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Optical Studies on Binary Mesophase Mixtures Containing p-Azoxyphenetole (PAP)

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The ordinary and extraordinary refractive indices in the nematic phase and the refractive index in the isotropic phase of binary mixtures of p-Azoxyphenetole (PAP) with 4,4′-di-n-propyloxyazoxybenzene (PDPAB), with 4,4′-di-n-butyloxyazoxybenzene (PBAB), with 4,4′-di-n-pentyloxyazoxybenzene (PPAB) and with 4,4′-di-n-hexyloxyazoxybenzene (PHAB) are reported. These refractive index data were used in a Vuks type analysis to obtain the values of the order parameters in PAP/PDPAB, PAP/PBAB, PAP/PPAB and PAP/PHAB mixtures. It is found that the order parameters in these four mixtures obey the additive rule.

1 INTRODUCTION

Optical and dilatometric studies of mixtures of p-azoxyanisole (PAA) and several other members of the homologous series of 4,4′-di-n-alkoxyazoxybenzenes have been reported.[1-4] The results of these studies have been used to determine the order parameters in these mixtures.[3-5] Chandrasekhar and Madhusudana[5] found that the order parameters of the PAA/p-azoxyphenetole (PAP) mixtures obeyed the additive relation

$$S_{\text{mix}} = xS_{\text{PAA}} + (1 - x)S_{\text{PAP}} \tag{1}$$

where x is the molar fraction of PAA in the mixtures and S_{PAA} (S_{PAP}) is the order parameter of the pure PAA (PAP) nematogen. Sungsittayakorn *et al.*,[3] and Denprayoonwong *et al.*,[4] found that the order parameters of PAA/4,4-di-n-pentyloxyazoxybenzene (PPAB) and PAA/4,4-di-n-hexyloxyazoxybenzene (PHAB) mixtures also follow the additive rule.

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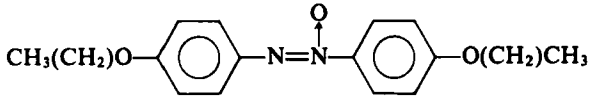
In this paper, we would like to present the results of some optical studies of binary mixtures of p-azoxyphenetole and four other members of the homologous series. Using our refractive index data in a Vuks[6] type analysis, we have calculated the order parameters of the four mixtures, PAP/4,4'-di-n-propyloxazoxybenzene (PDPAB), PAP/4,4'-di-n-butyloxyazoxybenzene (PBAB), PAP/PPAB and PAP/PHAB.

II EXPERIMENTAL

A Materials

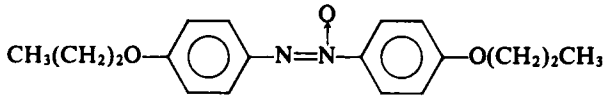
The structural formulas, transition temperatures and molar volumes just before the nematic-isotropic transition temperatures of the five 4,4'-di-n-alkoxyazoxybenzenes compounds are

p-azoxyphenetole (PAP)



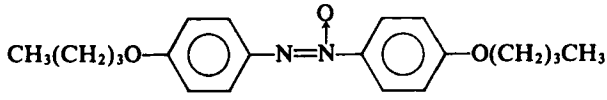
134°C nematic → 168°C isotropic Molar volume 267.3 ml/mole

4,4'-di-n-propyloxyazoxybenzene (PDPAB)



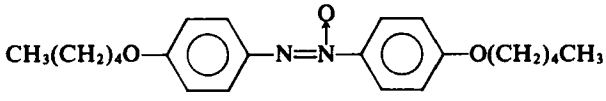
115°C nematic → 123°C isotropic Molar volume 299.0 ml/mole

4,4'-di-n-butyloxyazoxybenzene (PBAB)



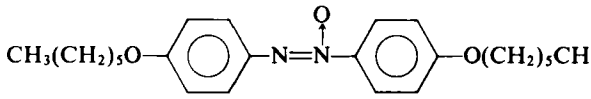
102°C nematic → 136°C isotropic Molar Volume 338.5 ml/mole

4,4'-di-n-pentyloxyazoxybenzene (PPAB)



79°C nematic → 123°C isotropic Molar Volume 368.9 ml/mole

4,4'-di-n-hexyloxyazoxybenzene (PHAB)



80°C nematic → 129°C isotropic Molar Volume 406.0 ml/mole

The nematogen PAP was purchased from Riedel Co; (Hannover, Germany) the nematogens PDPAB, PBAB and PPAB, for Eastman (Rochester, New York) and the nematogen PHAB, from Frinton Laboratories. (Frinton, New Jersey). The five nematogens were recrystallized at least two times from ethanol water mixtures before their use.

