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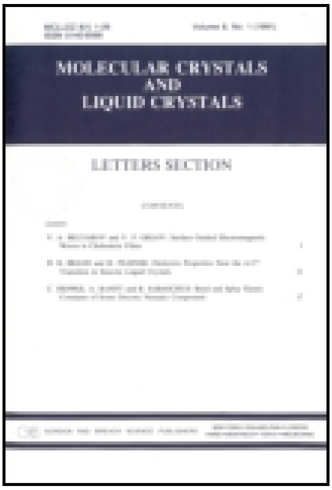

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Thermal Characterization and Mesomorphic Properties of Binary Mixture of Two Non-Mesogenic Compounds

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The binary mixture of two non-mesogenic compounds, viz., cetyl-dimethyl-ethyl-ammonium bromide (CDEAB) 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 CDEAB exhibits SmA, SmE, and SmB phases, sequentially when the specimen is cooled from its isotropic phase. Different liquid crystalline phases observed in the mixture were studied using differential scanning calorimetry (DSC), X-ray, and optical microscopic techniques. The temperature variations of optical anisotropy and electrical conductivity have 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; non-mesogenic; temperature dependence

Introduction

Liquid crystals are highly anisotropic fluids that exist between the boundaries of the solid phase and the conventional isotropic liquid phase. Thermotropic liquid crystals exhibit a mesomorphic behavior within a specific temperature range. They are either discotic, having a planar, disc-like, or cylindrical-shaped rod-like molecules [1,2]. The binary and ternary mixtures of some non-mesogenic compounds exhibit lyotropic and thermotropic mesophases [3,4]. The mesophases of thermotropic and lyotropic liquid crystals are thermodynamically stable but only partially ordered phases. Each mesophase is described by its degree of order. If the mesophase has orientational order only, it is called nematic (N), if it has both orientational and positional orders, it is called smectic (Sm). The nematic liquid crystal phase is technologically the most important mesophase. It is used in almost all commercially available liquid crystal displays [5–7].

The importance of liquid crystals lies in their extensive use in display devices, as well as many other scientific applications [8]. However, the use of liquid crystals in different devices depends upon various properties owned by them like order parameter, dielectric

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constant, dielectric anisotropy, birefringent behavior, elastic constants, etc. A particular application of liquid crystals requires a particular set of parameters of the liquid crystal in required range. Studies on physical properties of lyotropic/thermotropic liquid crystals are of importance because of their layered structure. Investigations of multi-component systems containing an amphiphile with water, cholesterol, ethylene glycol, and/or alcohol are of particular interest. Every component of such systems, with a degree of freedom, can modify not only the types and structures of the phases but also their various physical properties [9–12]. Liquid crystals are characterized by their phase transition behavior, which can be studied both by physically as well as chemically. The studies of physical and chemical properties are very useful as they provide impotent information regarding molecular structure, molecular dynamics, and type of molecular interactions in the sample and hence the probable liquid crystalline phases that could observed by the molecules of sample [13,14]. It is well established that some of the mixtures of amphiphilic substances form nematic, cholesteric, Twisted grain boundary (TGB), lamellar, hexagonal, and cubic structures of the liquid crystalline phases. In lamellar domain most of the defects are spherulitics, i.e., packing of spherical bilayers in the form of onions. The Friedel's oily streaks [15] are observed. Frequently, the mixtures of higher concentrations of amphiphilic compound exhibit a classical focal conic domain characterized by fan-shaped textures [16]. The micellar nematic phase has been encountered in the mixture of sodium oleate and glacial acetic acid [17]. It has also been demonstrated that the micellar nematic to cholesteric transition may be induced by the addition of optically active compounds [18].

