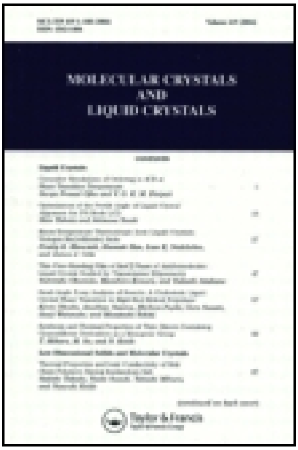

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Refractive Indices of p-Azoxyanisole (PAA), p-p'-di-n-pentyloxyazoxybenzene (PPAB) and Their Mixtures

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Refractive Indices of *p*-Azoxyanisole (PAA), *p*-*p*′-di-*n*-pentyloxyazoxybenzene (PPAB) and Their Mixtures

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The nematic isotropic phase boundary and refractive indices of p-azoxyanisole (PAA), *p*,*p*′-di-*n*-pentyloxyazoxybenzene (PPAB) and their mixtures are reported. The shape of the phase boundary of the PAA/PPAB system is explained in terms of the mixture theory of Humphries and Luckhurst. The optical data are used to calculate the mean polarizability of the mixtures and to calculate the order parameters on the basis of Vuks description of the local field. It is seen that the mean polarizabilities and order parameters of the PAA/PPAB mixtures of follow the additive rule.

I INTRODUCTION

Many studies[1-7] of the homologous liquid crystal series of *p*,*p*′-di-*n*-alkoxyazoxybenzenes have been reported in the literature. The nematic-isotropic transition temperatures,[4] ^{13}C NMR determined order parameters,[5] the entropies at the transition temperature,[6] and the splay elastic constants[7] of members of this series all show an even-odd effect. These even-odd effects indicate that the end chains of the molecules play a significant part in the stability of the mesophases. Marcelja[8] has developed a theory which predicts behaviors which are in agreement with the experimental observations of this series. Properties of binary mixtures of members of this series have also been reported. the phase diagrams of several binary mixtures of the *p*,*p*′-di-*n*-alkoxyazoxybenzenes have been given by Hsu and Johnson[9] and by Demus *et al.*[10] The nematic-isotropic phase boundary for *p*-azoxyanisole (PAA)/*p*-azoxy-

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phenetole (PAP) appears to be linear while the phase boundaries for the other mixtures are curved.

Refractive indices of PAA/PAP mixtures have been reported by Chatelain and Germain.[12] Chandrasekhar and Madhusudana[13] have analysed the index data in terms of a model in which the local field is isotropic[14] and have found that the optically determined order parameter of the PAA/PAP mixtures obey the following compositional dependence

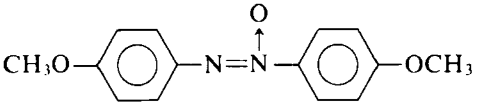
$$S_{\mathrm{mix}} = \tau S_{\mathrm{PAA}} + (1 - \tau) S_{\mathrm{PAP}} \tag{1}$$

where τ is the mole fraction of PAA in the mixture and where S_{PAA} and S_{PAP} are the order parameters of the two pure nematogen PAA and PAP, respectively. This additive character of the mixtures order parameter has also been observed by Ibrahim and Haase[14] in mixtures of 4-methoxybenzoic acid and 4-*n*-hexyloxybenzoic acid. They did not, however, give the phase diagram of this mixture.

We would like to report in this paper, our measurements of the refractive indices of the binary mixtures of *p*-azoxyanisole (PAA) and *p*,*p*′-*n*-di-*n*-pentyloxyazoxybenzene (PPAB). The phase diagram of this mixture has been reported on by Demus *et al.*[10] Dilatometric studies by Pongthana-ananta *et al.*,[16] of this system show that the molar volumes and the fractional volume changes (at the nematic-isotropic transitions) of the mixtures do not obey the additive rule and are, therefore, indicative of the non ideal nature of the PAA/PPAB mixture.

