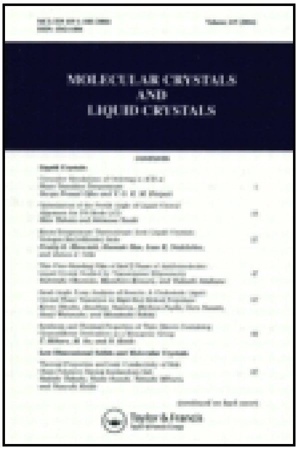

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# Refractive Indices, Lorentz Field Factors, Order Parameters In Pure and Binary Nematic Mixtures

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# REFRACTIVE INDICES, LORENTZ FIELD FACTORS, ORDER PARAMETERS IN PURE AND BINARY NEMATIC MIXTURES

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*Using the small angle prism technique refractive indices are measured at different temperatures in the nematic phase of (i) two nematogenic compounds, viz., hexylbenzoic acid (HBA) and diheptyl azoxybenzene (DHAB), and (ii) binary mixtures of HBA and octylbenzoic acid(OBA) (Mixture-I), and DHAB and nonylbenzoic acid (NBA) (Mixture-II). From the measured refractive index data and employing Neugebauer relations, anisotropy of Lorentz field factors and orientational order parameter have been estimated. The higher order parameter* $\langle P_4 \rangle$ *has also been computed using the Humphries-James-Luckhurst model and is compared with that of Maier-Saupe model.*

*Keywords*: nematics; optical textures; order parameter

## INTRODUCTION

There have been a number of experimental investigations on the birefringence of nematic compounds and their mixtures. Refractive indices and density are the essential parameters required to obtain the accurate value of the polarizability anisotropy. The order parameter [1–5] in nematic liquid crystals is one among the most important parameters. The order parameter of large number of nematic liquid crystals and their mixtures have been reported using optical anisotropy data [6–11]. Here, we have reported the anisotropy of Lorentz filed factors and the orientational order in the cases of: (i) hexylbenzoic acid (HBA), Diheptyl azoxybenzene (DHAB), (ii) two binary mixtures viz., the mixture of HBA and octylbenzoic acid(OBA) (Mixture-I), and of DHAB and nonylbenzoic acid (NBA) (Mixture-II). Further,

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the normalized distribution function f($\theta$) has been evaluated and hence the higher order parameter $\langle P_4 \rangle$ has also been computed . The temperature variation of these parameters and anisotropic pair potential has been discussed on the basis of Humphries-James-Luckhurst model for a nematic mixture.

## EXPERIMENTAL

The nematic compounds OBA and NBA were obtained from Merck chemical company, UK and the compounds HBA and DHAB were procured from M/s Sigma Aldrich chemical company USA. The solid-nematic (S-N) and nematic-isotropic (N-I) transition temperatures of all the pure and mixed systems were determined separately using DSC and the polarizing microscope. The refractive index measurements were made using Goniometer spectrometer and small angled prisms of angles 3–5°, at various temperatures in the nematic and isotropic phases for $\lambda$ 589.3 nm. The technique of measurement of refractive indices has been described in an earlier paper [12]. The densities at different temperatures in the nematic and isotropic phases were determined using capillary tube technique [12]. The measurement of the temperature, refractive index, and density are estimated to be accurate to ±0.1°C, 0.001 and 0.001 gm/cm$^3$ respectively.

