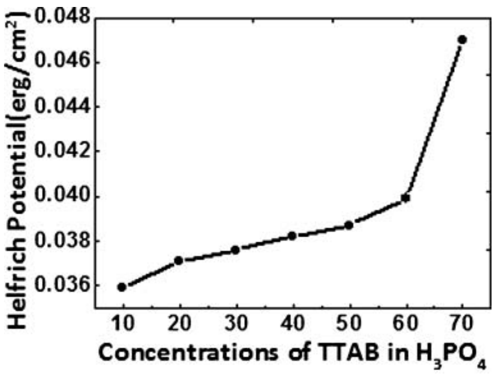

Figure 6. Variation of Helfrich potential with concentration of TTAB in H_3PO_4.

The variation of Helfrich potential along with the concentrations of TTAB is shown in Fig. 6 and, hence, it is very interesting to note that, the Helfrich potential values increase as the concentrations of the TTAB increase. This result invokes that in dilute region of the mixture $V(\xi)$ value decreases. This is supported by the nature of variation exhibited by the elastic modulus.

The elastic modulus (K) [16] of smectic compressibility is calculated using the relation

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

where k_c is curvature elastic modulus.

The elastic modulus is also estimated for the mixture of different concentrations at various temperatures. The graph obtained by plotting the elastic modulus as a function of the concentrations of TTAB is presented in Fig. 7. From the graph it is observed that, as the concentration of TTAB decreases, value of the bulk modulus also decreases.

The small values of electrical susceptibility, bulk modulus, and Helfrich potential in low concentrations are due to the lesser value of density in which the interaction of smectic layers with the neighboring layers appears to be very less.

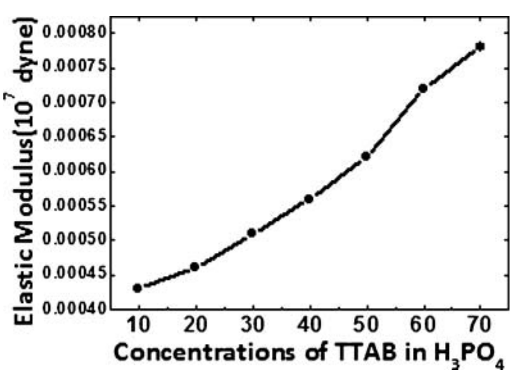

Figure 7. Variation of elastic modulus with concentration of TTAB in H_3PO_4.

Conclusions

The above studies apart from revealing numerous textures associated with various phases in mixture have enabled us to reach the following conclusions. Mixture with concentrations from 10% to 80% of TTAB in H_3PO_4 exhibits polymorphic smectic modifications at different temperatures. The drastic changes in the values of density, refractive index, and anisotropy of polarizability with temperature unambiguously correspond to smectic-E phase. The X-ray results also lend support to the above observations. This type of polymorphism is rare in the binary mixture of nonmesogenic compounds.

Acknowledgments

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