In the present study, we have considered the mixture of two non-mesogenic compounds, viz., cetyl-dimethyl-ethyl-ammonium bromide (CDEAB) and orthophosphoric acid (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 differential scanning calorimetry (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

The compound CDEAB used in this investigation was obtained from the Basic Pharma Life Science, Pvt. Ltd., India. They were further purified twice by re-crystallization 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 hr. The mixture of 15 different concentrations of CDEAB (by wt%) in H_3PO_4 was prepared and kept in desiccators 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 as a function of concentrations of CDEAB in H_3PO_4 as shown in Fig. 1. The phase diagram clearly indicates that the mesomorphism of the mixture is thermodynamically stable for lower and higher concentrations of CDEAB. The X-ray diffraction (XRD) studies were undertaken by using JEOL- X-ray diffractometer at various temperatures for

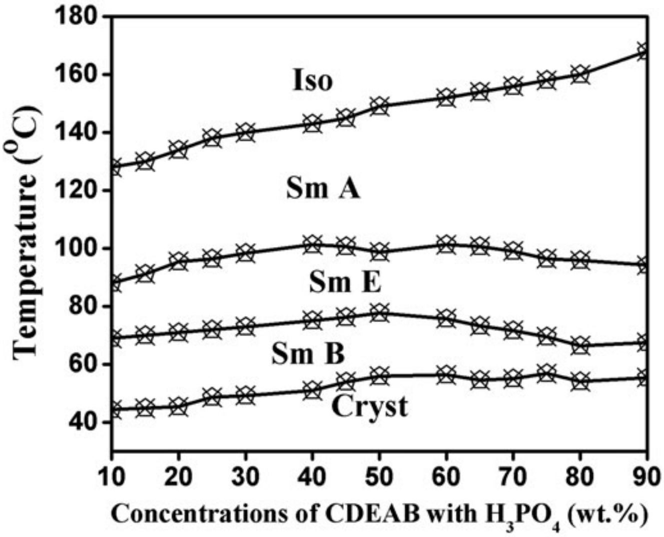

Figure 1. Partial phase diagram for the mixture of CDEAB in H_3PO_4.

different concentrations. The density and refractive indices of the mixtures were measured at different temperatures employing the technique described in our earlier paper [19].

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 CDEAB in H_3PO_4 as presented in DSC thermogram are shown in Fig. 2. The sequential representation of phases is as follows:

$$I - 143°\text{C SmA} - 101.3°\text{C SmE} - 75.2°\text{C SmB} - 51°\text{C}$$

On cooling the specimen from its isotropic melt, the setting point is marked by the genesis of nucleation at several points that appear as minute bubbles initially, but which progressively grow radially and form a focal conic fan texture of SmA phase in which the molecules are arranged in layers, the texture is shown in Fig. 3(a). This phase appears to be metastable and undergoes slow transformations to give a focal conic fan-shaped texture with radial striation on the fans, which are the characteristics of SmE phase as shown in Fig. 3(b). The SmE phase is also metastable and it transforms to focal conic fan-shaped texture on cooling the specimen. This texture corresponds to the paramorphotic [20] focal conic fan-shaped texture of highly ordered SmB phase as shown in Fig. 3(c), in which the molecules are arranged in hexagonal close-packed structure. On further cooling, i.e., the transition from SmE to SmB phase, it is observed that there is a drastic change in the values of density, refractive index, and electro conductivity of the sample. This anomalous

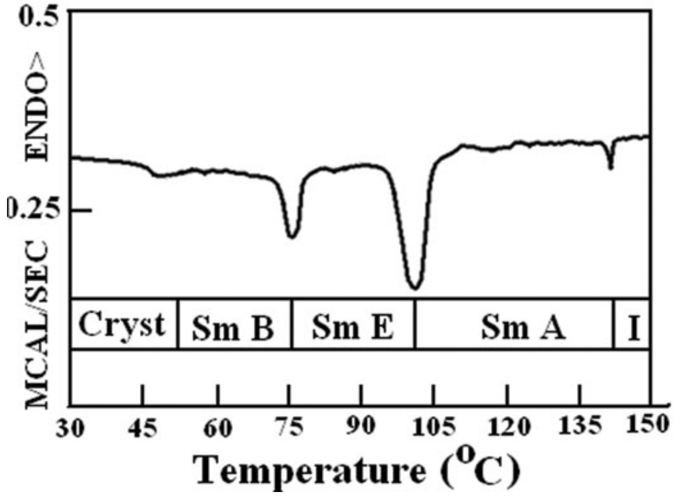

Figure 2. DSC thermogram for the samples of 40% CDEAB in H_3PO_4.

behavior is presumably associated with high degree of order of the molecular arrangement in SmB phase.