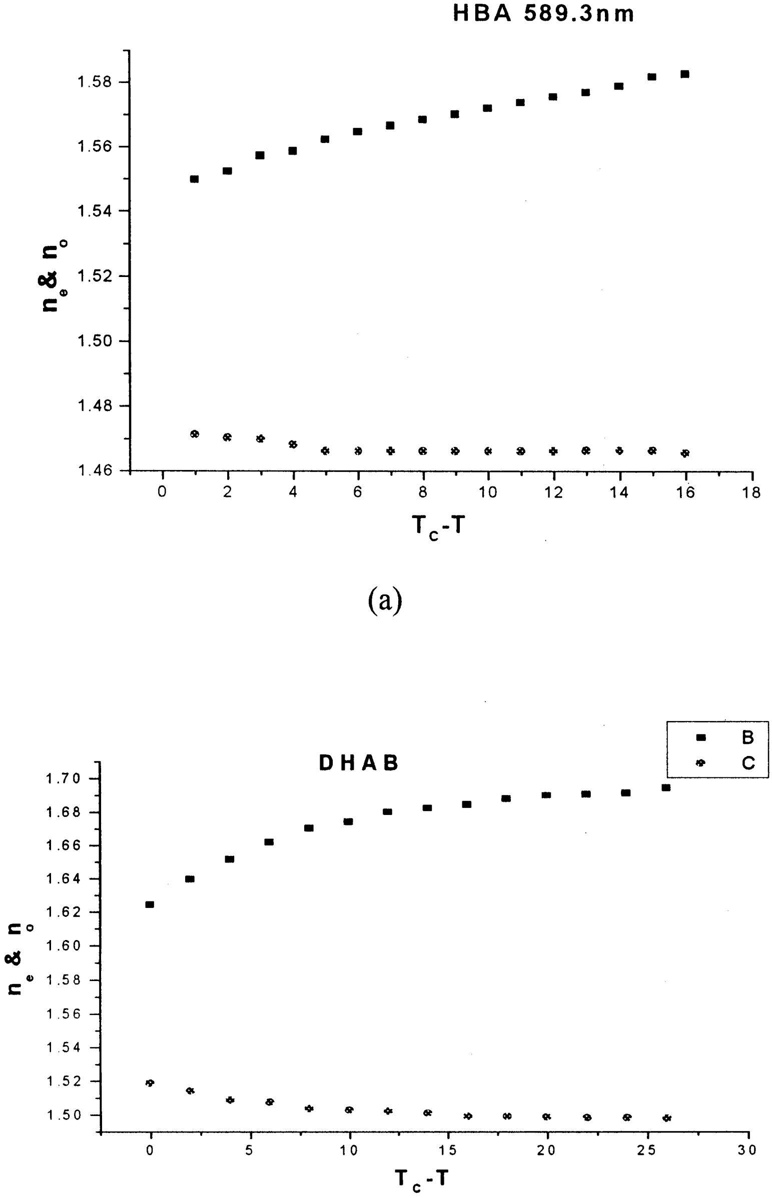
## RESULTS AND DISCUSSION

Table I gives the observed transition temperatures in the pure and mixed systems.

The observed transition temperatures for pure samples are in good agreement with the reported values. Figures 1(a) and 1(b) and 2(a) and 2(b) respectively give the measured refractive indices of pure and binary mixtures.

**TABLE 1**

| | Transition temperature (°C) | |
|---|---|---|
| Compound | S-N | N-I |
| HBA | 97.73 | 115.15 |
| DHAB | 35.18 | 71.02 |
| (Mixture-I) | 84.76 | 113.56 |
| (Mixture-II) | 58.38 | 86.45 |



(a)

(b)

