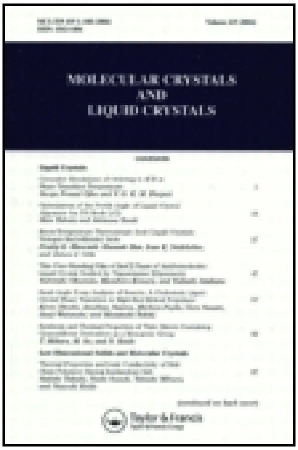


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Mesomorphic Behaviour of Lamellar Smectic Phases in the Binary Mixture of Non-Mesogenic Compounds

J. Mahadeva [a] , T. N. Govindaiah [b] , K. Rajashekara Prasad [c] & Nagappa [b]

[a] Department of Physics, PES College of Science, Mandya, India

[b] Department of Studies in Physics, University of Mysore, Mysore, India

[c] Department of Chemistry, K L College of Engineering, Vaddeswaram, India

Version of record first published: 05 Oct 2009

To cite this article: J. Mahadeva, T. N. Govindaiah, K. Rajashekara Prasad & Nagappa (2009): Mesomorphic Behaviour of Lamellar Smectic Phases in the Binary Mixture of Non-Mesogenic Compounds, Molecular Crystals and Liquid Crystals, 511:1, 218/[1688]-230/[1700]

To link to this article: http://dx.doi.org/10.1080/15421400903053883

Mol. Cryst. Liq. Cryst., Vol. 511, pp. 218/[1688]–230/[1700], 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903053883

Mesomorphic Behaviour of Lamellar Smectic Phases in the Binary Mixture of Non-Mesogenic Compounds

J. Mahadeva[1], T. N. Govindaiah[2], K. Rajashekara Prasad[3], and Nagappa[2]
[1]Department of Physics, PES College of Science, Mandya, India
[2]Department of Studies in Physics, University of Mysore, Mysore, India
[3]Department of Chemistry, K L College of Engineering, Vaddeswaram, India

The binary mixture of two non-mesogenic compounds viz., Sodium Oleate (NaOl) and Ethylene glycol (EG) exhibits a very interesting liquid crystalline smectic phases at large range of concentration and temperatures. The mixture with lower concentration of Naol exhibits an Iso – Sm A – Sm D – Sm B – Sm E – Cry., sequentially when the specimen is cooled from its isotropic phase. The phase transition temperature for different concentrations of these mixtures was determined using Polarizing microscope along with hot stage. The different phases of these mixtures are identified using X-ray and microscope techniques. The temperature variation of the optical anisotropy is discussed. Helfrich potential and elastic modulus is estimated in the smectic phase using Helfrich model.

Keywords: binary; lamellar; mesomorphic; non-mesogenic

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 the molecular ordering in the Iyotropic mesophase for the majority of the amphiphilic system corresponds to the smectic order [2]. The phase behavior of lyotropic systems of liquid crystals has been extensively studied [3,4], because of their different nature of liquid crystalline phases obtained at different temperatures and concentrations [5]. Both thermotropic and lyotropic system of liqud crystals give rise to several mesophases, which may be classified according to the

---

Address correspondence to J. Mahadeva, Department of Physics, PES College of Science, Mandya-571 401, India. E-mail: jmahadeva@yahoo.com

same space group in spite of their different shapes and chemical structure [6,7]. It is pertinent to mention here that there are lyotropic nematic and cholesteric phases encountered with soaps, water and long chain alchol systems [8–12]. Amongst the earlier investigations on such systems particular references must be made to the work of acimix [13] who used the mixture of 1-serine hydrochloride decy1 ester and orthophosphoric acid, which are non-mesogenic in nature. Nagappa *et al.* [10] have extensively studied the lytropic systems of cetyl alchohol and steryl alcohol with orthophosphoric acid, cetyl alchohol has been used as a solvent in forming the micellar phases.

