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PHYSICAL STUDIES OF BINARY MESOPHASE MIXTURES CONTAINING N-(p-PROPOXY-BENZYLIDENE)-p-PENTYLANILINE

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The applicability of the modified Lippincott δ-function model method is tested for binary mesophase mixtures. Using this method, the polarizabilities, polarizability anisotropies and order parameters of binary mesophase mixtures containing N-(p-propoxy-benzylidene)-p-pentylaniline are evaluated and compared with the reported values. A close agreement is observed between the estimated values and reported values.

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1. Introduction

From the technological point of view, the binary mixtures of liquid crystals are very important because of their application in display devices. Knowledge of the orientational order of the binary mesophase mixtures will be of immense importance to the technical personnel. Response of the display devices is mainly orientation dependent and in this respect the study of temperature dependence of the orientational order parameter is interesting.

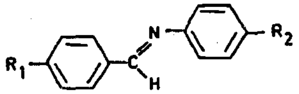
The orientational order parameter of a liquid crystal can be characterized by the molecular polarizabilities and their anisotropy. Molecular polarizabilities, though impossible to measure directly, can be calculated on the basis of different models. The authors developed a modified Lippincott δ-function model (MLδP) method [1] for the estimation of polarizabilities of liquid crystals and successfully applied the method for the different homologous series of liquid crystals [2–4].

In the present paper, the authors propose to test the applicability of the MLδP method to the binary mesophase mixtures. The binary mixtures selected for the study are

1. N-(p-propoxy-benzylidene)-p-pentylaniline (PBPA)/
/N-(p-ethoxy-benzylidene)-p-butylaniline (EBBA);

2. *N*-(*p*-propoxy-benzylidene)-*p*-pentylaniline (PBPA)/
/*N*-(*p*-butoxy-pentylidene)-*p*-pentylaniline (BBPA).

The structural formula and the solid-nematic (T_M) and nematic-isotropic (T_c) transition temperatures of these liquid crystals are presented in Fig. 1.



	R_1	R_2	T_M C ⟶ N	T_C N ⟶ I
BBPA	$O(CH_2)_3CH_3$	$(CH_2)_4CH_3$	42.0°C	80.5°C
EBBA	CH_3CH_2O	$(CH_2)_3CH_3$	34.0°C	78.0°C
PBPA	$CH_3(CH_2)_2O$	$(CH_2)_4CH_3$	23.0°C	69.1°C

Fig. 1. Structural formulae and transition temperatures of the liquid crystals.

2. Method

2.1. Estimation of mean polarizability

Applicable relations for the estimation of the mean polarizability in terms of the parallel bond component ($\sum \bar{\alpha}_{\|\mathrm{p}}$), the perpendicular bond component ($\sum \bar{\alpha}_{\perp}$) and the non-bond region electron contribution ($\sum \bar{\alpha}_{\|\mathrm{n}}$) are given in Eqs. (1)–(5):

$$\alpha_1 = \frac{1}{3}\left(\sum \bar{\alpha}_{\|\mathrm{p}} + \sum \bar{\alpha}_{\|\mathrm{n}} + \sum 2\alpha_{\perp}\right), \tag{1}$$

where

$$\sum \bar{\alpha}_{\|\mathrm{p}} = \frac{4nA\left[\exp(T-T_c)/T_c\right]}{a_0}\left(\frac{R^2}{4}+\frac{1}{2C_R^2}\right)^2 \exp\left\{-\left[\frac{(X_1-X_2)^2}{4}\right]\right\}. \tag{2}$$

Here n is the bond order, A is the δ-function strength, R is the bond length, X_1 and X_2 are Pauling's electronegativities for the atoms in the bond

$$\sum \bar{\alpha}_{\|\mathrm{n}} = \sum f_j \alpha_j . \tag{3}$$

Here f_j is the fraction of the non-bonded electrons of the j-th atom and α_j is its atomic polarizability.

$$\sum 2\bar{\alpha}_{\perp} = n_{\mathrm{df}} \frac{\sum X_j^2 \alpha_j}{\sum X_j^2}. \tag{4}$$

Here n_{df} is the number of degrees of freedom given as $n_{\mathrm{df}} = (3N - 2n_{\mathrm{b}})$. N is the number of atoms and n_{b} is the number of bonds in the liquid crystal.

$$\alpha = \alpha_1\left[1 - (m/\rho_1)(T - T_c)\right]. \tag{5}$$

Here m is the slope of the ρ versus t curve, T_c is the transition temperature, ρ_1 is the density in liquid phase, α_1 is the mean polarizability in liquid phase and α is the mean polarizability in liquid crystalline phase. Details of derivation of Eq. (5) are discussed in our paper [1].

