MOLECULAR POLARISABILITIES AND ORIENTATIONAL ORDER PARAMETERS OF BINARY MESOPHASE MIXTURES OF NEMATIC COMPOUNDS

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ABSTRACT

The mean molecular polarizabilities and orientational order parameters of the binary mixtures of three nematic compounds (EBBA/PBPA and BBPA/PBPA) are reported. The mean molecular polarizabilities and polarizability anisotropies are estimated using the molecular vibration approach and the order parameters are calculated using Vuks method. The variation of order parameter with temperature is studied and the results are found to be in accordance with additivity rule of mixtures

1. INTRODUCTION

It is an established fact that mixtures of liquid crystals are more suited for technological applications than pure materials. So, the study of physical properties of nematic liquid crystal mixtures as a function of composition attracted many workers and there have been many reports in recent years[1-3]. Also, another reason is that such systems are of considerable interest for theoretical studies in the field of molecular interactions. It has been shown that the deviations from the ideal behaviour of the mixtures containing molecules with strongly polar end groups can be attributed to the formation of different kinds of molecular associates[4,5]. Not only mixtures of terminal - polar compounds, but the systems containing weakly polar mesogens also should display a rich variety of thermodynamic properties owing to the strongly anisotropic molecular interactions.

In the present investigation polarisabilities, polarisability anisotropies and orientational order parameters of the binary mixtures of three nematic compounds (PBPA/EBBA) and (PBPA/BBPA) are evaluated. The study of polarizability is very important because the anisotropy of polarizability is necessary in evaluating the order parameter of the liquid crystals. There are different internal field models to evaluate the polarizabilities. But these models use the refractive indices and density data. In our recent communication[6] we have presented molecular vibration approach to evaluate molecular polarizabilities, using vibrational frequencies. In the present work, we have also made an attempt to apply our molecular vibration approach to the binary mixtures of liquid crystals by taking into consideration the additive rule of mixtures[7]. The structural formulae and the transition temperatures of the nematic compounds are shown in Figure.1.

2. THEORY

2.1 Estimation of mean molecular polarisability

The originality of the present method of molecular vibration approach lies in correlating bond polarizabilities and stretching and bending force constants. The fact that bond polarizabilities, molecular vibration parameters and related parameters like bond moments (μ) are used in explaining the apparent molar Kerr constant of tetrahedrally symmetric molecules, gives clue for a possible relationship between polarizability and molecular vibration parameters.

As the detailed derivation and details are reported elsewhere[8], we give the final equation which relates longitudinal (b_L) and transverse (b_T) bond polarizabilities with mean amplitude of vibration ($\sigma^{1/2}$) only

$$b_L+2b_T = C\, p^{j}\, j^{nr}\, \sigma^{1/2} \qquad (1)$$

where C is a constant equal to 5.24×10^{-15}, P is characteristic of the atom and is equal to 1, 1.2, 1.3, 1.4 and 1.5 accordingly as it belongs to 2nd, 3rd, 4th, 5th or 6th row in the periodic table, n is +1 or -1, according as the bond is nonhydride or hydride and r is the saturation factor.

So, the average polarizability (α) of the molecule is given by

$$\alpha = \frac{\Sigma n_i (b_L+2b_T)_i}{3} \qquad (2)$$

where n_i is the number of bonds of the type i.

Phaovilbul[9] et al observed that the order parameter and the dilatometric properties of PAA/ PPAB and PAA/PHAB mixture follow the additive rule. So for an ideal mixture we can express it as

$$\alpha_{mix} = x\alpha_1+(1-x)\alpha_2 \qquad (3)$$

where x is the molefraction 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 are estimated using Equations 1 and 2.

2.2 Estimation of molecular polarisability anistropy

It is difficult to estimate polarizability anisotropies without the density data. Of course we have Haller's [10] extrapolation method, in which log (α_e-α_o) is plotted against log (T_c-T) and when the straight line obtained is extrapolated upto log T_c, the limiting value of (α_e-α_o) is assumed to correspond to the value of ($\alpha_\parallel$-$\alpha\perp$) of the molecule. But the values

obtained by this method are found to have an error of around 10%. So, we adopted the procedure suggested by Shashidara Prasad[11], in which, to estimate $\alpha_{\parallel}$, the molecular axis is taken along the line joining the centre of two benzene rings. The polarizability parallel to the molecular axis is given by

$$\alpha_{\parallel} = \Sigma\beta_r\cos^2\theta+\Sigma\beta_t\sin^2\theta \quad (4)$$

where β_r and β_t are bond polarizabilities parallel and transverse to the bond respectively and θ is the angle between the bond and the molecular axis.