**FIGURE 1** Variation of refractive indices with temperature of (a) HBA and (b) DHAB.

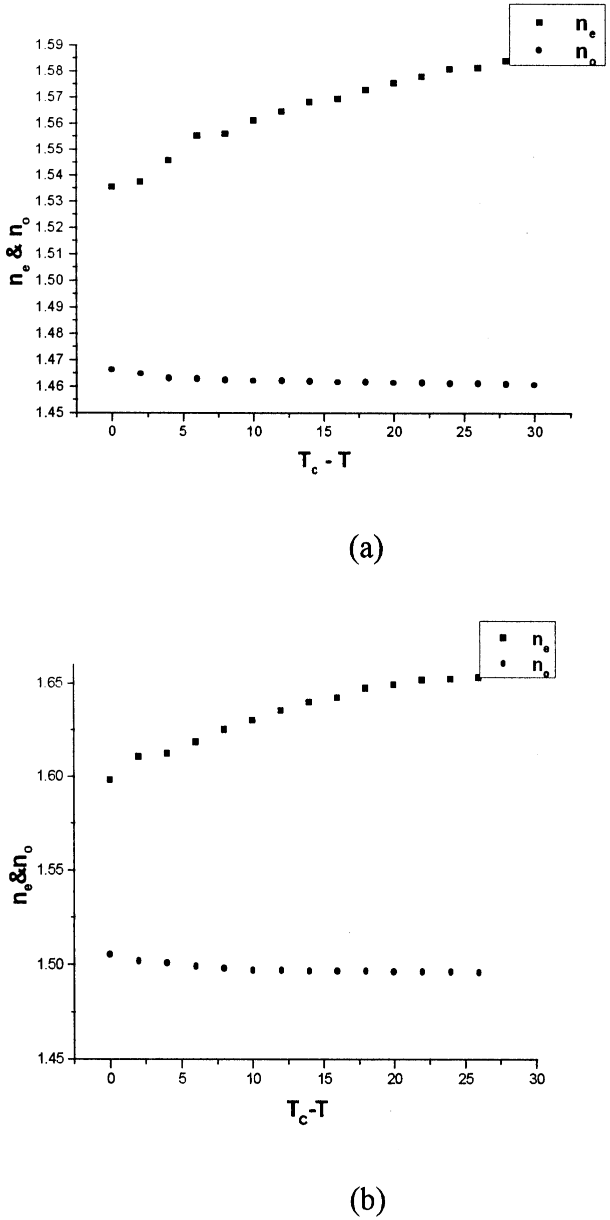


**FIGURE 2** Variation of refractive indices with temperature of (a) Mixture I and (b) Mixture II.

From the measured refractive index and density data Lorentz field factors $L_e$ and $L_o$ have been calculated using the following relations [13,14]

$$L_o = \frac{1}{4\pi\alpha_o N_{LC}}\left[1 - \frac{4\pi\alpha_o N_{LC}}{(n_o^2 - 1)}\right] \tag{1}$$

$$L_e = \frac{1}{4\pi\alpha_e N_{LC}}\left[1 - \frac{4\pi\alpha_e N_{LC}}{(n_o^2 - 1)}\right] \tag{2}$$

where, $N_{LC}$ is the number of molecules per unit volume of the nematic phase, $\alpha_o$ and $\alpha_e$ are the polarizabilities. The Lorentz field factors satisfy the relation $\mathbf{L_e + 2\ L_o = 1}$.

The following features have emerged from our calculation of Lorentz field factors. The Lorentz field factors $L_e$ in all the systems increases with increase of temperature. The anisotropy of Lorentz field factors ($\Delta$L) decreases with increase of temperature. The decrease in the anisotropy of Lorentz field factors is consistent with the expectation that the molecular distribution should be less anisotropic with increase of temperature. The anisotropy of molecular distribution drops to zero at the nematic isotropic transition temperature.

The orientational order parameter S[8] has been determined using the following relation :

$$S = \frac{\alpha_e - \alpha_o}{\alpha_{//} - \alpha_{\perp}}, \tag{3}$$

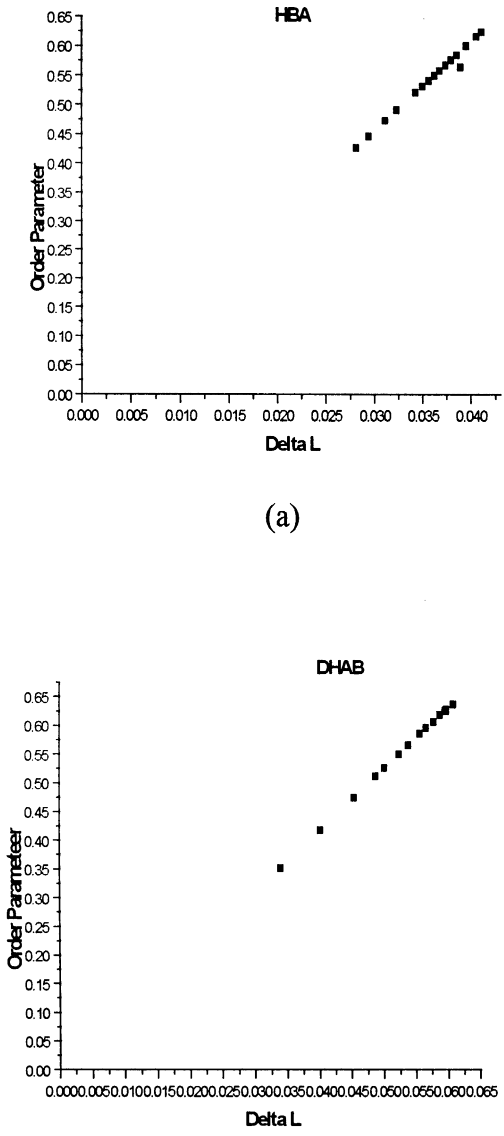
Here, the principal polarizabilities $\propto_e$ and $\propto_o$ were estimated using the measured refractive index and density data and employing the well-known Neugebauer relations [13,14]. The polarizability anisotropy $(\propto_{//} - \propto_{\perp})$ of the molecule has been computed using Hallers's extrapolation procedure [15].