The phase diagram is shown in Fig. 1 and it clearly illustrates that the lower and higher concentrations of CDEAB exhibit a wide variety of liquid crystalline phases. Here it is pertinent to remark that the SmB phase exists at room temperature for the concentrations from 10% to 90% of CDEAB. But above 90% of CDEAB, the mixture exhibits only a birefringent region and it is difficult to associate the texture with any of the liquid mesophase. The most remarkable feature of these CDEAB molecules is the tendency of

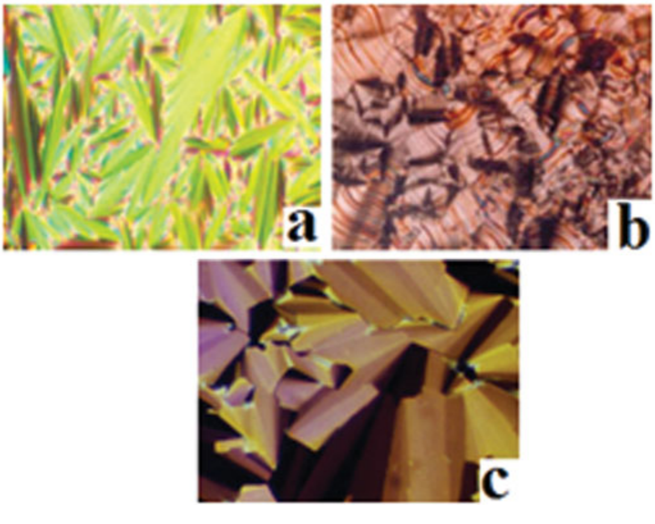

Figure 3. Microphotographs obtained in between the crossed polars. (a) Focal conic fan-shaped texture of SmA (Lamellar) phase (250X). (b) Focal conic fans with radial striation of smectic-E phase (250X). (c) Paramorphotic fan-shaped texture of highly ordered smectic-B phase (250X).

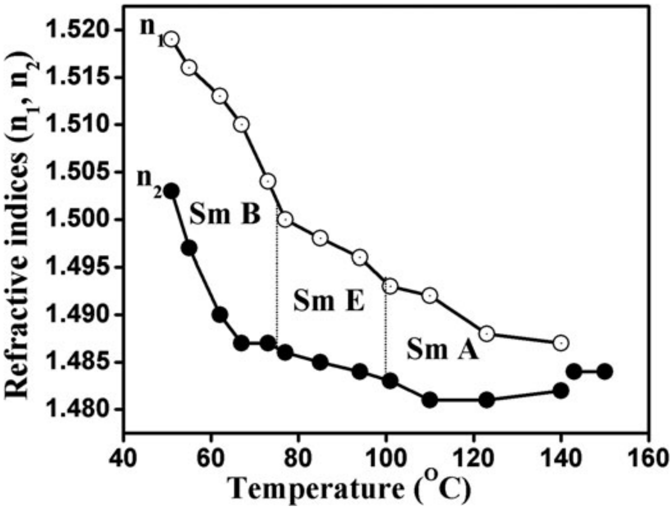

Figure 4. Temperature variations of refractive indices for the mixture of 40% CDEAB in H_3PO_4.

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 homogenous interfaces for higher concentrations of CDEAB. 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. [21] 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.

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 CDEAB in H_3PO_4 are shown in Fig. 4. The value of n_e is greater than n_o, indicating that the material is uniaxially positive. The values of electrical susceptibility for 40% of CDEAB in H_3PO_4 have been calculated using Neugebauer relation [22] 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 CDEAB, the value of electrical susceptibility decreases with temperature because the effective optical anisotropy associated with the molecules of CDEAB also decreases.