From the value of $\alpha_{\parallel}$ from Equation 4, the molecular polarizability anisotropy ($\Delta\alpha$) can be written as

$$\Delta\alpha = 3/2(\alpha_{\parallel}-\alpha) \quad (5)$$

here α is the mean molecular polarizability estimated from the molecular vibration method.

Applying the additivity rule, the polarizability anisotropy of the mixture can be expressed as

$$\Delta\alpha_{mix} = x\Delta\alpha_1+(1-x)\Delta\alpha_2 \quad (6)$$

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

2.3 Estimation of order parameter

The orientational order parameter S is written as [12]

$$S=1/2<(3\cos^2\theta-1)> \quad (7)$$

where θ is the angle between the director and the major axis of the rod like molecule.

According to Vuk's[13] the ratio of the average local electric field to the applied is same for the two cases when the applied field is parallel and perpendicular to the optic axis of the medium.

According to Vuk's model the order parameter is given by

$$S = \frac{a}{(aII - a\perp)}\frac{(n_e^2 - n_o^2)}{n^2 - 1} \quad (8)$$

where a is the mean polarizability estimated from the molecular vibration method and $n^2 = (n_e^2+2n_o^2)$. XX and YY are the polarisabilities in a direction parallel and perpendicular to the optic axis. The variation of refractive indices with temperature is taken from the work of Nagappa et al[14]. From this the variation of order parameter with temperature is also studied.

3. RESULTS AND DISCUSSION

The estimated values of mean polarizabilities and polarizability anisotropies of pure compounds are given in Table 1, along with the reported values[15]. The mean molecular polarizabilities and polarizability anisotropies of the two binary systems are presented in the Table 2. Variation of mean polarizabilities with concentration in two mixtures is shown in Figure 2. From the estimated polarizabilities it is clear that polarizabilities are almost independent of temperature. The estimated values of α_{mix} lie in between the α values of pure compounds. The values of polarizabilities estimated by the present method are also in good agreement with the reported values[15]. The variation of polarizability anisotropy with concentration is shown in Figure 3. From the data, we can observe higher values of anisotropies for the second mixture PBPA/BBPA. It is a known fact that binary mixtures of liquid crystals exhibit a pronounced minimum in their clearing temperature, as a function of concentration. The presence of a guest component increases the nematic range of the binary mixture. A similar behaviour can be found in the present mixtures also.

To estimate the order parameters of the mixtures, Vuk's model is chosen. Madusudhana[16] showed that one percent error in the density measurements (which enters into the calculations of the order parameters through the determination of mean polarisabilities) gives rise to nearly eleven percent error in the order parameter when the anisotropic internal field model (Neugebauer's approach[17]) is used, but the same density error gives rise to only one percent error when the Vuk's approach is used.

The variation of order parameters with reduced temperature, is studied and shown in Figures 4 and 5. It is observed that the S-values of pure nematic compounds have higher values than the mixtures i.e., the order parameters of different concentrations lie in between the S-values of the pure compounds and the law of additivity is found to be valid. From the plots (4 and 5) it is also observable that the order parameters decrease with temperature as one observes in a pure nematic compound. In most of the liquid crystalline phases, motions of parts of the molecule e.g., free rotation about the single bonds (as in the case of the CH_2 groups at the end of the molecule), are always possible. The fractional number of molecules in which such motions takes place and the amplitudes of such motions increase with increase temperature. As a result there should be a small but systematic decrease in the optical anisotropy with increasing temperature and hence the order parameter also shows the same behaviour with increasing temperature except at the nematic-Isotropic transition.

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Table 1. Mean molecular polarisabilities (α x 10^{24} cm^3) and polarisability anistropies ($\Delta\alpha$ x 10^{24} cm^3) of pure liquid crystalline compounds.