Figure 3(a) and 3(b) represent the variation of orientational order parameter S with $\Delta L(L_o - L_e)$ in the cases of HBA and DHAB respectively. The order parameter determined from experimental refractive index and density data for the mixtures I and II is compared with that estimated using Humphrie-James-Lukhurst model and Maier-Saupe model [see Figure 4(a) and 4(b)]. Figure 5(a) comparison of the orientational order parameter of mixture II and that of the constitutent pure components.

In accordance with the Maier-Saupe model, the distribution function f($\theta$) of the nematogenic system can be assumed to form a Gaussian distribution function [16] around the director and can be written as

$$f(\theta) = \frac{1}{\sigma}\{\exp -(\theta^2/2\sigma^2) + \exp[-(\theta - \pi)^2/2\sigma^2]\} \qquad [4]$$

where, $\sigma$ in the standard deviation. Using this relation f($\theta$) for all the



(a)

(b)

**FIGURE 3** Variation of order parameter with Lorentz anisotropy of (a) HBA and (b) DHAB.

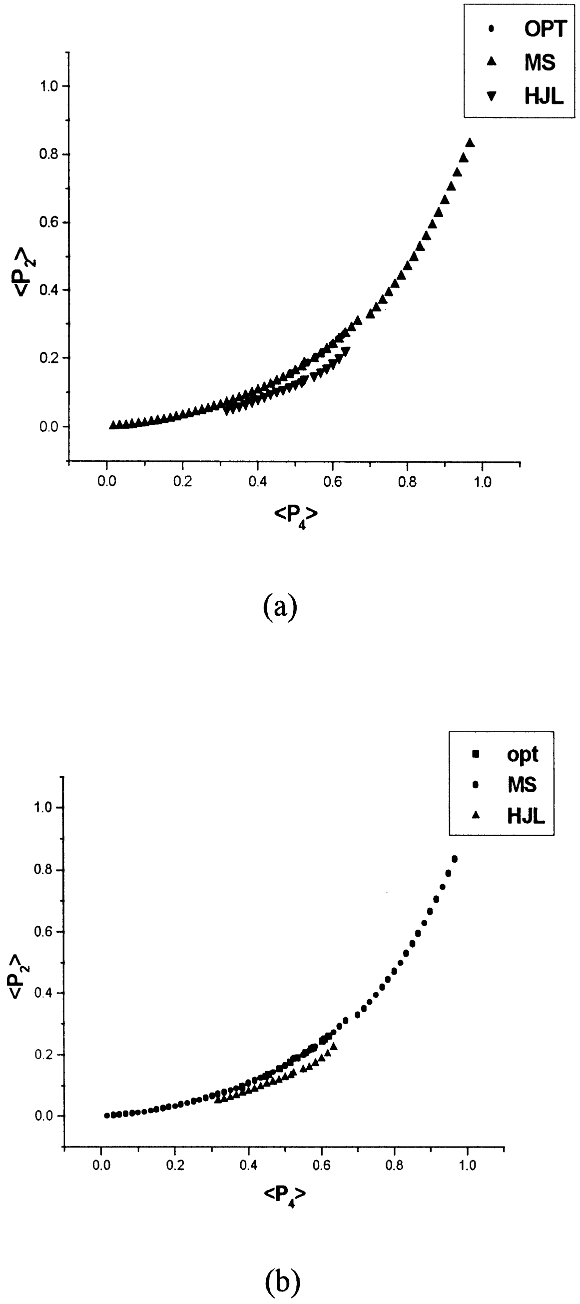
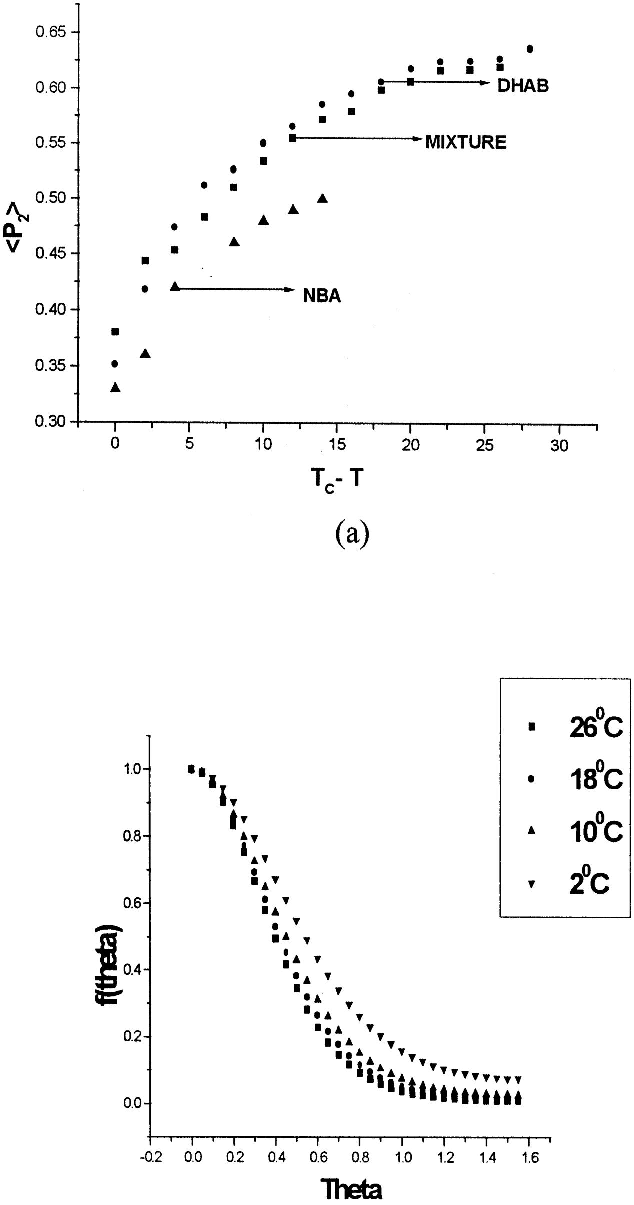