The studies of Chandrasekhar and Madhusudana [5] showed that the order parameters of the *p*-azoxyanisole (PAA)/p, p'-di-*n*-ethoxyazoxy benzene (PEAB) mixtures obey additive relations. Phaovibul et al. [6] and Denprayoonwong et al. [7] also found that the order parameter and the dilatometric properties of PAA/p, p'-di-*n*-pentyloxyazoxy benzene (PPAB) and PAA/p, p'-di-*n*-hexyloxyazoxy benzene (PHAB) mixtures also follow the additive rule. Applying the additive rule, the mean polarizabilities of the mixture can be expressed as

$$\alpha_{\text{mix}} = X\alpha_1 + (1 - X)\alpha_2, \tag{6}$$

where X is the mole fraction of the component having a mean polarizability α_1 and $(1 - X)$ is the mole fraction of the second component in the mixture. The values of α_1 and α_2 can be estimated from Eq. (5) using the MLδP method. The necessary data on bond lengths are taken from CRC handbook [8]. The density data and the transition temperatures of these liquid crystals are taken from the reported data [9].

2.2. Estimation of molecular polarizability anisotropy

As it is well known [10], we need a molecular polarizability ellipsoid rather than the average polarizability to study the directional properties of the anisotropic crystals. In the calculations of the polarizability we take the molecular axis along the line joining the centres of the two benzene rings, and assume the molecule to be rigid. The polarizability contribution parallel to the molecular axis of the polarizability ellipsoid of a polyatomic molecule is given by

$$\alpha_{\parallel} = \sum \overline{\alpha}_{\parallel} \cos^2 \theta + \sum \overline{\alpha}_{\perp} \sin^2 \theta \tag{7}$$

(summed over all bonds), where θ is the angle between a bond and the molecular axis, $\overline{\alpha}_{\parallel}$ and $\overline{\alpha}_{\perp}$ are respectively the parallel bond component and the perpendicular bond component of the polarizability obtained from the MLδP method.

In the absence of the conformed molecular structures of many of these substances, for the sake of uniformity and simplicity the bond angles are assumed to be 109° for the bonds involving tetrahedral linkage and in all other cases as 120°. Standard values of the bond lengths are assumed and the angles between the various bonds and the molecular axis were determined by drawing a figure of the molecule. The molecular axis is taken to be along the line joining the outer *para* carbon atoms of the two benzene rings assuming the molecule to be rigid.

Using the values of $\alpha_{\parallel}$ obtained from Eq. (7), the molecular polarizability anisotropy can be calculated as

$$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} = (3/2)(\alpha_{\parallel} - \overline{\alpha}), \tag{8}$$

where $\overline{\alpha}$ is the mean polarizability from the MLδP method. $\alpha_{\perp}$ can be calculated as

$$\alpha_{\perp} = \alpha - (1/3)(\alpha_{\parallel} - \alpha_{\perp}).$$

From the additivity rule the molecular polarizability anisotropy of the mixture can be represented as

$$\Delta\alpha_{\text{mix}} = X\Delta\alpha_1 + (1 - X)\Delta\alpha_2,$$

where $\Delta\alpha_1$ is the polarizability anisotropy of the component of mole fraction X and $\Delta\alpha_2$ is the polarizability anisotropy of the second component of mole fraction $(1-X)$.

2.3. Estimation of order parameters

The orientational order parameter S is defined as [11, 12]

$$S = (3/2)\langle\cos^2\theta\rangle - 1/2, \tag{10}$$

where θ is the angle made by the long molecular axis with the preferred direction and the brackets denote an average over the molecules in a macroscopic volume.

The principal polarizabilities of the molecules, the anisotropic nature of the polarization field in the medium and the orientational order parameter S determine the birefringence of nematic liquid crystals. For calculations of the polarizabilities of the molecules and the order parameter S from birefringence data, the Lorenz–Lorentz formula cannot be employed because its validity is restricted to cases of the spherical (or cubic) symmetry in connection with the molecular arrangement. According to the Vuks formula [13] the ratio of the average local electric field to the applied field is the same for the cases when the applied fields is (i) parallel and (ii) perpendicular to the optical axis of the medium. Neugebauer [14, 15] has considered in detail the form of the polarization field in anisotropic media. In a nematic medium, as a result of the anisotropic distribution of the molecules the average local electric field has the form $E+\gamma P$, where E is the applied field, P — the polarization and γ is a factor which is different for the directions parallel and perpendicular to the optical axis.

In the present study the order parameters of the above systems were evaluated, using both the isotropic internal field model of Vuks and the anisotropic internal field model of Neugebauer.

In the Vuks method the order parameter is given by [16]:

$$S = \frac{\alpha}{\alpha_\parallel - \alpha_\perp}\frac{n_e^2 - n_0^2}{n^2 - 1}, \tag{11}$$

where $n^2 = (1/3)(n_e^2 + 2n_0^2)$. α is the mean polarizability, $\alpha_\parallel$ - $\alpha_\perp$ is the polarizability anisotropy evaluated using MLδP method.