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

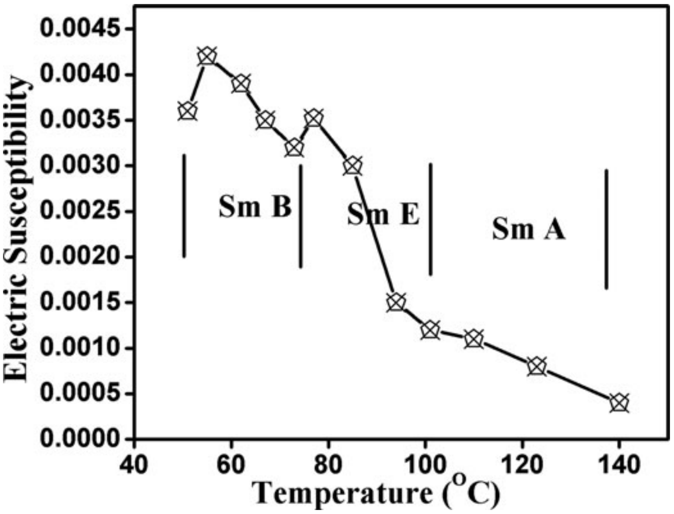

Figure 5. Temperature variation of electric susceptibility for the mixture of 40% CDEAB in H_3PO_4.

to understand the molecular arrangement in the mixture of CDEAB in H_3PO_4. The X-ray traces presented in Figs. 6(a) and Figs. 6(b) are taken for 40% of CDEAB in H_3PO_4 at temperatures 108°C and 120°C, display two sharp peaks at $2\theta = 7.8^\circ$ and 7°, which are the characteristics of SmA phase at respective temperatures. The peaks at angle 30.7° and 31.3° 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. Here, it is pertinent to remark that there is one auxiliary peak observed in Fig. 6(a) at temperature 108°C that represents a preceding phase. 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 CDEAB in H_3PO_4 exhibits a lamellar mesophase at different temperatures. At higher temperature, CDEAB molecules are arranged alternatively in planar double layer separated by H_3PO_4 layers leading to SmA phase. From the skeletal structure of CDEAB, the molecule length turns out to be 24.63 Å, which is approximately half of the effective d spacing obtained from XRD recording.

Helfrich Potential and Elastic Modulus

The free energy of steric inter-membrane interactions exists between undulating neighboring membranes, when they are side by side in the multilayer systems [23]. The undulation modes in multilayer systems can be treated in terms of the de Gennes theory [24] 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 $\beta = 3\pi^2/128$, $(k_0/k_B\ \mathrm{T}) = 0.75$ (the repulsive force between the membrane), $k_0 =$ bare bending constant, and k_B is the Boltzmann 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