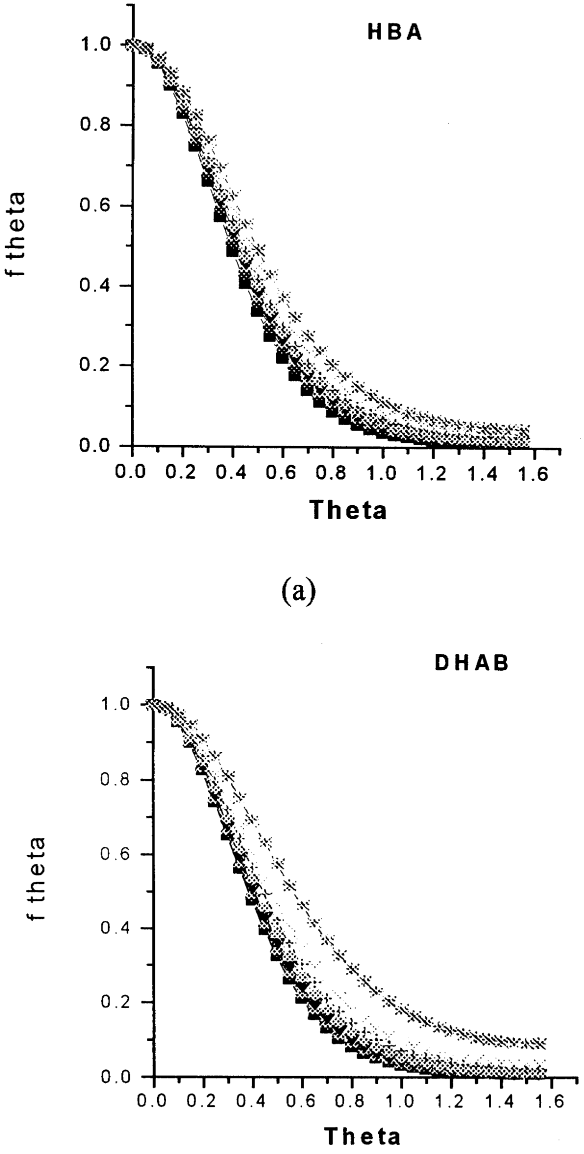
**FIGURE 4** Comparison of order parameter from different approaches of (a) Mixture I and (b) Mixture II.



(a)

(b)

**FIGURE 5** (a) Comparison of order parameter of Mixture II with pure nematics. (b) Distribution function at different temperatures of Mixture I.