B Experimental Procedure

The transition temperatures of the mixtures were observed by microscopic observation using a Reichart No. 285167 heating-stage microscope, the temperatures being measured with a Mettler TM16 thermometer. The refractive in dices were measured using the minimum deviation method. The angles were determined with an AO Spencer Spectrometer. The details of the method can be found in Refs. 3 and 4. The accuracy of the refractive indices is estimated to be ±0.005 while the accuracy of the temperature readings for the refractive index measurements is estimated to be ±0.5 degree.

III RESULTS AND DISCUSSIONS

We have plotted on Figure 1, the temperature dependence on n_o(the ordinary refractive index), n_e(the extra ordinary refractive index) and n_i(the refractive index of the isotropic phase) for the PAP/PDPAB mixtures. On Figure 2, the same information for the PAP/PBAB mixtures is plotted; on Figure 3, the refractive indices for the PAP/PPAB mixtures are plotted while on Figure 4, the refractive indices for the PAP/PHAB mixtures are plotted. The refractive index data can be used in conjunction with density data to determine the order parameter

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

where θ is the angle between the long axis of the molecule and the average direction of the molecular alignment. The connection between the order parameter and the optical properties of the system is the relation

$$S\Delta\alpha = (\alpha_e - \alpha_o) \tag{3}$$

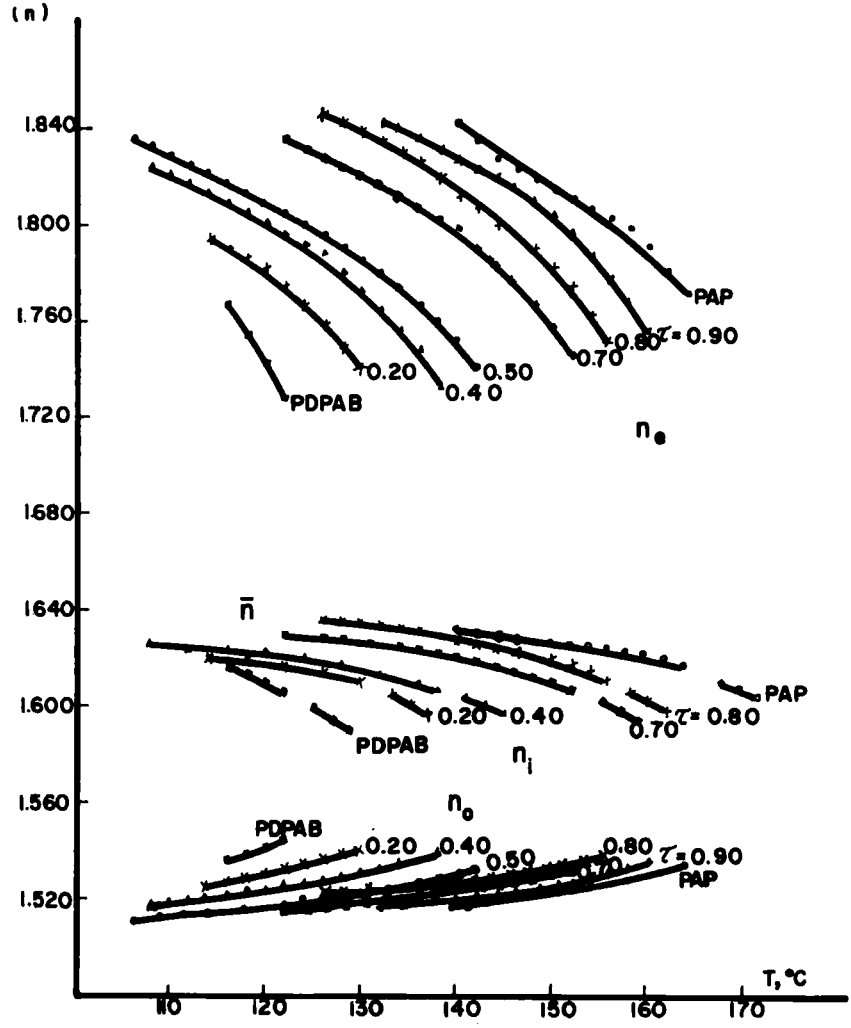


FIGURE 1 Refractive Indices of PAP/PDPAB Mixtures. The curves give the temperature dependences of n_o, the ordinary refractive index of the nematic phase, of n_e, the extra ordinary refractive index of the nematic phase and of n_i, the refractive index of the isotropic phase. $\bar{n}$ is the average value in the nematic phase and is equal to $(n_e^2 + 2n_o^2)/3$.