Lyotropic mesophases are characterized by lamellar, hexagonal and cubic structures. In lamellar domain most of the defects are spherulitic or batonnets where the molecular packing with spherical bilayers in the form of onions. The Friedels oily streaks [14–16] are also observed. Occasionally the mixtures of higher concentrations of amphiphilic compounds exhibit classic focal conic domains, which are characterized by a fan shaped texture.

In the present study we have considered the mixtures of two non-mesogenic compounds viz., sodium oleate (NaOl) and Ethylene glycol (EG). The polymorphic smectic modifications of the liquid crystalline phases are observed using microscopic technique and these results are verified from the result of X-ray studies.

EXPERIMENTAL STUDIES

The sodium oleate (NaOl) used in this investigation was obtained from the British Deug house Led., England. The samples were further purified twice by re-crystallization with benzene. M/S SISCO Research Laboratory, Bombay, India, supplied ethylene glycol. The Ethylene glycol was used after boiling it at 433 K for 6 hours. The structural

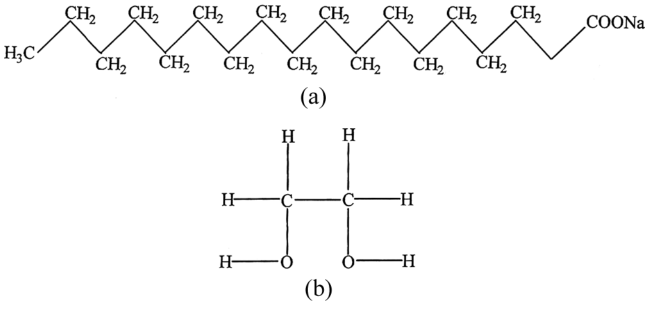


FIGURE 1 (a) Structural formula of the sodium oleate (NaOl) molecule; (b) Structural formula of the Ethylene glycol (EG) molecule.

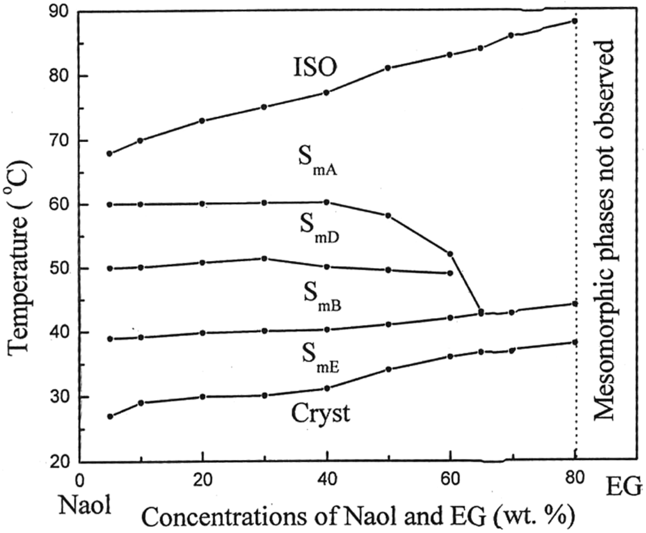


FIGURE 2 Partial phase diagram for the mixture of NaOl and EG.

formulae of sodium oleate and ethylene glycol are shown in Figure 1(a, b). The mixture of fifteen different concentrations of Naol (by wt%) in EG were prepared and kept in a desiccator's for a long time. The isotropic-liquid crystalline phase transition temperatures of these concentrations were measured using Leitz-polarizing microscope with conventional hot stage. The sample was sandwiched between the slide and cover, slip, which was sealed for the microscopic observation. The phase diagram shown in Figure 2, obtained by plotting the isotropic liquid crystalline phase transition temperatures of the mixture determined by the DSC studies as a function of concentrations of lyotropic liquid crystals. The phase diagram clearly indicates that the mesomorphism of these mixtures is thermodynamically stable for lower concentrations of Naol. The X-ray diffractometer recording for different concentrations of lyotropic liquid crystals at various temperatures were taken by using Jeol X-ray diffractometer. The density and refractive indices of these mixtures were measured at different temperatures employing the technique described in our earlier paper [17].

