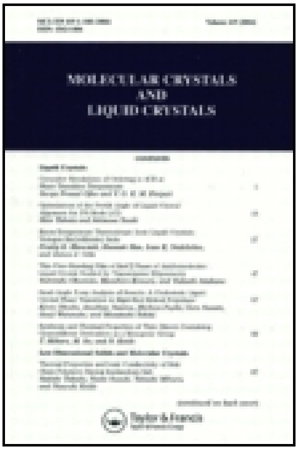

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Order Parameter of Mixtures of Nematic Compounds

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Order Parameter of Mixtures of Nematic Compounds

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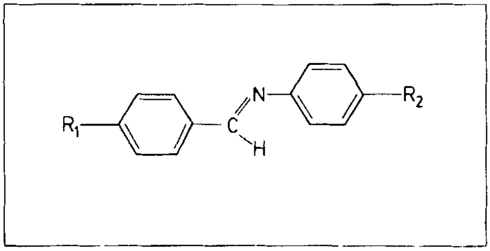
The orientational order parameters of the binary mixtures of three nematic compounds are calculated using the measured densities and refractive indices. The order parameter values are found to be in good agreement with the Maier-Saupe theoretical values.

INTRODUCTION

Nematic liquid crystals are characterised by the presence of an orientational order of elongated rod-like molecules. Nematic phase is the least ordered of all liquid crystalline phases. All anisotropic properties such as refractive index, elastic constant, magnetic susceptibility etc., of the nematic phase are in some form related to the orientational order parameter. In the present investigation refractive indices and densities of binary mixtures of three Schiff base nematic compounds are measured at different temperatures. The orientational order parameters are determined from these measurements. In addition to this the thermal properties of *N*-(*p*-propoxybenzylidene)*p*-pentylaniline are studied by DSC and compared with microscopic observations.

EXPERIMENTAL

The Schiff base nematic compounds used in this investigation are *N*-(*p*-ethoxybenzylidene)*p*-*n*-butylaniline (EBBA), *N*-(*p*-butoxybenzylidene)*p*-pentylaniline) (BBPA) and *N*-(*p*-propoxybenzylidene)*p*-pentylaniline (PBPA). The structural formulae and transition temperatures of nematic compounds are shown in Figure 1. These samples were obtained from M/s Eastman Organic Chemicals, USA. Mixtures of PBPA in EBBA and BBPA in PBPA of six concentrations were prepared and are denoted as "A" and "B" respectively. The components of mixtures were well mixed in the molten state and allowed to cool very slowly. The



	R_1	R_2	
BBPA	$O(CH_2)_3CH_3$	$(CH_2)_4CH_3$	$K \xrightarrow{22.3^\circ} S \xrightarrow{42^\circ} N \xrightarrow{81.5^\circ C} I$
EBBA	CH_3CH_2O	$(CH_2)_3CH_3$	$K \rightarrow S_G \xrightarrow{34^\circ C} N \xrightarrow{78^\circ} I$
PBPA	$CH_3(CH_2)_2O$	$(CH_2)_4CH_3$	$K \rightarrow S_E \xrightarrow{6^\circ C} S_G \xrightarrow{23^\circ} N \xrightarrow{69.3^\circ} I$

FIGURE 1 Structural formulae and transition temperatures of nematic compounds BBPA, EBBA and PBPA.

TABLE I

Thermodynamic data of PBPA

Temperature in K	Enthalpy (ΔH) Kilocal/mol	Entropy (ΔS) cal/Kelvin/mole
343.00 (I-N)	0.655	1.90
293.10 ($N-S_G$)	3.168	10.90
279.50 (S_G-Solid)	2.190	7.835

transition temperatures T_{NI} of nematic compounds and their mixtures of different concentrations were determined using a polarizing microscope and a hot stage. The temperatures at which phase transition occurs in the case of PBPA were determined by differential scanning calorimetry using Perkin-Elmer DSC-2 Instrument facility at the Raman Research Institute. The exothermic DSC curve of PBPA consists of three transition peaks at temperatures 341.1 K, 293.1 K and 279.5 K respectively corresponding to isotropic-nematic, nematic-smectic G and smectic G-solid phase transitions. The values of phase transition temperatures were found to be in good agreement with the values obtained from the optical texture studies. The average values of enthalpies and entropies are shown in Table I. These results were compared with the lower members of the series homologous with MBBA.[1] This indicates that the melting enthalpy increases with decreasing chain length. It is also found that the melting enthalpy for smectic G to nematic phase transition is greater than that for solid to smectic G transition.