where α_e and α_o are the effective polarizabilities and $\Delta\alpha$ is the molecular polarizability anisotropy. Depending on whether the internal fields are taken to be isotropic or anisotropic, the dependence of the difference of the effective polarizabilities $(\alpha_e - \alpha_o)$ will be given by the Vuks model formula[6] or by the Neugebauer model formula.[7]

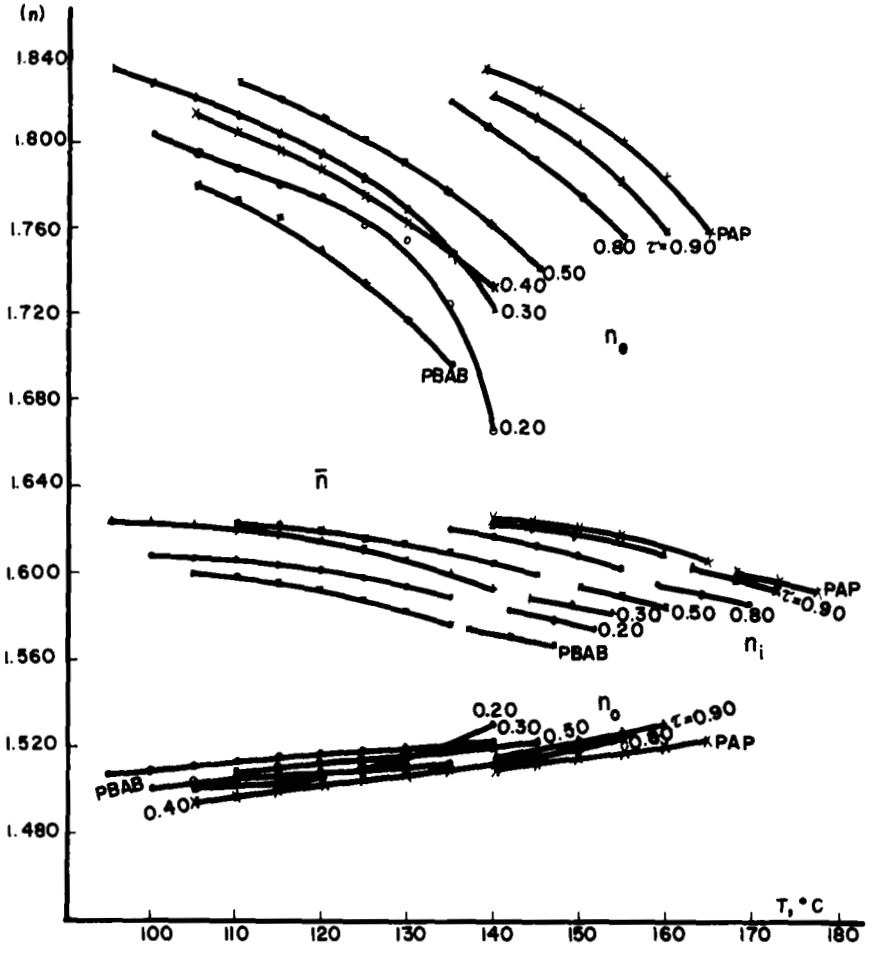


FIGURE 2 Refractive Indices of PAP/PBAB Mixtures. The curves give the temperature dependences of n_o, n_e, n_i and $\bar{n}$.

For reasons to be discussed later, we will assume that the internal fields are isotropic even though the liquid crystalline phase is highly anisotropic. This means that we are assuming that the liquid crystalline phase can be described by the Vuks model. According to this model, the difference between the effective polarizabilities is

$$\alpha_e - \alpha_o = \frac{3}{4\pi}\frac{1}{N}\frac{n_e^2 - n_o^2}{\bar{n}^2 + 2} \tag{4}$$

where N is the number of molecules per unit volume and $\bar{n}^2 = (n_e^2 + 2n_o^2)/3$.