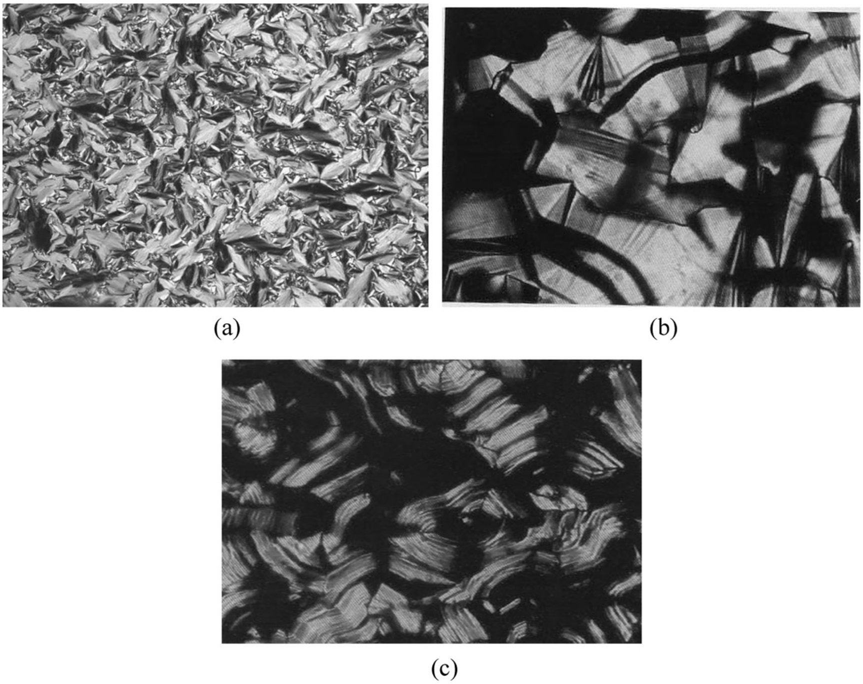
RESULTS AND DISCUSSION

Optical Texture Studies

The optical texture study of the various smectic modifications and the corresponding phase transition temperatures for 40% of lyotropic liquid crystals are given below.

Iso 77.2°C → SmA 60.14°C → SmD 50.03°C → SmB 40.23°C
→ SmE 31.07°C → Cry

On cooling the specimen from its isotropic liquid state 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 (Lamellar) phase in which the molecules are arranged in layers shown in Figure 3(a). This phase under goes slow transformations to an isotropic viscous smectic-D phase [17]. The optically extinct smectic-D phase is submitted to 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


(a) (b)

(c)

FIGURE 3 (a) Microphotographs of focalconic fan shaped texture of smectic-A (Lamellar) phase (250×); (b) Microphotographs of paramarphic smectic-B (250×); (c) Microphotographs of focalconic fans with radial striations of the smectic-E phase (250×).

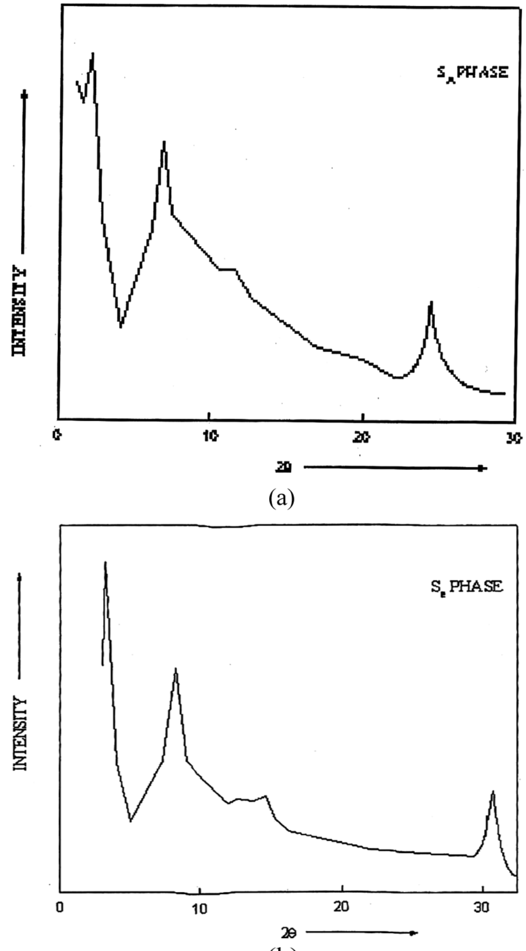
smectic-D phase transform to focal conic fan shaped texture on cooling the specimen. This texture corresponds to the paramorphotic [18] focal conic fan shaped texture of the ordered smectic-B phase shown in Figure 3(b). And then on further cooling of the sample radial striations on the fans were developed which is the characteristics of smectic-E phase shown in Figure 3(c).