It is well known that binary mixtures of liquid crystals exhibit a pronounced minimum in their clearing temperature T_{NI}, as a function of concentration as shown in Figure 2. The presence of guest component enhances the nematic range of the binary mixture. In the case of the mixture of BBPA in PBPA, the nematic-smectic B transition temperature was found to be greatly depressed, and the mixtures with low percentages of BBPA provide room temperature nematic phase.

The densities of mixtures at different temperatures were determined by measuring the length of a pellet of known mass of the specimen taken in a calibrated capillary tube. The values of densities are accurate to 0.001 gm/cc. The refractive indices were measured using the well known low angled hollow prism method[2] for the wavelength 589 nm.

RESULTS AND DISCUSSION

The orientational order parameter S is given by[3]

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

where θ is the angle between the director and the major axis of the rodlike molecule. The relation between the order parameter and the polarizability anisotropy in the

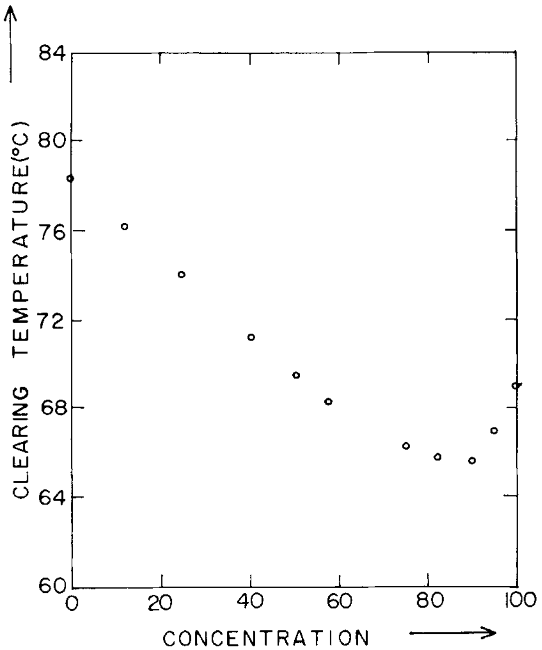


FIGURE 2 Clearing temperature as a function of the Wt.% of PBPA in EBBA of the mixture A.

