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Optical studies on smectic phases in mixture of non-mesogenic compounds

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ABSTRACT

The binary mixture of two non-mesogenic compounds viz., sodium oleate (Naol) and Ethylene glycol (EG) exhibit a smectic phases are at large range of concentrations and at different temperatures. The mixtures with lower concentrations of Naol in EG exhibit an Iso-SmA-SmD-SmB-SmE-Cryst phases sequentially when the specimen is cooled from its isotropic phase. The phase transition temperatures for different concentrations of' Naol in EG were measured using polarizing microscope. The different smectic phases are observed by using microscopy techniques and hence it has been verified by optical anisotropic studies. Helfrich potential and elastic moduli are estimated in the lamellar phase using Helfrich model.

KEYWORDS

Phase transition;
Smectic;
Optical anisotropy;
Helfrich and elastic studies.

INTRODUCTION

The study of binary and ternary mixtures of some non-mesogenic compounds creates a new era in the field of liquid crystals[1]. It is well known that: molecular ordering in the lyotropic mesophase for the majority of amphiphilic system corresponds to smectic order. Both thermotropic and lyotropic system of liquid crystalline materials gives rise to several mesophases which may be classified according to the same space group in spite of their different shapes and chemical structure[2]. This type of work are carried out with greater convenience if one chooses a mixture of non-mesogenic compounds of different nature that exhibit a several mesophases for large range of concentrations and temperatures.

In the present study, we have been considered two non-mesogenic compounds; namely, sodium oleate (Naol) and Ethylene glycol (EG). Polymorphic smectic modifications of the liquid crystalline phases were observed by using microscopic technique and they have been verified from the results of optical anisotropic techniques. Helfrich potential and elastic modulii have been estimated in the lamellar smectic phases using Helfrich model with approximation.

EXPERIMENTAL STUDIES

The sodium oleate (Naol) used in this investigation was obtained from the British Drug house Ltd., England and the Ethylene glycol (EG) supplied by MIS SISCO research laboratory, Bombay, India. These chemicals are further purified twice with recrystallization method using benzene as a solvent. The structural formulae for sodium oleate (Naol) and ethylene glycol molecules are as shown in Figure

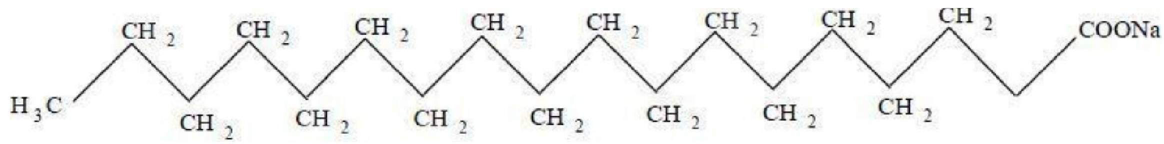

Figure 1a : The structural formula for sodium oleate

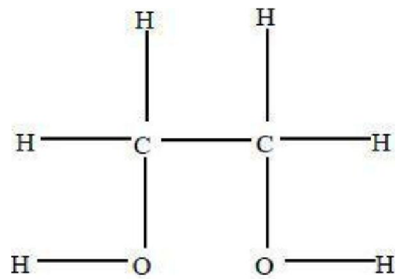

Figure 1 b :The structural formula for ethylene glycol molecules

1(a, b). The different concentrations of given mixture exhibit a polymorphic modifications of the smectic phases; they were observed using Leitz-polarizing microscope in conjunction with hot stage. The density and refractive indices of these mixtures are measured at different temperatures employing the technique[3].

RESULTS AND DISCUSSION

Optical studies

For the observation of optical textures: the sample was taken in the form of thin film between slide and cover glass and hence it was sealed. The various smectic modifications and the corresponding phase transition temperatures of 40% of Naol in EG are

83^0C 67.5^0C 54.3^0C $40.8\,^0$C 31^0C

Iso————SmA————SmD————SmB————SmE————Cryst

On cooling the specimen from its isotropic melt, a focal conic fan shaped texture is observed which is the characteristic of smcctic-A (Lamellar) phase in which the molecules are arranged in layers as shown in Figure 2(a). On further cooling, the observed lamellar smectic phase changes over to an isotropic viscous srnectic-D phase[4]. Sequentially on cooling specimen: smectic-D phase slowly transform to focal conic fan texture, which is the characteristic of highly ordered smectic-B phase in which the molecules are arranged in hexagonal closed packed system. Again on cooling, the focal conic fans are crossed by a number of arcs, which are the characteristic of srncctic-E phase as shown in Figure 2(b).