The textures obtained in the polymorphic smectic-A, smectic-B and smectic-E phases are similar to those described in our earlier studies [19]. The isotropic-liquid crystalline phase transition temperature of these mixtures was obtained from the microscopic studies. The phase diagram shown in Figure 2, illustrates that, the lower and higher concentrations of sodium oleate exhibits a wide variety of liquid crystalline phases. Here it is pertinent to remark that the smectic-E phase exhibit at room temperature for the concentrations from 10% to 80% of Naol. But above 80% of Naol, the mixture exhibits only a birefringent region and it is difficult to associate the texture with any of the mesophases.

X-Ray Studies

X-ray studies are useful for the identification of various types of arrangement of molecules in the liquid crystalline phases. Using XRD data an attempt has been made to understand the molecular arrangement in the mixture of lyotropic liquid crystals. The X-ray diffraction patterns were recorded using JEOL, (Japan). X-ray diffractometer (target Fe $\lambda = 1.934\,\text{Å}$). The mixture of 40% sodium oleate (NaOl) in ethylene glycol (EG) were filled in the sample holder and a diverging X-ray beam was made to fall on the mixture. The X-ray diffractometer traces were obtained for various concentrations of the mixtures at different temperatures for the smectic-A and smectic-E phases.

The XRD recordings are obtained for the sample of 40% NaOl in EG at 345 K and 308 K, which are shown in Figures 4(a, b). The recordings at these temperatures correspond to the smectic-A and smectic-E phases. It is observed that the peaks are very sharp in the smectic-E phase [20], because of the fact that the smectic-E phase is highly ordered. The effective ‘d’ Spacing in smectic-E phase is calculated using Bragg’s equations $n\,\lambda = 2d\sin\theta$ and are shown in Table 1. The inner sharp ring in the X-ray recordings corresponds to the first order diffraction from the smectic layer like planes. from which d is calculated. The intermolecular distance is calculated from the outer ring, which appears to be sharp owing to the fact that with in the plane of each layer there is a regular arrangement of molecule in the lateral directions.



(a)

(b)

FIGURE 4 (a) X-ray diffraction patterns for the mixture of 40% NaOl in EG at 343 K; (b) X-ray diffraction patterns for the mixture of 40% NaOl in EG at 308 K.

At higher temperatures the NaOl molecules are arranged alternatively a planar double layer separated by EG layers leading to the smectic-A phase. The molecular length of NaOl is 2.3 μm, which is calculated from the skeletal structure of NaOl using the bond length and bond angle of CH_2-CH_2. The effective 'd' spacing obtained from X-ray diffraction recordings at 308 K approximately corresponds to twice the molecular length of NaOl. The area per polar group (S) in

TABLE 1 Spacing Determined Using XRD Recordings, Calculate Values of S, the Interfacial Area Per Polar Group and d_{hc}, the Average Thickness of Hydrocarbon Layers Obtained for Different Concentrations of Naol and EG