(a)

(b)

**FIGURE 6** Distribution function at different temperatures of (a) HBA and (b) DHAB.

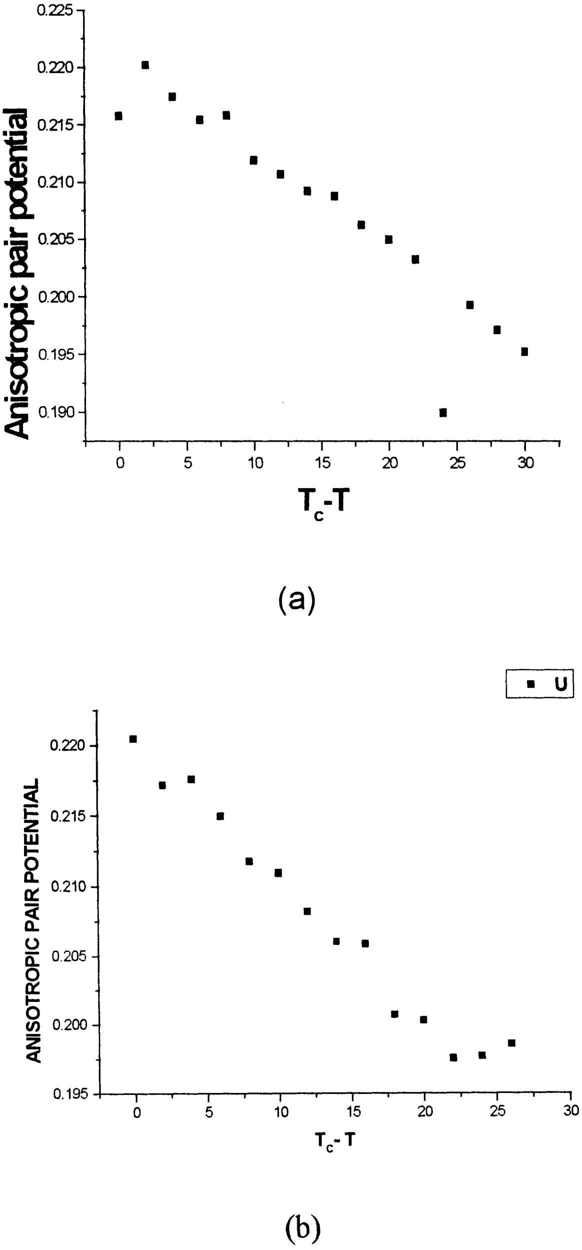


**FIGURE 7** Variation of anisotropic pair potential with temperature of (a) Mixture I and (b) Mixture II.

systems has been estimated at various values of $\theta$ and at different temperatures in the nematic phase.

Figures 5(b), 6(a) and 6(b) give the variation of $f(\theta)$ with $\theta$ respectively in mixture I, HBA and DHAB.

The orientation order parameter or the second moment in terms of $f(\theta)$ is worked out using the order parameter obtained from the refractive index data, and employing the one dimensional minimization program of SIMPLEX [17]. The second moment $\langle P_2 \rangle$ is given by

$$\langle P_2 \rangle = \frac{\int_0^{\pi/2} P_2(\cos\theta) f(\theta) \sin\theta \, d\theta}{\int_0^{\pi/2} f(\theta) \sin\theta \, d\theta} \qquad [5]$$

The higher order parameter $\langle P_4 \rangle$ is given by

$$\langle P_4 \rangle = \frac{\int_0^{\pi/2} P_4(\cos\theta) f(\theta) \sin\theta \, d\theta}{\int_0^{\pi/2} f(\theta) \sin\theta \, d\theta} \qquad [6]$$

Using Humphries, James and Luckhurst model [18] which assumes the order parameter determined from the refractive index data, anistotropic pair potential associated with the binary mixtures at different temperature in the nematic phase has also been calculated and shown respectively in Figure 7(a) and 7(b).

Plot of $\langle P_4 \rangle$ vs $\langle P_2 \rangle$ dependence in Figures 4(a) and 4(b) show the similarity of results between pure compounds on one hand and mixtures on the other. This implies that pair correlations are quite important in these systems and they can have influence on the interpretation of data. Here solute molecules is not sensitive to pair correlations. The fact that the curves $\langle P_4 \rangle$ vs $\langle P_2 \rangle$ agree with Maier-Saupe model implies that

$$P_4 \geq (35{P^2}_2 - 10\,P_2 - 7)/18 \qquad [7]$$

Any deviation from this, implies that the $\theta$ fluctuations are large in the nematic phase of mixtures.

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