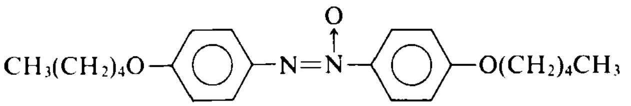
II EXPERIMENTAL PROCEDURE

The two pure nematogen constituents, whose structural formula, nematic region and molecular weight are
4-4′-di-methoxyazoxybenzene (*p*-azoxyanisole) PAA



nematic range 118–135°C
molecular weight 258.28

and
p-*p*′-di-*n*-pentyloxyazoxybenzene PPAB



nematic range 79–122°C
molecular weight 370.49

were obtained from Riedel Co. (W. Germany) and Eastman Kodak Co. (U.S.A.), respectively. Both nematogens were recrystallized twice from waterethanol mixtures and dried under vacuum before their use. Each mixture was prepared by mixing accurately weighed quantities of the two mesogenic components in a semi-micro test tube and then heated to the isotropic phase to insure homogeneous mixtures. The components were weighed to an accuracy of ±0.0001 gm.

The nematic-isotropic transitions of each mixtures were observed with a Reichert heating stage microscope while the temperatures were being measured by a Mettler TM16 thermometer. The accuracy of our temperature measurements was estimated to be ±0.5°C.

The refractive indices for the 5893 Å sodium line were measured using the minimum deviation method of Pellet and Chatelain.[17] The values of the prism angle and minimum deviation angles were read from an AO Spencer spectrometer (American Optical Corp, Scientific Instrument Division) to an accuracy of ±0.5 minute of arc. Using a prism angle of 230 minutes, the errors in the determination of the refractive indices are estimated to be ±0.006.

III RESULTS AND DISCUSSION

In Figure 1, we have plotted the temperature dependence of n_0 (the ordinary refractive index, n_e (the extra ordinary refractive index) and n_i (the refractive index for the isotropic liquid) for PAA, PPAB and their mixtures. Our measured values for the refractive indices for PAA and PPAB are in good agreement with the values reported by de Jeu and Bordewijk.[2] Knowing the values of the refractive indices and densities of the PAA/PPAB systems, the mean (or average) polarizability $\bar{\alpha}$ can be calculated from the Lorentz-Lorenz relation for the isotropic phase or from the Born relation for the nematic phase, i.e.,

$$\frac{4\pi}{3}\frac{N_0}{M}\bar{\alpha} = \left[\frac{1}{\rho_i}\frac{n_i^2 - 1}{n_i^2 + 2}\right]_{\text{liquid}} = \left[\frac{1}{\rho_n}\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\right]_{\text{nematic}} \tag{2}$$

where N_0 is Avogadro's number; M, the molecular weight, ρ, the density and where $\bar{n}^2 = (n_e^2 + 2n_0^2)/3$. Since the mean polarizability is a property of a single isolated molecule and not of the system, both the Lorentz-Lorenz and the Born relations should yield the same value.[13] We find, for example, that the Lorentz-Lorenz relation gives the values of 32.24×10^{-24} cc and 32.25×10^{-24} cc at the temperatures 137°C and 139°C, respectively, for the mean polarizability of PAA, while the Born relation gives the values 32.22×10^{-24} cc, 32.20×10^{-24} cc and 32.26×10^{-24} cc at the temperatures 135°C, 130°C and 124°C respectively. The results of similar calculations of the mean polarizabilities of PAA/PPAB mixtures are shown in Figure 2. Our calculated values for α of PAA and PPAB are 32.24×10^{-24} cc and 48.38×10^{-24} cc, respectively. These values are close to the values of 31.9×10^{-24} cc and 49.5×10^{-24} cc reported by Hanson and Shen.[1] Our values for $\bar{\alpha}$ indicate that the mean polarizability per