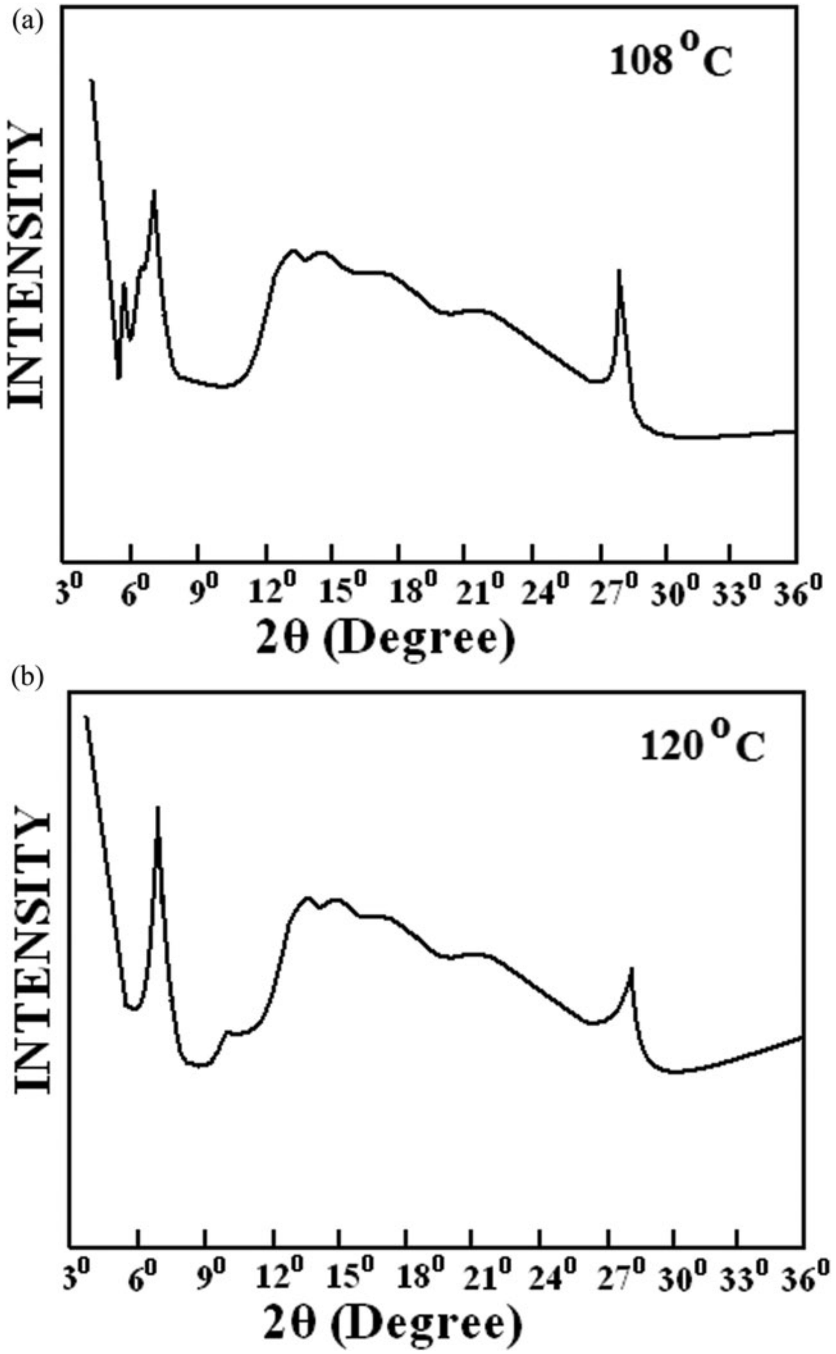

Figure 6. (a) XRD traces obtained for the mixture of 40% CDEAB in H_3PO_4 at temperature 108°C. (b) XRD traces obtained for the mixture of 40% CDEAB in H_3PO_4 at temperature 120°C.

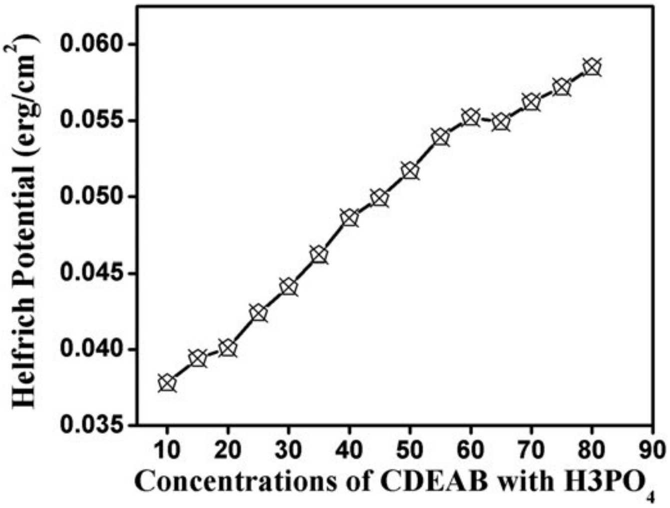

Figure 7. Variation of Helfrich potential with concentrations of CDEAB in H_3PO_4.

$\pi/2$. ξ is the mean membrane separation. Here, it has been considered that the value of "ξ" is equal to the value of "*d*" [25].

The variation of Helfrich potential along with the concentrations of CDEAB is shown in Fig. 7 and, hence, it is very interesting to note that the Helfrich potential values increase as the concentrations of the CDEAB 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) [25] 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 CDEAB is presented in Fig. 8. From the graph, it is observed that as the concentration of CDEAB 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.