Compound	**Mean Polarisability (α)**		**Polarisability Anistropy ($\Delta\alpha$)**	
	Present Method	Reported[15] Values	Present Method	Reported[15] Values
EBBA	38.27	37.89	22.50	23.12
PBPA	43.05	43.92	23.96	24.31
BBPA	44.33	43.01	23.21	23.96

Table 2. Mean Molecular Polarisabilities (α x 10^{24} cm^3) and polarisability anistropies ($\Delta\alpha$ x 10^{24} cm^3) of the Binary Mixtures

System	Mean Polarisability (α)	Polarisability Anistropy ($\Delta\alpha$)
I		
0.76EBBA/0.24PBPA	39.42	23.20
0.50EBBA/0.50PBPA	40.67	23.41
0.25EBBA/0.75PBPA	41.86	23.62
II		
0.81PBPA/0.19BBPA	43.29	24.11
0.60PBPA/0.40BBPA	43.56	24.15
0.40PBPA/0.60BBPA	43.69	24.19
0.20PBPA/0.80BBPA	44.07	24.26

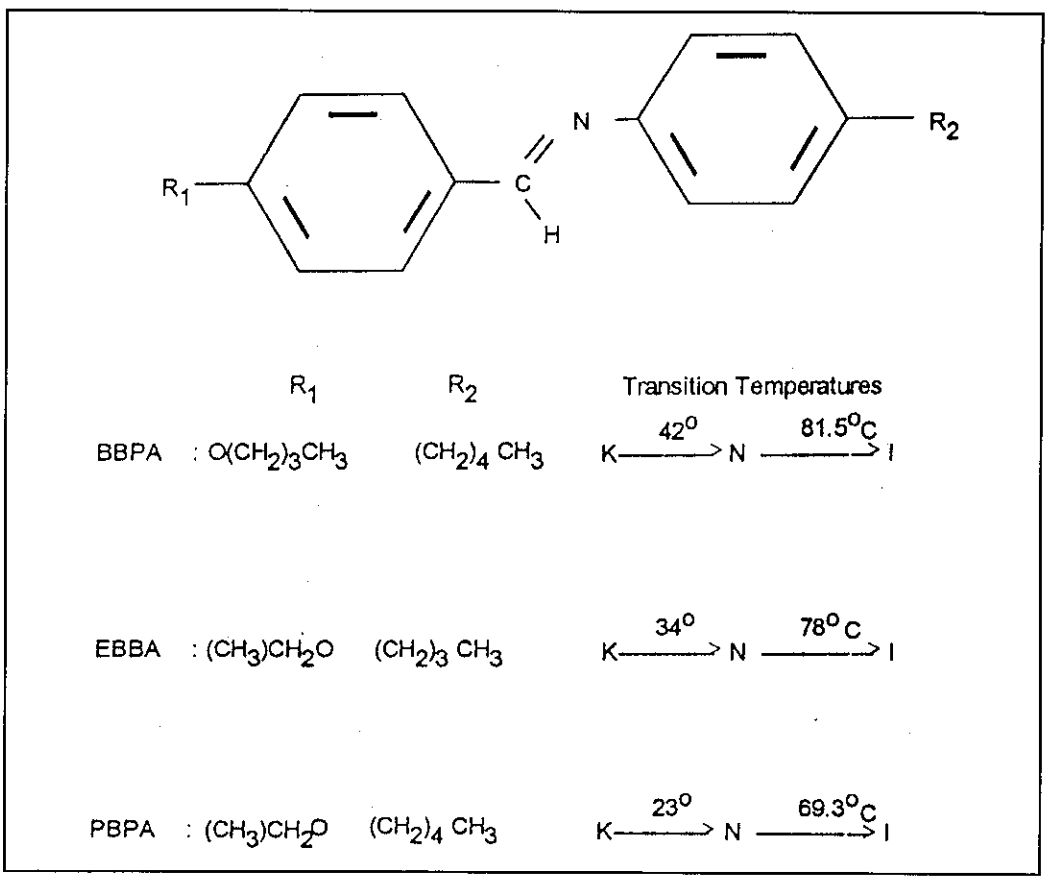

Figure 1. Structural formulae and transition temperatures of the three nematic compounds.

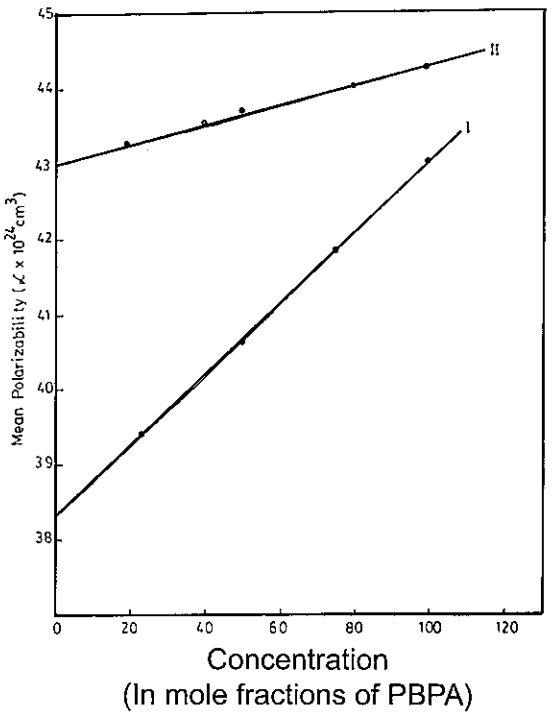

Figure 2. Variation of Polarizability with concentration in the two mixtures.