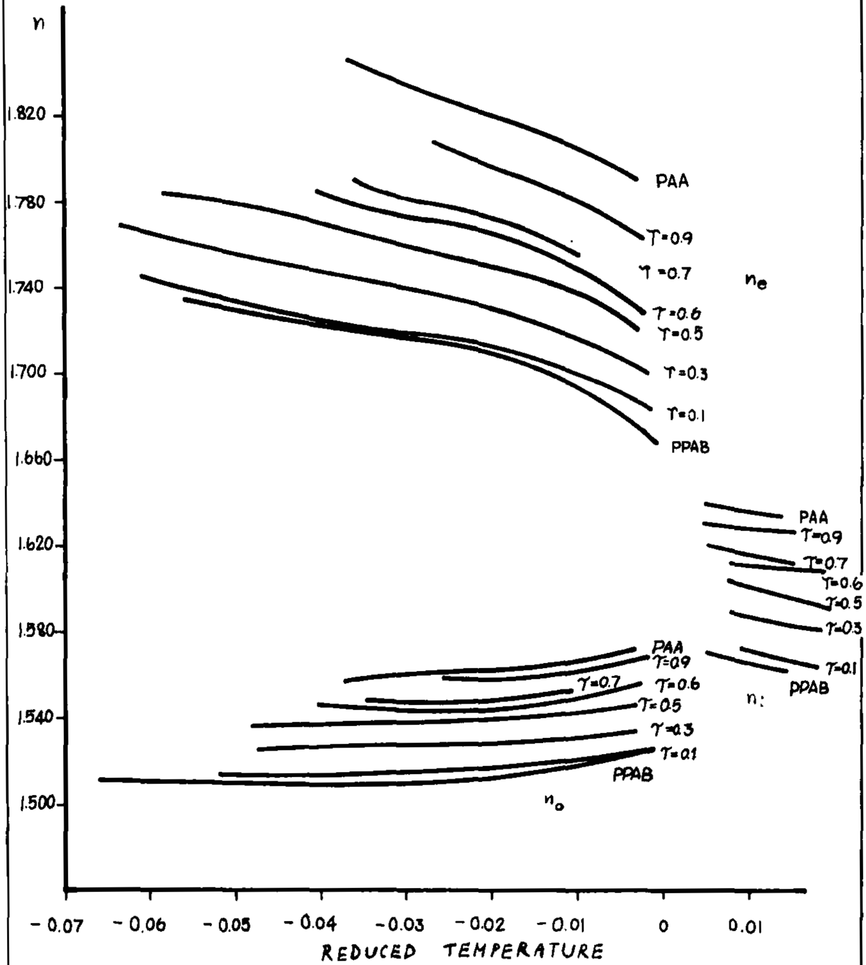


FIGURE 1 Refractive indices of PAA, PPAB and their mixtures. The accompanying numbers give the mole fraction of PAA in the mixtures.

methylene group is 2.02×10^{-24} cc while Hanson and Shen's values give a value 2.2×10^{-24} cc. The mean polarizability calculated from the bond polarizability data[15] is 1.84×10^{-24} cc. Figure 2 indicates that the mean polarizability of the PAA/PPAB mixtures follow the additive rule.