In the Neugebauer method, the order parameter is given by [16]:

$$S = \left(\frac{\alpha}{\alpha_\parallel - \alpha_\perp}\right) f(B), \tag{12}$$

where

$$f(B) = (9/4B)[(B^2 - (10/3)B + 1)^{1/2} + B/3 - 1]$$

and

$$B = \frac{n^2-1}{n^2+2}\left(\frac{n_e^2+2}{n_e^2-1} + 2\frac{n_0^2+2}{n_0^2-1}\right).$$

3. Results and discussion

The mean polarizabilities and polarizability anisotropies of EBBA, BBPA, PBPA estimated from the MLδP method are presented in Table I along with the reported values [9]. The estimated values of mean polarizability and polarizability anisotropies of the binary mesophase mixtures are presented in Table II. The refractive indices of these mixtures were measured by using the well known low angle hallow prism method [17]. Using the mean polarizability, the polarizability anisotropy and the refractive indices data the order parameters of these binary mesophase mixtures are evaluated using the Vuks and Neugebauer methods and presented in Figs. 2 and 3 along with the reported data [18]. The solid line represents the variation of the order parameter with the temperature as per the reported data. A close agreement is found between the parameters evaluated

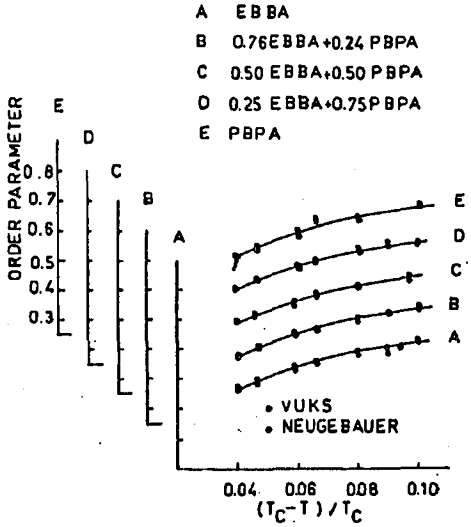


Fig. 2. Order parameters in EBBA/PBPA mixtures.

TABLE I

Molecular polarizabilities and polarizability anisotropies (all $\times 10^{24}$ cm^3) of EBBA, BBPA and PBPA.

Compound	$\sum \bar{\alpha}_{\parallel p}$	$\sum \bar{\alpha}_{\parallel n}$	$\sum 2\bar{\alpha}_{\perp}$	α		$\Delta\alpha$	
				Present	Reported value	Present	Reported value
EBBA	76.37	1.63	36.11	37.89	38.45	23.12	22.68
BBPA	88.42	1.63	42.87	43.92	43.18	24.31	24.14
PBPA	86.08	1.63	42.21	43.01	44.04	23.96	23.57

from this method and the reported values, which confirms the applicability of the present method to the binary nematic mixtures.

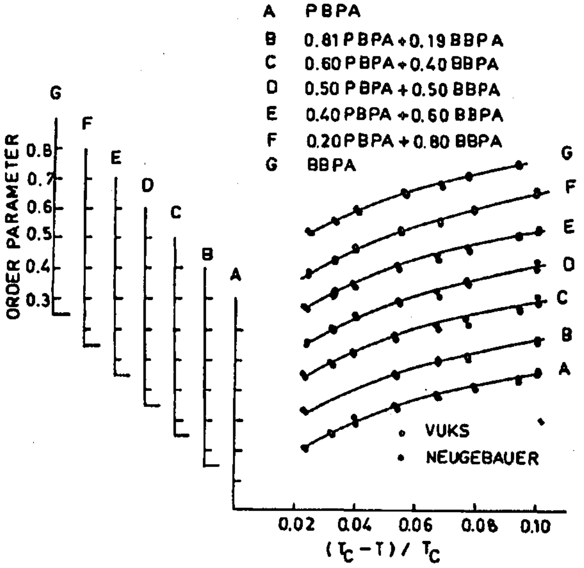


Fig. 3. Order parameters in BBPA/PBPA mixtures.

TABLE II
Molecular mean polarizabilities ($\alpha \times 10^{24}$ cm^3) and polarizability anisotropies ($\Delta\alpha \times 10^{24}$ cm^3) of binary mesophase mixtures.

System	α	$\Delta\alpha$
0.76 EBBA + 0.24 PBPA	39.12	23.32
0.50 EBBA + 0.50 PBPA	40.45	23.54
0.25 EBBA + 0.75 PBPA	41.73	23.75
0.81 PBPA + 0.19 BBPA	43.18	24.03
0.60 PBPA + 0.40 BBPA	43.37	24.10
0.40 PBPA + 0.60 BBPA	43.56	24.17
0.20 PBPA + 0.80 BBPA	43.74	24.24

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