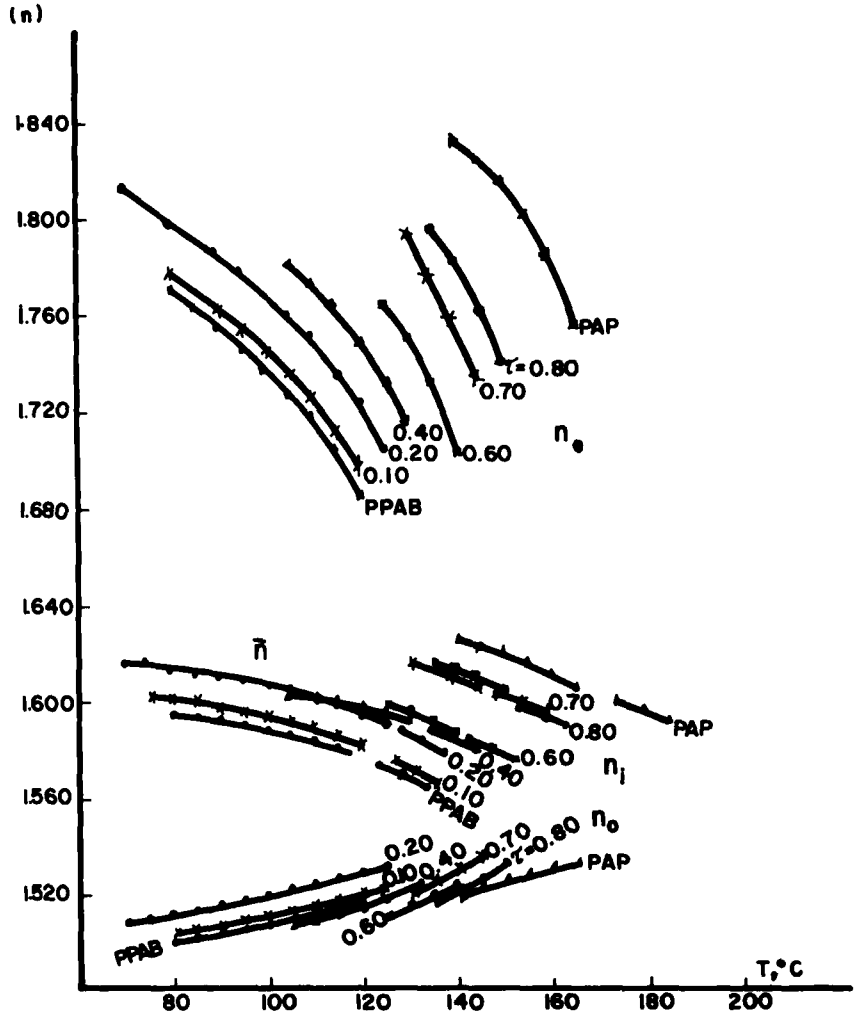


FIGURE 3 Refractive Indices of PAP/PPAB Mixtures. The curves give the temperature dependences of n_o, n_e, n_i and $\bar{n}$.

Since the mean polarizability $\bar{\alpha}$ is also related to the refractive indices via the Lorentz-Lorenz relation

$$\bar{\alpha} = \frac{3}{4\pi} \frac{1}{N} \frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} \tag{5}$$

Eq. (4) can be rewritten as

$$\alpha_e - \alpha_o = \bar{\alpha} \frac{n_e^2 - n_o^2}{\bar{n}^2 - 1} \tag{6}$$