The refractive indice and density data may also be used to determine the

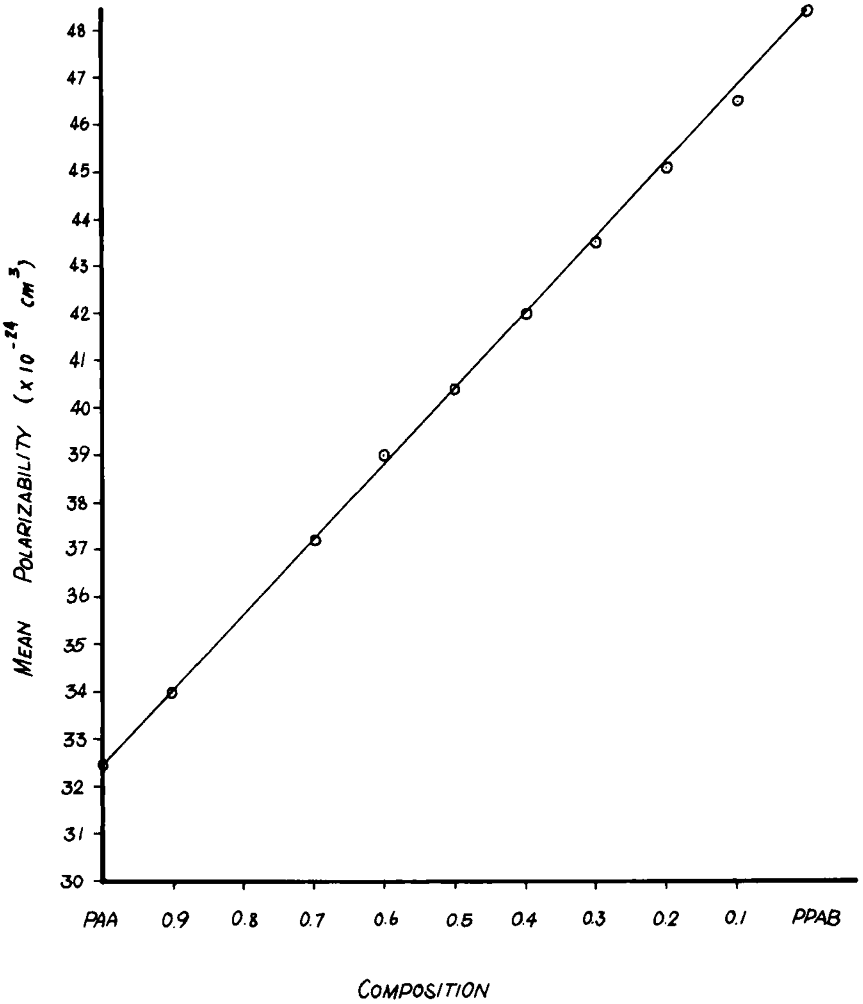


FIGURE 2 Composition dependence of the mean polarizability. The points were obtained by substituting the data of Figure 2 into equation (5).

order parameter

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

where θ is the angle between the long axis of the molecule and the average direction of the molecular alignment, which is related to the polarizability through the relation[4]

$$S \Delta \alpha = (\alpha_e - \alpha_0) \tag{4}$$

where α_e and α_0 are the effective polarizabilities and $\Delta \alpha$ is the polarizability anisotropy. In the Vuks model[14] which assumes that even in a strongly anisotropic liquid, the local field is isotropic, the differences in the effective polarizabilities ($\alpha_e - \alpha_0$) can be calculated from the optical measurements by the relationships

$$\frac{n_e^2 - 1}{\bar{n}^2 + 2} = \frac{4}{3}\pi N\left(\bar{\alpha} + \frac{2}{3}(\alpha_e - \alpha_0)\right) \tag{5a}$$

$$\frac{n_0^2 - 1}{\bar{n}^2 + 2} = \frac{4}{3}\pi N\left(\bar{\alpha} - \frac{1}{3}(\alpha_e - \alpha_0)\right) \tag{5b}$$

These two relationships can be combined to give

$$\alpha_e - \alpha_0 = S\Delta\alpha = \frac{3N_0M}{4\pi\rho}\left[\frac{n_e^2 - n_0^2}{\bar{n}^2 + 2}\right] \tag{6}$$

In order that S can be determined, the polarizability anisotropy $\Delta\alpha$, must be known. Chandrasekhar and Madhusudana,[13] who were the first to apply the above model to liquid crystal mixtures, were able to calculate $\Delta\alpha$ for the PAA/PAP mixtures from the solid state refractive indices data taken by Chatelain and Germain.[12] Chandrasekhar and Madhusudana found that the polarizability anisotropy for the PAA/PAP system followed the additive rule. In the absence of solid state data, Haller *et al.*[18] proposed that the anisotropy $\Delta\alpha$ can be obtained by extrapolating the plot ot $S\Delta\alpha$ versus the reduced temperature $T_{red} = (T - T_t)/T_t$ down to $T = 0$°K and assume that $S = 1$ at $T = 0$°K. However, such an extrapolation[19] of $S\Delta\alpha$ values for the homologous series trans-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes produced a set of scattered $\Delta\alpha$ values which did not follow any systematic pattern. De Jeu and Classen[3] discarded a similar extrapolation of magnetic susceptibility data to find the magnetic susceptibility anisotropies for the homologous series *p, p′*-di-*n*-alkyl and *p,p′*-di-*n*-alkoxyazoxybenzenes because the extrapolations yield a set of scattered values. Chang *et al.*[20] assumes that the small variation in the chain lengths of the end groups of the homologous series *p*-alkoxybenzylidene butylaniline does not cause an appreciable variation in the anisotropy of the molecular polarizability and so the polarizability anisotropies for every member of the series has approximately the same value as the anisotropy of the first member of the series. Karat and Madhusudana[21] have calculated from the bond polarizability data that the addition of an extra methylene (CH_2) group in the end chains leads to an increase in the polarizability anisotropy of $+0.27 \times 10^{-24}$ cc., if the additional C—C bond is along the molecular axis, and is -0.1×10^{-24} cc., if the C—C bond is at a large angle to the long axis. According to this scheme, the polarizability anisotropy for PAP would be 35.24×10^{-24} cc. This is very close to the value 35.1×10^{-24} cc. obtained by Chandrasekhar and Madhusudana[13] from the solid state data. The above