Naol content (wt %)	D (10^{-1} nm)	Volume fraction (φ)	D (10^{-1} nm)	d_{hc} (10^{-1} nm)	d_{aqg} (10^{-1} nm)	S (10^{-2} nm^2)	
	SmE phase					SmE phase	SmA phase
10	32.57 (15.82)	0.8625	4.10	28.09	4.4784	23.78	–
20	34.43 (15.84)	0.8664	4.71	29.83	4.5999	22.35	48.94
30	36.93 (13.68)	0.8600	4.90	31.76	5.1702	20.92	44.29
40	41.78 (13.20)	0.8610	4.51	35.97	5.8074	18.56	41.97
50	50.37 (13.76)	0.8600	4.63	43.33	5.0518	15.39	34.98
60	36.95 (15.84)	0.8631	4.07	31.89	5.0585	20.99	–
70	36.93 (15.85)	0.8630	4.65	31.87	5.0594	20.98	–

different lamellar phases was calculated using the standard method [21]. Hence we observe that the molecular area of polar head at high temperature is equal to twice the molecular area of the crystallized aliphatic chains at lower temperatures [22].

Figure 5 shows a planar bimolecular leaflets alternating with ethylene glycol regions in one-dimensional liquid crystalline lattice d_{hc} designates the pure NaOl region and circles denotes the interface between the hydrocarbons and ethylene glycol. The interfacial area per molecule (S) is calculated and these values are shown in Table 1.

Optical Anisotropy

The results of this investigation are further supported by the birefringence studies. The refractive indices for extraordinary ray (n_e) and

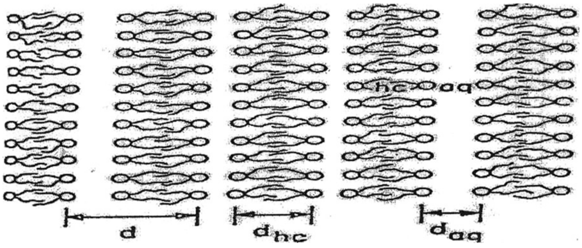


FIGURE 5 Planar bimolecular leaflets alternating with EG regions in one-dimensional liquid crystal lattice.

ordinary ray (n_o) of the mixtures were measured at different temperatures for the different concentrations using Abbe Refractometer and precision Gonioneter spectrpmeter. The temperature variation of refractive indices for 30%, 40% and 50% of sodium in ethylene glycol are shown in Figure 6(a–c). The value of n_1 is greater than n_2, indicating that the material is uniaxial positive. We are unable to measure the third component of index n_3 in biaxial smectic-E phase.

The electrical susceptibility χ is related to $N\alpha$ i.e., $\chi_e = N\alpha_e$, $\chi_o = N\alpha_0$ and $\Delta\chi = \chi_e - \chi_{o.}$ Here α_e and α_0 are the effective polarizabalities of extraordinary and ordinary rays respectively, N is the number of molecules per unit volume. The values of χ_e and χ_o at various temperatures are calculated using Neugebauer relation [23]

$$n_e^2 - 1 = 4\pi\chi_e(1 - 4\pi L_e\chi_e)^{-1} \tag{1}$$

$$n_0^2 - 1 = 4\pi\chi_0(1 - 4\pi L_0\chi_0)^{-1} \tag{2}$$

Here L_e and L_o are the Lorenz field factors for the extraordinary and ordinary vibrations. By use of the equation,

$$L_e + 2L_o = 1$$

And from the relations 1 and 2 we get

$$1/\chi_e + 2/\chi_o = 4\pi/3[(n_e^2 + 2)/(n_e^2 - 1) + 2(n_o^2 + 2)/(n_o^2 - 1)]$$