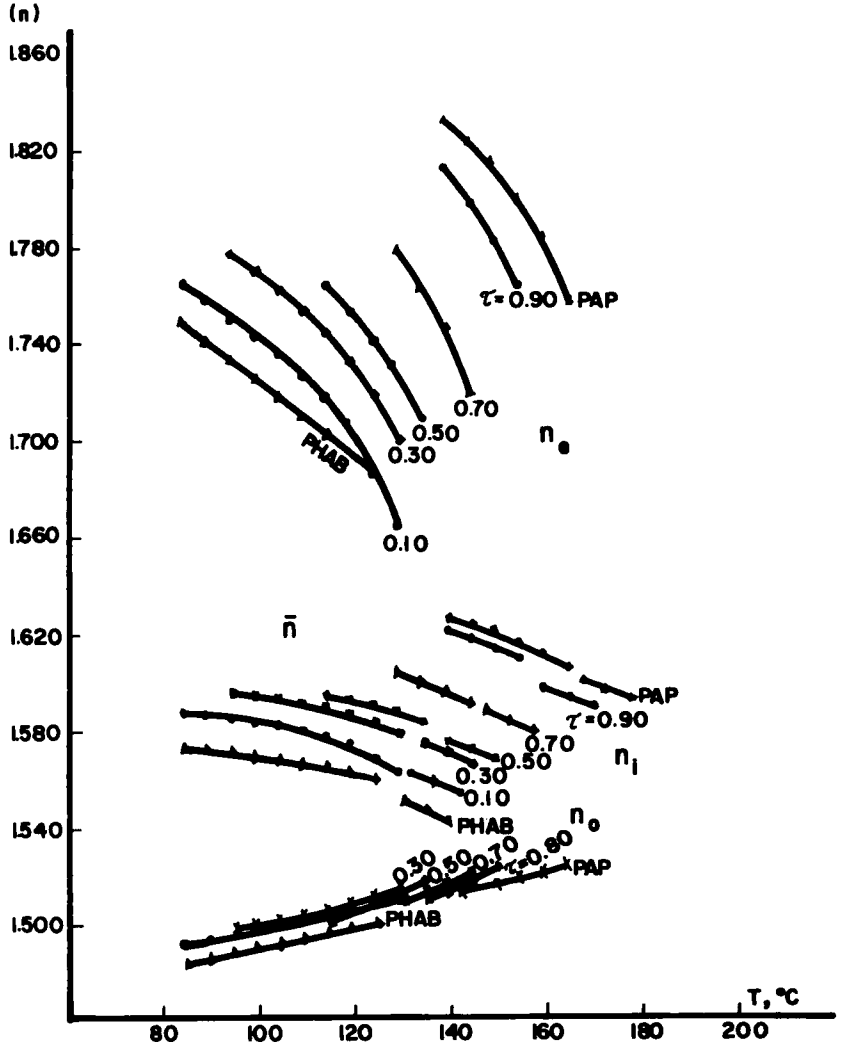


FIGURE 4 Refractive Indices of PAP/PHAB Mixtures. The curves give the temperature dependence of n_o, n_e, n_i and $\bar{n}$.

Having both the optical and density data, the mean polarizabilities can be calculated. Using the density data reported by de Jeu *et al.*,[8] and the present optical data, we find the mean polarizabilities of PAP, PDPAB, PBAB, PPAB and PHAB to be 37.04×10^{-24} cm^3, 41.16×10^{-24} cm^3, 45.07×10^{-24} cm^3, 48.38×10^{-24} cm^3, and 52.4×10^{-24} cm^3, respectively. These values agree quite well with the values 36.8×10^{-34} cm, 40.48×10^{-24} cm^3, 44.16×10^{-24}

cm^3, 47.84×10^{-24} cm^3 and 51.52×10^{-24} cm^3 calculated from bond polarizability data.[9]

In the absence of density data from which the mean polarizabilities of our mixtures can be calculated, Eq. (6) may still be used if reasonable assumptions about the mean polarizabilities of the mixtures are made. The first assumption is that the mean polarizabilities of the mixtures are temperature independent. This assumption is support by our present analysis of the pure nematogens optical data and our previous analysis of PAA/PPAB mixtures[3] and PAA/PHAB[4] mixtures. The second and more crucial assumption is that the mean polarizabilities of the mixture follow the additive rule

$$\bar{\alpha}_{mix} = x\,\bar{\alpha}_1 + (1 - x)\,\bar{\alpha}_2 \tag{7}$$

where x is the mole fraction of the component having a mean polarizability $\bar{\alpha}_1$ and $(1 - x)$ is the mole fraction of the second component in the mixture. Chandrasekhar and Madhusudana[5] analysis of the PAA/PAP and our analyses of PAA/PPAB[3] and PAA/PHAB[4] indicate that the mean polarizabilities of mixture do obey Eq. (7). With these assumptions, Eq. (6) may be used to determine the differences $(\alpha_e - \alpha_o)$ of the mixtures.