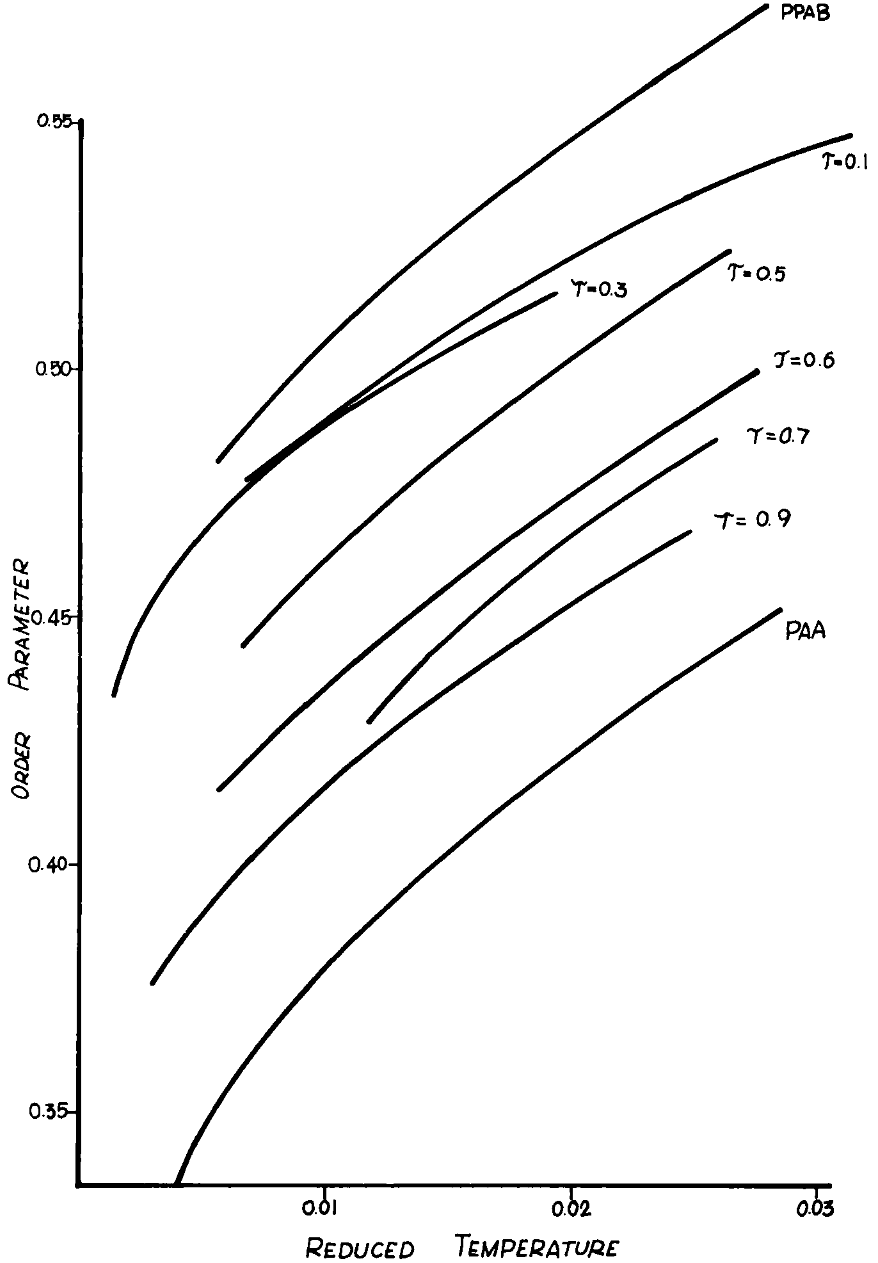


FIGURE 3 Temperature dependence of the order parameters of PAA, PPAB and their mixtures.