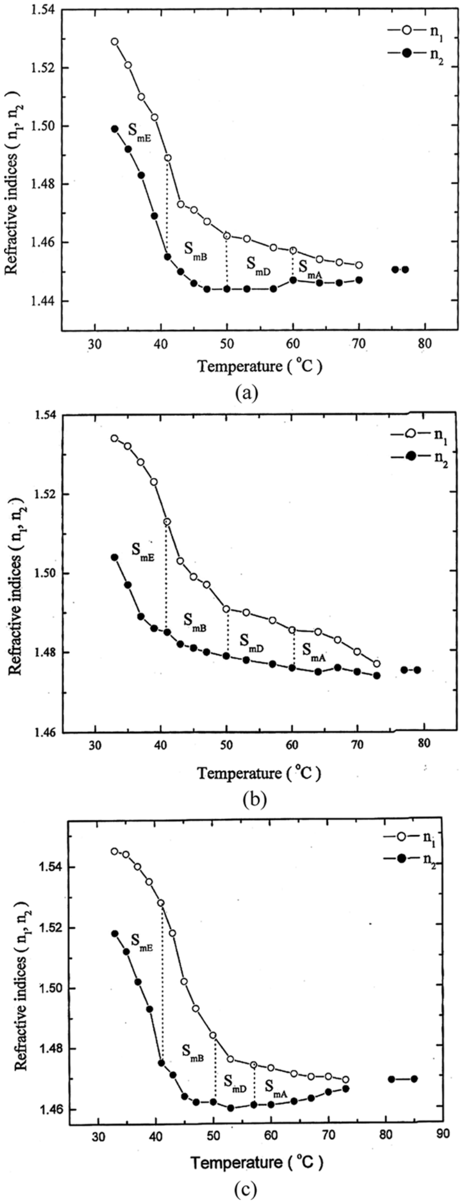
Further, the Born relation [24] given below is valid

$$(\chi_e + 2\chi_o)/3 = 3/4\pi[(n^2 - 1)/(n^2 + 2)]$$

Here $n^2 = n_e^2 + 2n_o^2/3$ and also it may be noted that

$$\chi_e - \chi_o/\chi = N(\alpha_e - \alpha_o)/N\alpha = (\alpha_e - \alpha_o)\alpha$$

The plot of $\Delta\chi$ as a function of temperatures for 30%, 40% and 50% of NaOl in EG are shown in Figure 7(a–c). From these figures it is observed that wherever there is a phase transition the value of $\Delta\chi$ changes appreciably, which indicates that each change corresponds to the various modification in smectic phases. Further with increase in concentrations of NaOl the values of $\Delta\chi$ increases and it decreases with the increase of temperature, because the effective optical anisotropy associated with the temperature.



(a)

(b)

(c)

FIGURE 6 (a) Temperature variation of refractive indices for the mixture of 30% NaOl in EG; (b) Temperature variation of refractive indices for the mixture of 40% NaOl in EG; (c) Temperature variation of refractive indices for the mixture of 50% NaOl in EG.

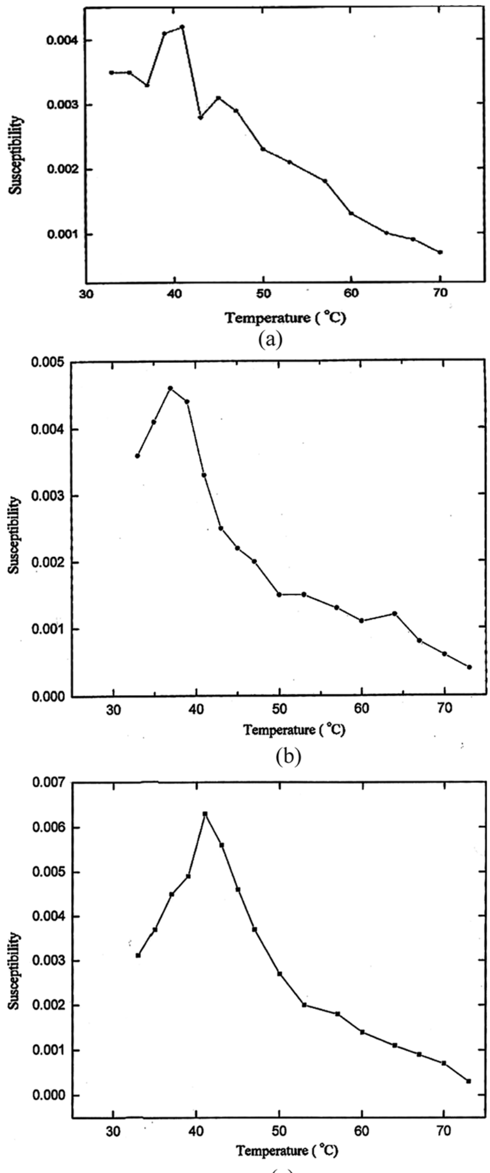


FIGURE 7 (a) Temperature variation of susceptibility for the mixture of 30% NaOl in EG; (b) Temperature variation of susceptibility for the mixture of 40% NaOl in EG; (c) Temperature variation of susceptibility for the mixture of 50% NaOl in EG.