Optical anisotropic studies

The refractive indices of a liquid crystal are mainly determined by the molecular structure, wavelength and operating temperature. As the wavelength increases, the refractive indices decrease. The decreasing rate depends on the liquid crystal molecular structures. The wavelength and temperature-dependent refractive indices are fundamentally interesting and practically important for optimizing the display performances and other photonic devices

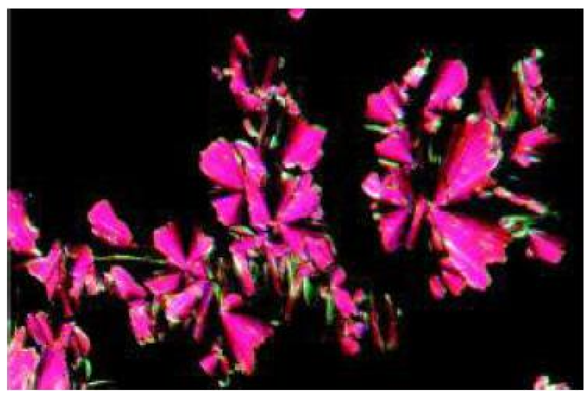

Figure 2a : Focal conic fan-shaped texture of lamellar SmA phase (250X)

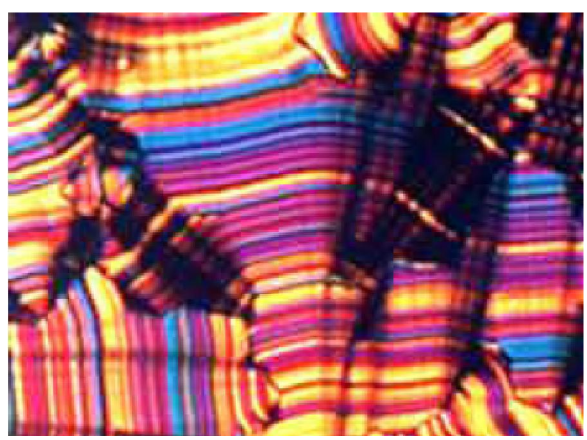

Figure 2b : Focal conic fans with radial striation of smectic-E phase (250X)

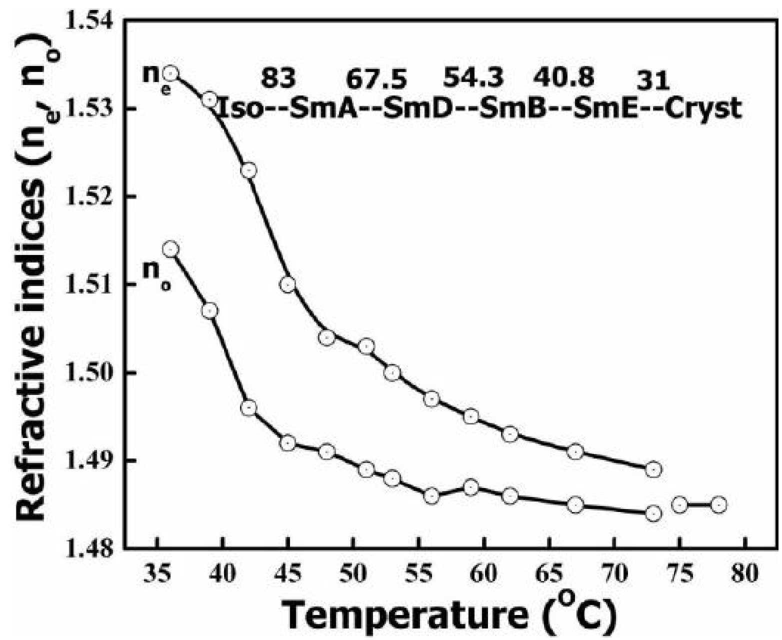

Figure 3 : Temperature variations of refractive indices for the mixture of 40% Naol in EG.