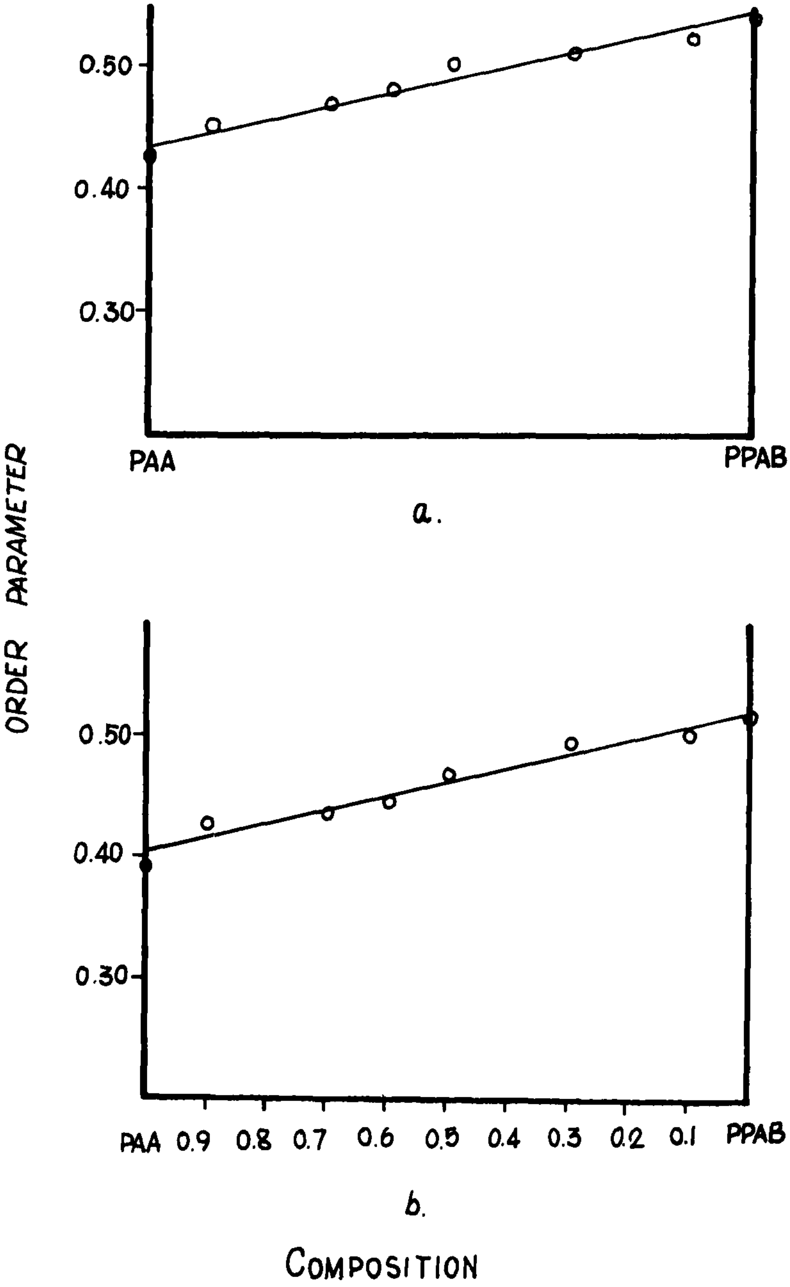


FIGURE 4 Composition dependence of the order parameters of PAA, PPAB and their mixtures. a. At the reduced temperature $T_{red} = -0.020$. b. At the reduced temperature $T_{red} = -0.011$.

scheme would give the value 35.92×10^{-24} cc. as the polarizability anisotropy of PPAB.

In the absence of solid state refractive indices data for PPAB, we have used the above value in our calculations of the order parameter. For the anisotropy of the various PAA/PPAB mixtures, we have assumed that the polarizability anisotropy is given by

$$\Delta\alpha_m = \tau\Delta\alpha_{\mathrm{PAA}} \text{ and } (1 - \tau)\,\Delta\alpha_{\mathrm{PPAB}} \qquad (7)$$

We believe that the above assumption may at most lead to an error of only a few percent. (We note that the mean polarizabilities of the PAA/PPAB mixtures appears to follow an additive rule (See Figure 2)). The results of substituting our refractive index data and the density data of Ref. 16 into Eq. (6) and then using Eq. (7) gives the order parameters for the various PAA/PPAB mixtures shown in Figure 3. We have taken the values of the order parameters at the reduced temperatures $T_{\mathrm{red}} = -0.011$ and -0.02 and plotted them on Figure 4. We find that the order parameters for the PAA/PPAB mixtures appear to follow the additive rule.

We close by noting that the refractive index data can also be analysed in terms of the Neugebauer model[22] which takes the local field to be anisotropic. Van Hecke[19] finds however that Neugebauer type analysis of the birefringence data of the homologous series trans-4-ethoxy-4′-*n*-alkanoxyazobenzenes does not produce the even-odd effect obtained from a Vuks type analysis of the same data.

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