The polarizability anisotropies of the mixture have to be known if the order parameters are to be calculated by Eq. (3). Direct measurements of the polarizability anisotropies require that the refractive indices of the solid phase be known. Lacking this type of data, the polarizability anisotropies must be indirectly determined. Haller *et al.*,[10] proposed that the extrapolation of the calculated $(\alpha_e - \alpha_o)$ down to 0°K would give a value for $\Delta\alpha$. However, this method has been criticised[8,11] since it produces contradictory results when applied to homologous series of liquid crystals. Karat and Madhusudana[12] and others propose instead that the polarizability anisotropies can be calculated from bond polarizability data. According to their scheme, $\Delta\alpha_{PAP} = 35.24 \times 10^{-24}$ cm^3, $\Delta\alpha_{PDPAB} = 35.04 \times 10^{-24}$ cm^3, $\Delta\alpha_{PBAB} = 35.58 \times 10^{-24}$ cm^3, $\Delta\alpha_{PHAB} = 35.38 \times 10^{-24}$ cm^3 and $\Delta\alpha_{PHAB} = 35.92 \times 10^{-24}$ cm^3. The value for PAP is close to the value determined by Chandrasekhar and Madhusudana[5] from solid state data. For the mixtures, we will assume that the polarizability anisotropies are given by

$$\Delta\alpha_{mix} = s\,\Delta\alpha_1 + (1 - x)\Delta\alpha_2 \tag{8}$$

Chandrasekhar and Madhusudana found the anisotropies of the PAA/PAP mixtures follow this rule. Ibrahim and Haase[13] also found that the anisotropies of benzoates mixtures obeyed the additive rule.

The actual mean polarizabilities and polarizability anisotropies of the mixtures may deviate from the above two additive rule. Becuase of the possible errors that these two assumptions may introduce, the Vuks model was chosen to describe the internal fields in the mixtures. Madhusudana[14] recently

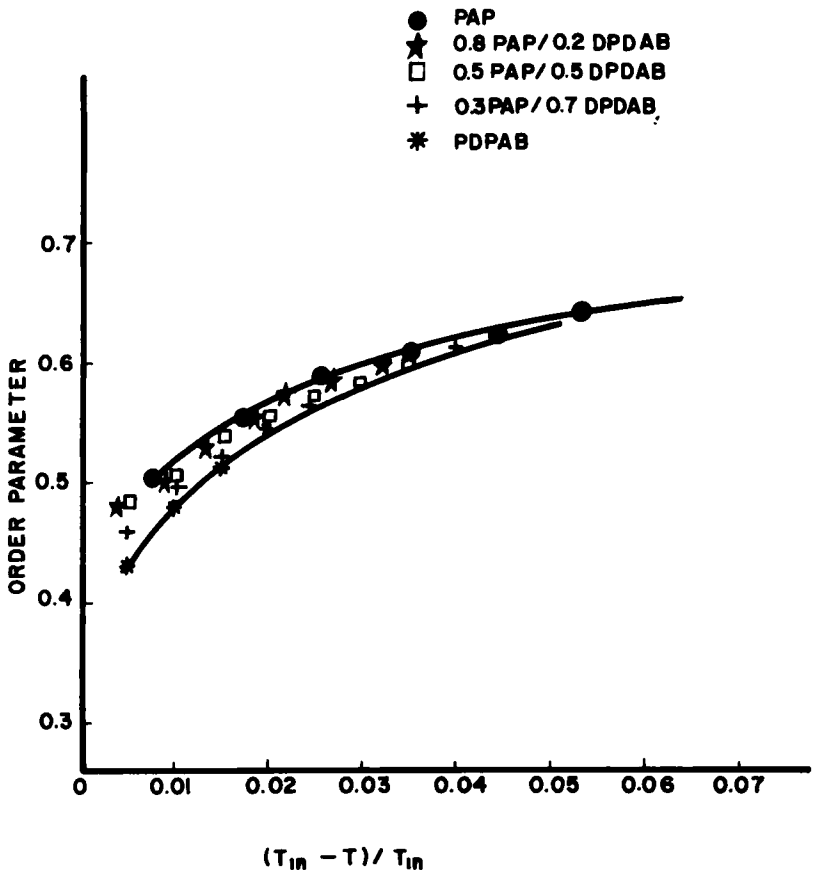


FIGURE 5 Order Parameters In PAP/PDPAB Mixtures. The points are the results of substituting some of the data given on figure 1 into Vuks equations.

showed that an one percent error in the density measurements (which enters into the calculations of the order parameter through the determination of the mean polarizabilities) gives rise to an eleven percent error in the order parameter when the anisotropic internal field description (the Neugebauer approach) is used but that the same density error gives rise to only an one percent error when the Vuks approach is used.