Conductivity Measurements

To obtain reliable data on the phase behavior with temperature, electrical conductivity measurements are necessary. A small change in electrical conductivity with temperature relates to the phase behavior of the lyotropic and thermotropic systems [26]. The temperature variations of electrical conductivity are as shown in Fig. 9. The changes were observed in electrical conductivity, the values correspond to different liquid crystalline phase transitions of the thermotropic and lyotropic system at various temperatures and they were also identified by DSC and optical texture studies. It was observed that a change in electrical

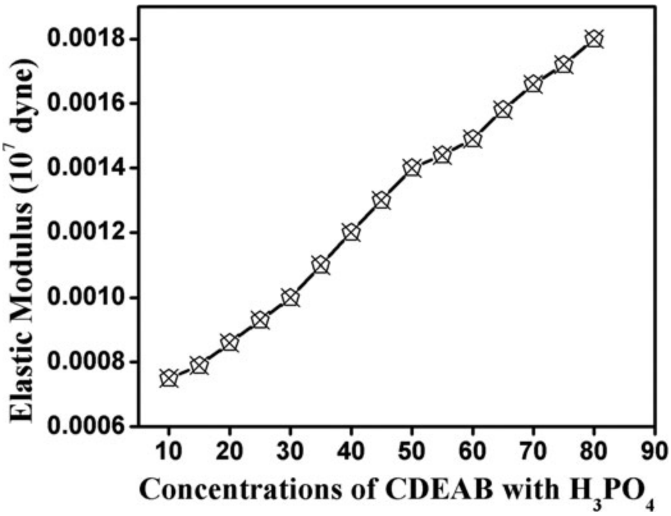

Figure 8. Variation of elastic modulus with concentrations of CDEAB in H_3PO_4.

conductivity at temperatures 58°C, 85°C, and 110°C corresponds to the phase transition from crystalline to SmB, SmB to SmE, and SmE to SmA phases, respectively. This type of behavior is generally observed in hexagonal, cubic, and lamellar phases of lyotropic and thermotropic systems [27,28].

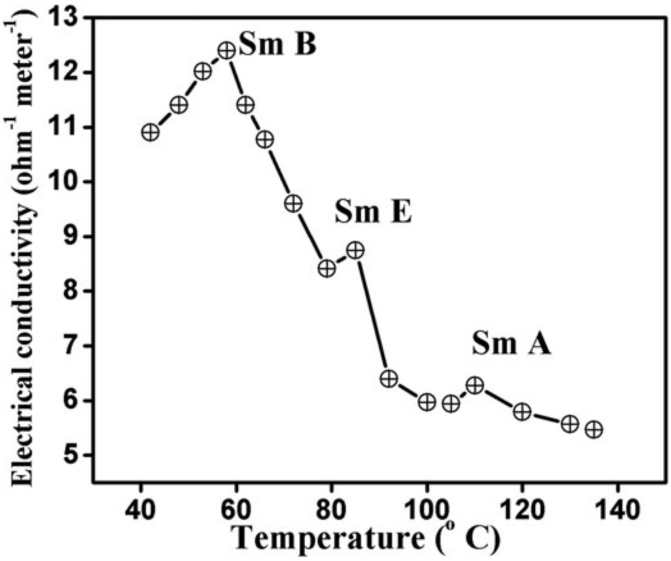

Figure 9. Temperature variation of electrical conductivity σ (Ω^{-1} m^{-1}) for the sample of 40% of CDEAB in H_3PO_4.

Conclusions

Microscopic investigation of the binary mixture of CDEAB and H_3PO_4 shows the existence of SmA, SmE, and SmB phases for all concentrations of CDEAB. The phase behavior is discussed with the help of phase diagram. The drastic changes in the values of density, refractive index, anisotropy of polarizability, and electrical conductivity with the variation of temperature unambiguously correspond to polymorphic smectic phases, respectively. Drastic changes in electrical conductivity are expected to be due to changes in the dimension of disks along with changes in the orientation order of the arrangement. X-ray and DSC studies also lend support to these observations.