HELFRICH POTENTIAL AND ELASTIC MODULUS

The free energy of steric interactions between undulating membranes, when they are side by side in the multiplayer systems [25]. The undulation modes in multiplayer systems can be treated in terms of the de Gennes theory [26] of fluctuations in smectic phase, which invokes curvature elasticity and smectic compressibility.

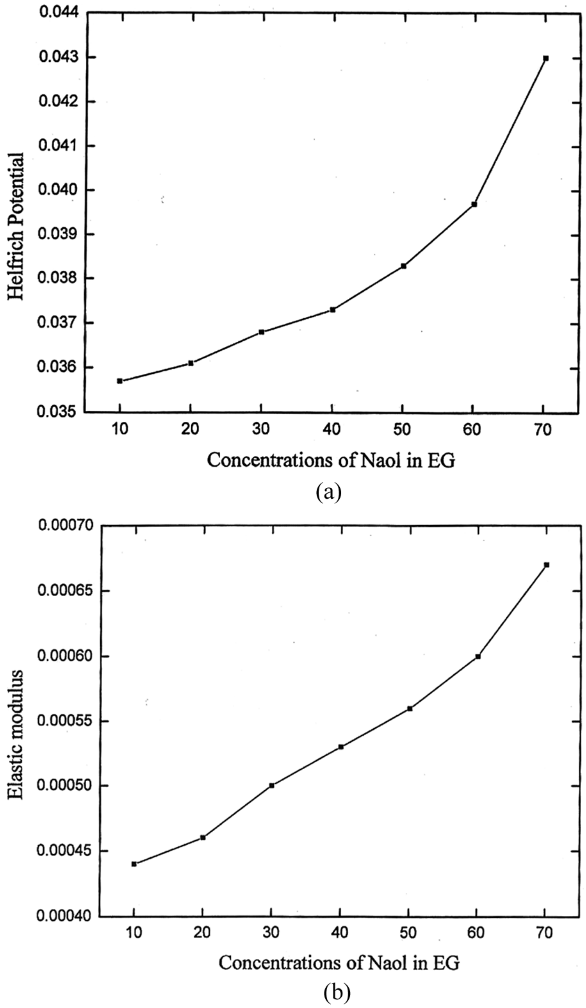


FIGURE 8 (a) Variation of Helfrich potential with concentrations of NaOl and Eg; (b) Variation of elastic modulus with concentrations of NaOl and Eg.

To estimate the Helfrich potential ($V(\zeta)$), we consider the free energy per unit area.

$$V(\zeta) = \beta(K_BT)^2/K_0\zeta^2$$

Where $\beta = 3\pi^2/128$, $(K_0/K_BT) = 0.75$ (The repulsive force between the membrane K_0 is bare bending constant, K_B is the Boltzman constant.

The $V(\zeta)$ 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 $\pi/2$. ζ is mean membrane separation. Here it has been consider ζ is equal to d [27], and its value is 27.78 Å.

The $V(\zeta)$ of layers at different concentration of NaOl at different temperature in smectic phase is calculated. The variations of elastic modulus along with the concentration of Naol as shown in Figure 8(a) 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 $V(\zeta)$ value decreases.

The elastic modulus (K) [27] of smectic compressibility is calculated using the relation,

$$K = [3\pi^2/64][(K_BT)^2/K_cd]$$

where K_c is curvature modulus.

The elastic modulus is estimated for the mixture of different concentrations at various temperatures. The graph is obtained by plotting the elastic modulus as a function of the concentrations as shown in Figure 8(b). From the graph it is observed that as concentration of Naol decreases. The values of the bulk modulus also decrease. The reason is the smectic layers have no interaction with the neighboring layers in the dilute regions. The Helfrich steric contribution is small, for a particular form of dislocations.