The results of our calculations of the order parameters are shown on Figures 5, 6, 7 and 8. On Figure 5, we have plotted the temperature dependence of the order parameters of several PAP/PDPAB mixtures. The temperature dependence curves for the pure nematogens PAP and PDPAB are similar to the curves obtained by de Jeu and Claassen[8] from magnetic susceptibility studies on the 4,4'-di-n-alkoxyazoxybenzene homologous series. The temperature

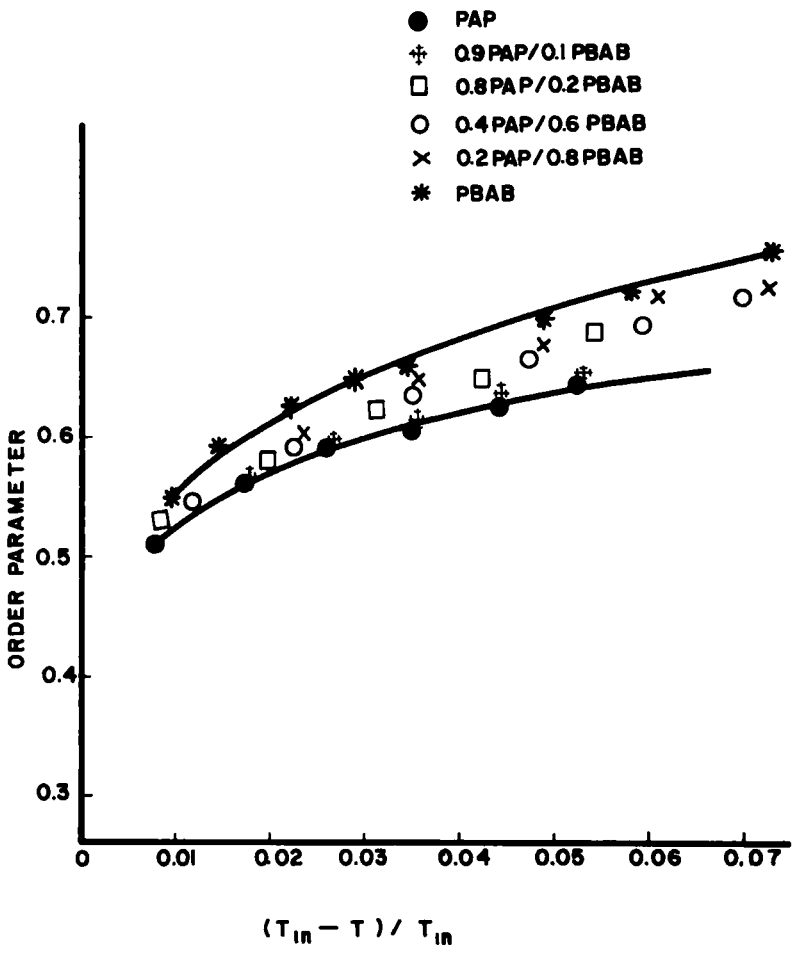


FIGURE 6 Order Parameters In PAP/PBAB Mixtures. The points result when some data points given in figure 2 are substituted into Vuks equations.

dependences of the order parameters in PAP/PBAB, PAP/PPAB and PAP/PHAB mixtures are found in Figures 6, 7 and 8, respectively. The temperature dependence curves for the pure nematogens PBAB, PPAB and PHAB are similar to the curves obtain by de Jeu and Claassen. All four of these figures indicate that the order parameters of the mixture follows the additive rule, Eq. (1). The clearest evidence for this is seen in Figure 6, the order parameter curves for the PAP/PBAB mixtures. At the reduced temperature $(T_{IN} - T)/T_{IN} = 0.035$ we clearly see that the experimental points are lying in the proper sequence.