References

[1] Kılı, Ç. M., & Çınar, Z. (2007). *J. Mol. Struct.*, *808*, 53.

[2] Gray, G. W. (1987). *Thermotropic Liquid Crystals,* 1st ed., pp. 1–22, John Wiley and Sons: New York.

[3] Forrest, B. J., & Reeves, L. W. (1981). *Chem. Rev., B 1*, 1.

[4] Collings, P. J., & Hird, M. (1997). *Introduction to Liquid Crystals*, Taylor and Francis: Bristol, PA.

[5] Kim, J. H., Vorflusev, V., & Kumar, S. (2004). *Displays*, *25*, 207.

[6] Kuo, W. H., Lin, P. H., & Hwang, S. L. (2007). *Displays*, *28*, 35.

[7] Hsieh, K. L. (2008). *Expert System, Appl.: Int. J.*, *34*, 952.

[8] Brown, G. H. (Ed.) (1975). *Advance in Liquid Crystal*, Vol. 2, pp. 325–329, Academic Press: New York.

[9] Kasianova, I., Kharatyian, E., Geivandov, A., & Palto, S. (2010). *Liq. Cryst.*, *37*, 1439.

[10] Felekis, T., Tziveleka, L., Tsiourvas, D., & Paleos, C. M. (2005). *Macromolecules*, *38*, 1705.

[11] Miller, C. A. (1976). In: *Dynamic Phenomena in Lyotropic Liquid Crystals - Review*, Friberg, S. (Ed.), *Lyotropic Liquid Crystals and Structure of Biomembranes. Advances in Chemistry Series*, Vol. 152, p. 1, American Chemical Society: Washington, DC.

[12] Sousa, M. E., Chan, C., Jian, K., Gao, Y., Hurt, R. H., Crawford, G. P., & Yang, N. (2005). *Mol. Cryst. Liq. Cryst.*, *435*, 107/767.

[13] Garg, A. K., Agrawal, V. K., & Bahadur, B. (1985). *Mol. Cryst. Liq. Cryst.*, *130*, 1.

[14] Smyth, C. P. (1955). *Dielectric Behaviour and Structure*, pp. 89–92, McGraw Hill: New York.

[15] Friedel, G. (1972). *Ann. Phys. France*, *2*, 273.

[16] Marthandappa, M., Nagappa, Somashekar, R., & Lokanatha Rai, K. M. (1992). *Phys. Stat. Solidi (A)*, *129*, 389.

[17] Nagappa, Hanumantha Naik, R., Jagadeesh, K. N., Shivaprasad, A., Somashekar, R., & Lokanatha Rai, K. M. (1995). *Mol. Cryst. Liq. Cryst.*, *260*, 631.

[18] Helfrich, W. Z., & Servuss, R. M. (1984). *II Navocemento*, *3*, 137.

[19] Nagappa, Nataraju, S. K., & Krishanamurti, D. (1986). *Mol. Cryst. Liq. Cryst.*, *133*, 31.

[20] Fantel, K., Mandell, L., & Ekwall, P. (1968). *Acta Chem. Scand.*, *22*, 3209.

[21] Marthandappa, M., Nagappa, & Lokanatha Rai, K. M. (1991). *J. Phys. Chem.*, *1013*, 95.

[22] Neugebauer, H. E. J. (1954). *Can. J. Phys.*, *32*, 1.

[23] Helfrich, W. Z. (1978). *Natureforschung*, *33a*, 305.

[24] de Gennes, P. G. (1969). *J. Phys. Paris, Colloque*, *4*, 64.

[25] de Gennes, P. G., & Prost, J. (1993). *The Physics of Liquid Crystals*, p. 103, Clarendon Press: Oxford, UK.

[26] Marthandappa, M., Nagappa, & Lokhanatha Rai, K. M. (1991). *J. Phys. Chem.*, *95*, 6369.

[27] Franeois, J. (1971). *Kolloid, Z. Z. Polym.*, *246*, 606.

[28] Govindaiah, T. N., Sreepad, H. R., Sathyanarayana, P. M., Mahadeva, J., & Nagappa. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 24.