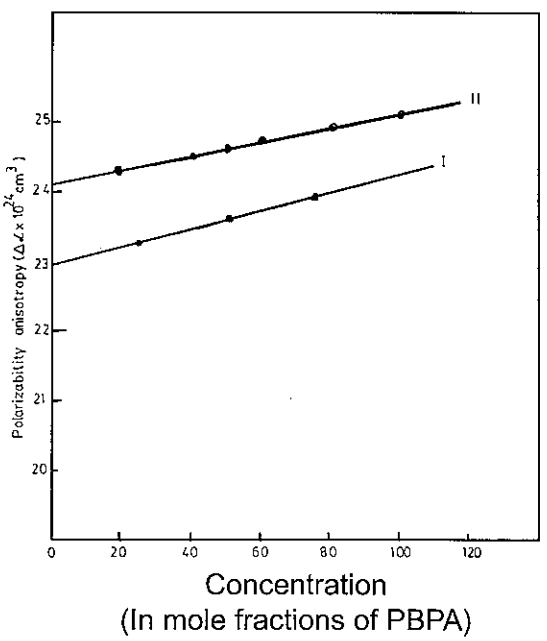

Figure 3. Variation of Polarizability Anisotropy with concentration in the two mixtures.

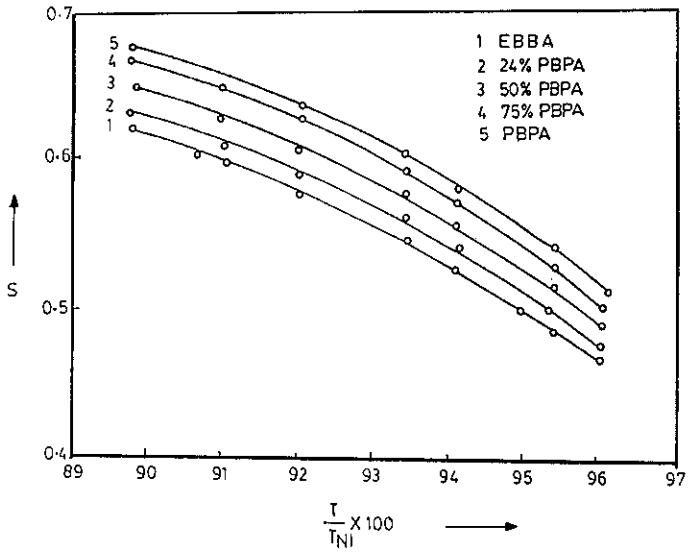

Figure 4. Variation of Order Parameter with Reduced Temperature in Mixture I

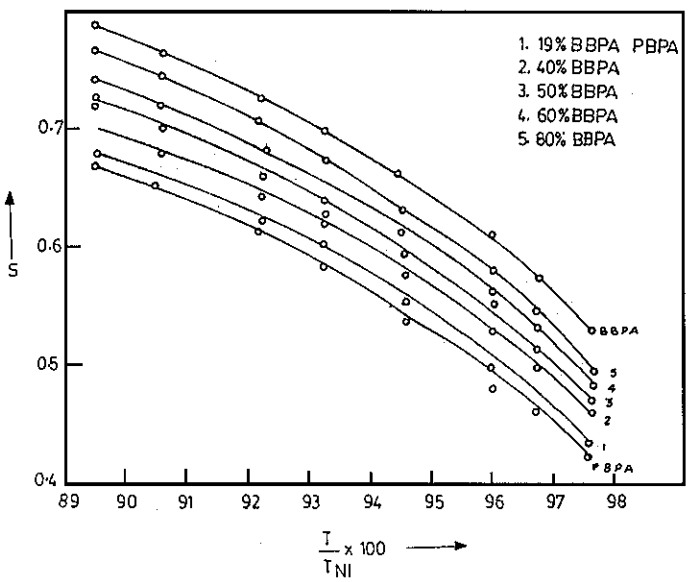

Figure 5. Variation of Order Parameter with Reduced Temperature in Mixture II