CONCLUSIONS

The above studies apart from revealing numerous textures associated with various phases in mixtures have enabled us to reach the following conclusions. Mixtures with different concentrations from 5–65% of NaOl in EG exhibit polymorphic modifications of the smectic phases depending on the temperatures. The drastic change in the values of density, refractive index anisotropy of polarizability with temperature unambiguously corresponds to smectic-E phase. The mixture with concentrations of 66% NaOl in EG and above exhibit a smectic-A and smectic-E phases respectively, when the sample is cooled from isotropic liquid phase. The X-ray results also lend support to the above observations. This type of polymorphism is very rare in the binary mixture of non-mesogenic compounds.

REFERENCES

[1] Benton, W. J. & Millar, C. A. (1983). *J. Phys. Chem.*, *82*, 1981.
[2] Skoulios, A. & Guillon, D. (1988). *Mol. Cryst. Liq. Cryst.*, *165*, 317.
[3] Gulerene, Y. & Marcerah, J. P. (1983). *Phys. Rev. Lett.*, *51*, 2109.
[4] Melnik, G., Photinces, P. J., & Saupe, A. (1988). *J. Chem, Phys.*, *88*, 4046.
[5] Latapanikar Sharma, V. K., Geetadatta, Usha Deniz K., Parvathanathan, P. S., Ranathan, K. V., & Khetrapal, C. L. (1995). *Mol. Cryst. Liq. Cryst.*, *260*, 611.
[6] Ekwall, P. (1995). *Advances in Liquid Crystals*, *1*, 1.
[7] Lawrence, A. S. E. (1970). In: *Liquid Crystals and Ordered Fluids*, Johnson, J. F. & Porter, R. S. (Eds.), Plenum Press: New York, 289.
[8] Luzzati, V. (1968). In: *Biological membranes*, Academic Press: London, 71.
[9] Somashekhar, R., Sthyanarayana, C. H., & Madhava, M. S. (1985). *Mol. Cryst. Liq. Cryst.*, *129*, 79.
[10] Marthandappa, M., Nagappa, & Lokhanatha Rai, K. M. (1991). *J. Phys. Chem.*, *95*, 6369.
[11] Vorlander, D. & Gahren, A. (1907). *Ber. Dtsch. Chem. Ges.*, *40*, 1966.
[12] Kravchenkov, V. M. & Pastukova, I. S. (1952). *Zh. Prikl. Khim.*, *25*, 313.
[13] Acimix. (1987). *Liq. Cryst.*, *4*(2), 549.
[14] Prathiba, R. & Madhusudana, N. V. (1992). *J, Physiquell.*, *2*, 383.
[15] Gray, G. W. & Goodby, J. W. G. (1984). *Smectic Liquid Crystals*, Leon and Hill: Glassgow.
[16] Friedel, G. (1972). *Ann Phys. France*, *2*, 273.
[17] Nagappa, Nataraju, S. K., & Krishnamurthy, D. (1986). *Mol. Cryst. Liq. Crystal*, *133*, 31.
[18] Fantel, K., Mandell, L., & Ekwall, P. (1968). *Acta. Chem. Scand.*, *22*, 3209.
[19] Franeois, J. (1969). *J. Phys. Radium.*, *30*, 89.
[20] Devries, A. (1975). *Pramana. Suppl*, *1*, 93.
[21] Parsigian, V. A. (1967). *Science*, *156*, 939.
[22] Vincen, J. M. & Skoulios, A. (1966). *Act, Crystallogr.*, *20*, 432.
[23] Neugebauer, H. E. J. (1954). *Canad. J. Phys.*, *32*, 1.
[24] Born, M. (1916). *Sitz. De Phys. Maths.*, *25*, 614.
[25] Helfrich, W. Z. (1978). *Naturfersch.*, *33a*, 305.
[26] de Gennes, P. G. (1969). *J. Phys. Paris, Colloque.*, *4*, 64.
[27] de Gennes, P. G. & Prost, J. (1998). *The Physica of Liquid Crystal*, Clarenden Press: Oxford, UK, 103.