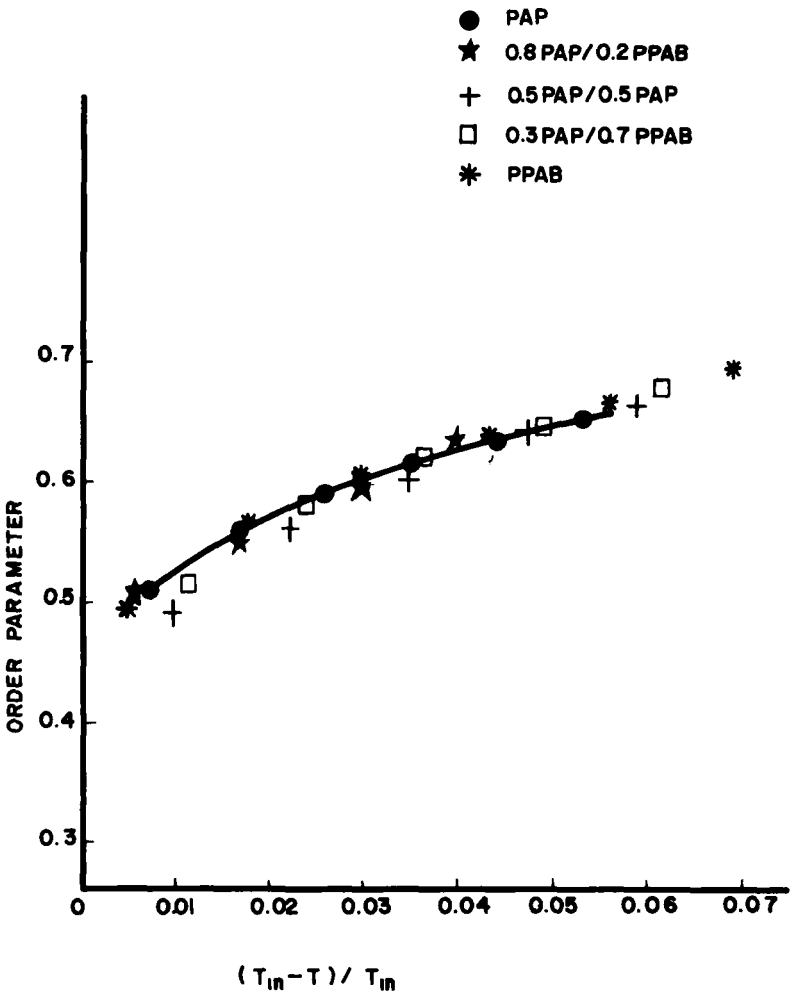


FIGURE 7 *Order Parameters In* PAP/PPAB Mixtures. The points are the order parameters determined by substituting some data points of figure 3 into Vuks equations.

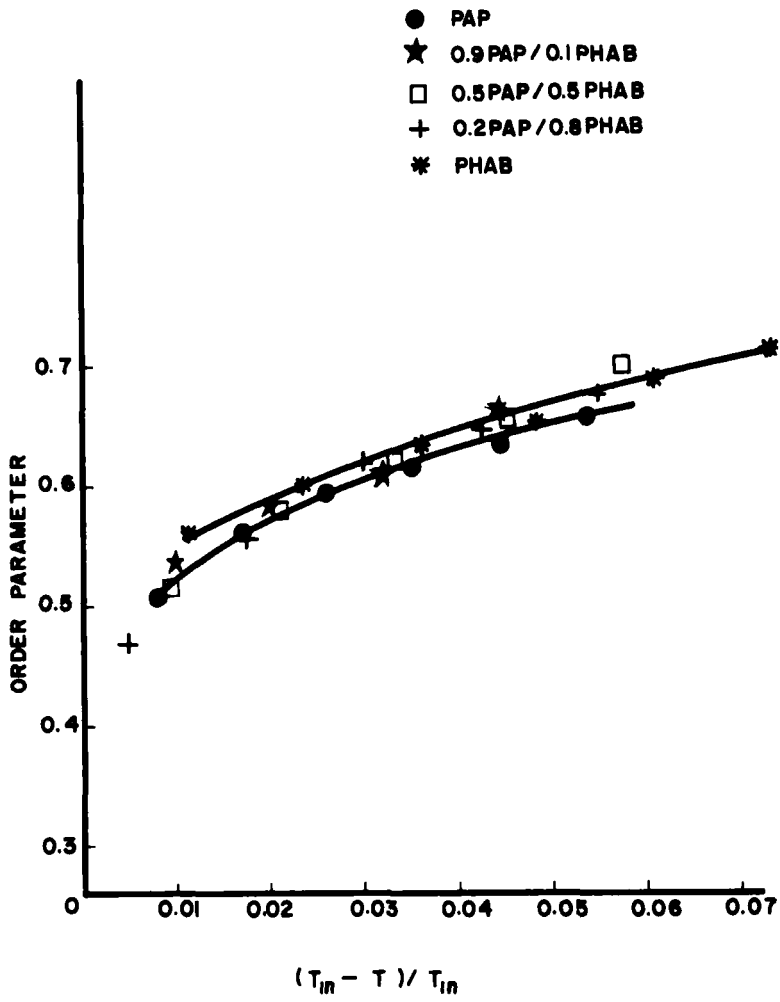


FIGURE 8 Order Parameters In PAP/PHAB Mixtures. The points are the results of substituting some data points of figure 4 into Vuks' equation.

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