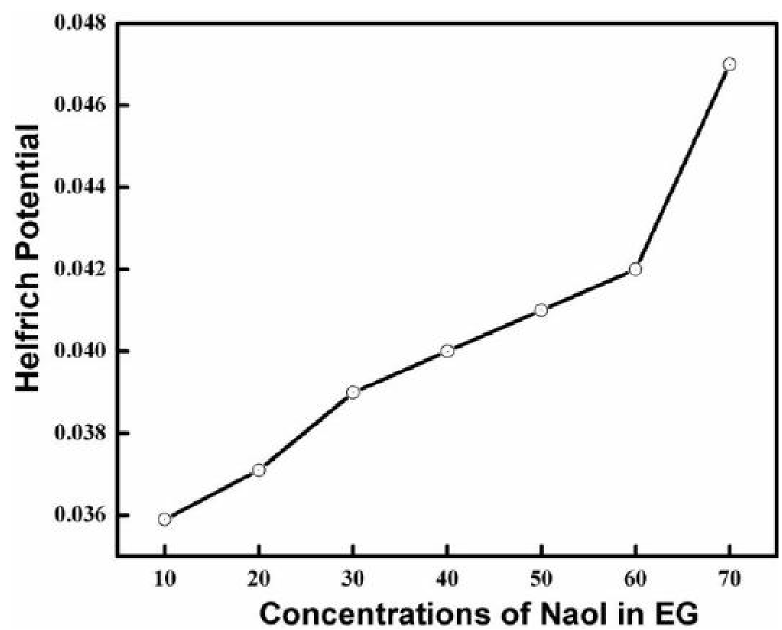

Figure 4 : Variation of helfrich potential with concentrations of Naol in EG.

employing liquid crystals[5, 6].

Results of this investigation are further supported by the optical studies[7, 8]. 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. Temperature variations of refractive indices for the mixture of 40% Naol in EG are as shown in Figure 3. The value of n_e is greater than n_o indicating that the material is uniaxial positive. From the figure, it can be observed that wherever there is phase transition, the value of refractive indices changes appreciably, which indicates that the changes correspond to polymorphic smectic modifications. Further, with increase in the concentration of Naol the value of refractive indices decreases with temperature, because the effective optical anisotropy associated with the molecules of Naol also decreases[9-11].

Helfrich potential and elastic modulus

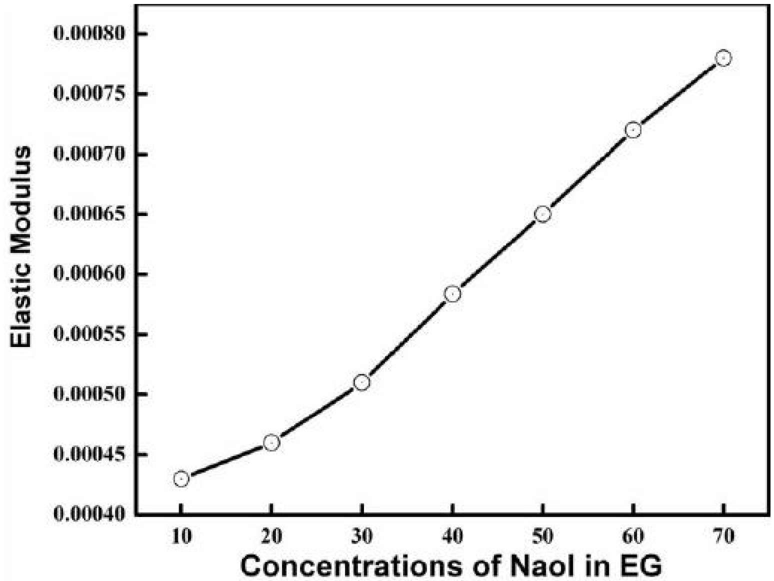

Figure 5 : Variation of elastic modulus with concentrations of naol in EG

The free energy of steric inter-membrane interactions between undulating the neighbouring membranes, when they are side by side in the multilayer systems[12]. The undulation modes are in multilayer systems can be treated in terms of the de Gennes theory[13] 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,

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

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

The V(ξ) 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 π/2. ξ mean membrane separation. Here it has been considered that the value of ξ is equal to the value of d[14].

The variations of Helfrich potential along with the concentrations of Naol in EG as shown in Figure 4 and hence it is very interesting to note that, the Helfrich potential values increases as the concentrations of the Naol increases. This result invokes that in dilute region of the mixture V(ξ) value decreases.

The elastic modulus (K)[14] of smectic compressibility is calculated using the relation,

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

where k_c is curvature elastic modulus.

The elastic modulus is also estimated for the mixture of different concentrations at various temperatures. The presented graph Figure 5 is obtained by plotting the elastic modulus as a function of the concentrations of Naol in EG. From the graph it is observed that as concentration of Naol decreases, the values of the bulk modulus also decrease. The reason is that: the smectic layers have no interaction with neighboring layers in dilute regions. The Helfrich steric contribution is small for a particular form of dislocations.

CONCLUSIONS

The above studies apart from revealing numerous optical textures associated with various liquid crystalline smectic phases in the given mixture have enabled us to reach the following conclusions. The given mixtures of all concentrations exhibits induced polymorphic smectic modifications at different temperatures. The drastic changes in the values of density, refractive index, and anisotropy of polarizability with the variation of temperature suggest that, the size of aggregates goes on increasing and while the mixture is cooled from its isotropic phase. But below a particular temperature, the size of aggregates becomes so large, that the specimen moves toward crystalline nature. This type of induced polymorphism is rare in mixture of non-mesogenic compounds.

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