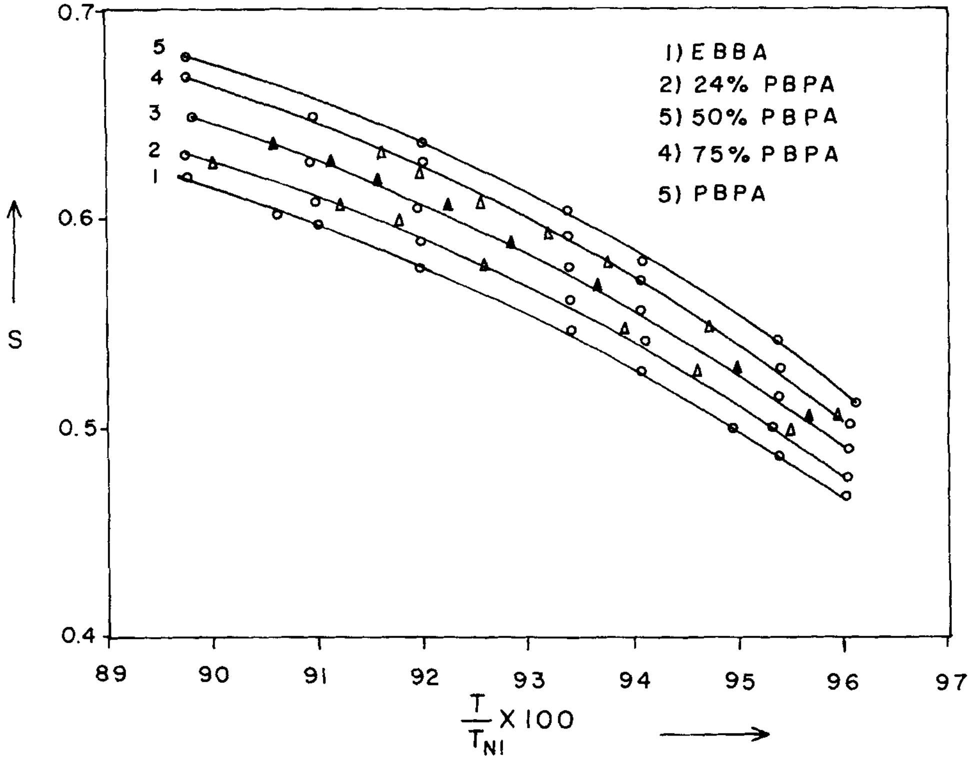


FIGURE 3 Orientational order parameter S from calculated and experimental values versus reduced temperature T/T_{NI} for the mixture A. ((○)—Experimental, (△)—Calculated.)

nematic and crystalline phase is given by

$$S = \frac{(\alpha_e - \alpha_o)}{(\alpha_\parallel - \alpha_\perp)} \tag{2}$$

From the measured refractive index and density data in the nematic and isotropic phases, it is possible to calculate the effective polarizabilities α_e and α_o of nematic compounds and of their binary mixtures using Neugebauer relations at various temperatures. In order to estimate the polarizability anisotropy $(\alpha_\parallel - \alpha_\perp)$ of the molecules of nematic compounds the additive rule of bond polarizability is employed.[4] It also facilitates further comparisons with the values of $(\alpha_\parallel - \alpha_\perp)$ calculated from refractive index and density data in the crystalline phase of the compounds. The values of $\alpha_\parallel$ and $\alpha_\perp$ of the molecules of nematic compounds enable the calculation of $\alpha_\parallel$ and $\alpha_\perp$ of the binary mixtures using the additivity relations

$$\alpha_\parallel = \frac{N_1(\alpha_\parallel)_{\text{EBBA}} + N_2(\alpha_\parallel)_{\text{PBPA}}}{N_1 + N_2} \tag{3}$$

$$\alpha_\perp = \frac{N_1(\alpha_\perp)_{\text{EBBA}} + N_2(\alpha_\perp)_{\text{PBPA}}}{N_1 + N_2} \tag{4}$$

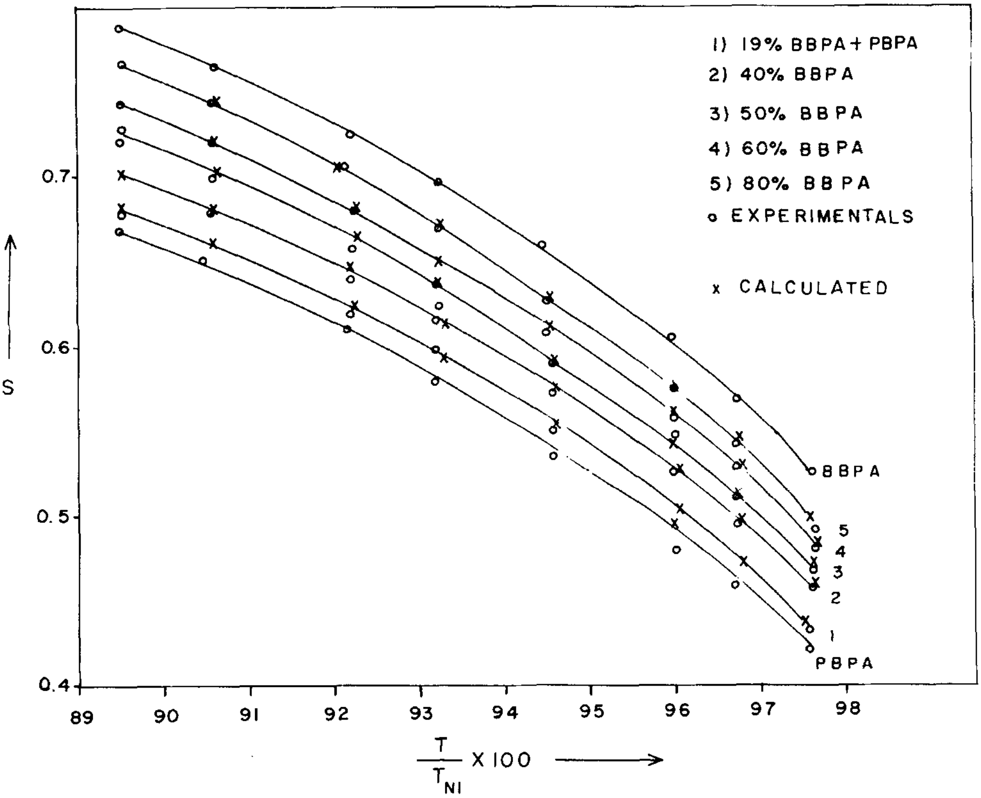


FIGURE 4 Orientational order parameter from calculated and experimental values versus reduced temperature T/T_{NI} for the mixture B.

where N_1 and N_2 are the number of molecules per unit volume of the compounds EBBA and PBPA respectively.

Following Haller *et al.*,[5] $\log(\alpha_e - \alpha_o)$ was plotted versus $\log(T_c - T)$. This yields a straight line which is extrapolated up to $\log(T_c)$. The limiting value of $(\alpha_e - \alpha_o)$ was assumed to correspond to the value of the difference $(\alpha_\parallel - \alpha_\perp)$ of the molecule. This was done for A and B mixtures and these values were found to be in good agreement with the values calculated from additivity relations (3) and (4).

In order to estimate the orientational order parameter of mixtures of various concentrations, we have considered the S_{NMR} of EBBA and S-factors of PBPA and BBPA from index data of our studies. The S-factors of mixtures of different concentrations $(S_{mix})_{cal}$ at various temperatures were calculated using the additivity relation,[2]

$$\langle S_{mix}\rangle_{cal} = \frac{S_1N_1 + S_2N_2}{N_1 + N_2} \tag{5}$$

where S_1 and S_2 are the order parameters of the two pure nematic compounds. Using the density and refractive index data, the values of $(S_{mix})_{index}$ for different

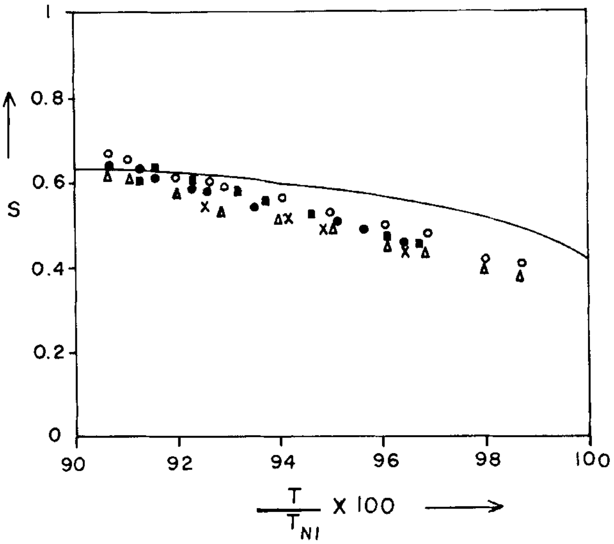


FIGURE 5 The temperature dependence of S for PBPA (○), EBBA (△), 24% PBPA (×), 50% PBPA (●), and 75% PBPA (□). The solid curve is from the Maier-Saupe theory.

concentrations at various temperatures were calculated using equation (2). $(S_{\mathrm{mix}})_{\mathrm{cal}}$ and $(S_{\mathrm{mix}})_{\mathrm{index}}$ are drawn as functions of reduced temperatures (T/T_{NI}) for A and B mixtures (see Figures 3 and 4). The S-factors of pure nematic compounds have also been shown for comparison. From Figures 3 and 4 it is observed that S-factors of different concentrations lie in between the S factors of the pure compounds and the law of additivity (Equation 5) is found to be valid. The experimental order parameter values are plotted against the reduced temperature along with the Maier-Saupe theoretical values in Figure 5. It is seen that the experimental order parameter values agree well with Maier-Saupe[6] theoretical values except near the nematic-isotropic (NI) transition temperature, where the experimental S-factors are significantly lower than the theoretical values.[7] This discrepancy may be attributed to the enhanced vibrations of the aliphatic chain part of the molecules, and the more pronounced fluctuations of the director in the vicinity of the NI transition. Therefore the mean field theory is expected to underestimate the temperature variation of S near NI transition.

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