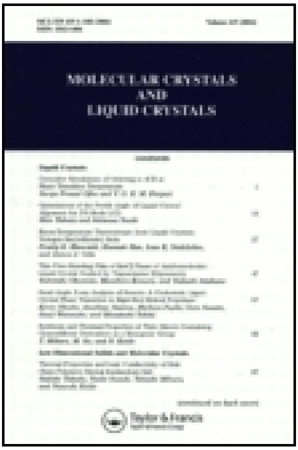

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Optical and Dilatometric Properties of Binary Mixtures of PAA and PHAB

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The nematic isotropic phase boundary, dilatometric properties and refractive indices of *p*-azoxyanisole (PAA), *p,p'*-di-*n*-hexyloxyazoxybenzene (PHAB) and their mixtures are reported. The refractive index and density data are used to calculate the mean polarizabilities of the PAA/PHAB mixtures and to calculate the temperature dependence of the order parameters of the PAA/PHAB mixtures using both the Vuks and the Neugebauer descriptions of the local field. It is seen that the PAA/PHAB mixture order parameters at the reduced temperature $t = 0.013$ appear to follow the additive rule.

I INTRODUCTION

The homologous series of liquid crystals *p,p'*-di-*n*-alkoxyazoxybenzene has been well studied. The nematic isotropic transition temperatures,[1] densities,[2] refractive indices,[3,4] entropy changes at the nematic isotropic transition temperatures,[5] the latent heat of transition at the nematic-solid phase transition,[6] ^{13}C NMR studies,[7] magnetic susceptibilities,[8] d.c. Kerr effect,[9] Raman emission spectra,[10] and the splay elastic constants[11] of most members of this series have been reported. Many of these properties exhibit the odd-even effect. The existance of an even-odd effect in the observed properties of this homologous series has led Marcelja[12] to develop a theory in which the end chains of the molecules take an active part in the anisotropic interaction. Prior to this theory, the end chains were assumed to "merely take up space."[13]

Studies of the properties of binary mixtures have not been as extensive. Chatelain and Germain[14] measurements of the refractive indices of binary mixtures of *p*-azoxyanisole (PAA) and *p*-azoxphenetole (PAP), Hsu and

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Johnson[15] and Demus *et al.*,[16] measurements of the phase boundaries of eutectic mixtures of the *p,p'*-di-*n*-alkoxyazoxybenzenes, are among the few reported. Using Chatelain and Germains data, Chandrasekhar and Madhusudana[17] were able to determine the order parameters of various PAA/PAP mixtures. They found that the PAA/PAP mixtures order parameter obeyed the empirical relation

$$S_{\text{mix}} = \tau S_1 + (1 - \tau) S_2 \tag{1}$$

where τ is the mole fraction of constituent 1 in the mixture and where S_1 and S_2 are the order parameters for the two pure nematogens. Smith[18] has shown that the nematic-solid phase boundary of the PAA/PAP system can be explained by the Chatelier-Schröder-van Laar equations.[19] By assuming that the other mixtures of the *p,p'*-di-*n*-alkoxyazoxybenzenes are only weakly non ideal, Demus *et al.*,[16] were able to obtain an modified Chatelien-Schröder-van Laar equation which yielded eutectic points in close agreement with the measured values.

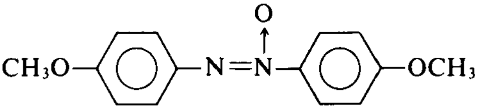
Humphries and Luckhurst[20] have developed a theory for liquid crystals which appeared to be able to explain the shape of the nematic-isotropic phase boundaries of the *p,p'*-di-*n*-alkoxyazoxybenzene mixtures reported by Hsu and Johnson.[15] They found that the deviation from the geometric mean approximation (which in their theory led to a linear nematic isotropic phase boundary) increased as the difference between the number of methylene ($—CH_2$-) groups in the alkoxy end chain of the two molecules became larger. To obtain their least square best fits, Humphries and Luckhurst assumed that the densities of the higher members of the homologous series are the same as that of PAA and that the molar volumes of the binary mixtures are additive. The densities of the *p,p'*-di-*n*-alkoxyazoxybenzenes given by Linsert[21] clearly show that the first assumption is wrong while the recent dilatometric studies of Phaovibul *et al.*[21] on PAA/PPAB indicate that the additive rule is nearly obeyed away from the nematic-isotropic transition but not close to the transition.

We would like to report in this paper, our measurements of the dilatometic propertis and the refractive indices of binary mixtures of *p*-azoxyanisole (PAA) and *p,p'*-di-*n*-hexyloxyazoxybenzene (PHAB). The phase boundaries of this system have already been obtained by Hsu and Johnson.[15] Of all the systems studied by them, the nematic isotropic phase boundary of the system PAA/PHAB deviates most from the linear phase boundary approximation.

II EXPERIMENTAL PROCEDURES

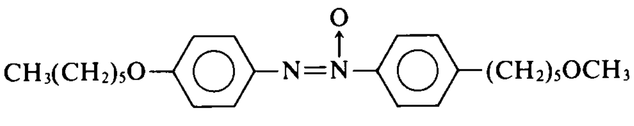
A Materials

The structural formulas, transition temperatures and molecular weights of the liquid crystals used in this study are *p*-azoxyanisole (PAA)



118°C crystalline to nematic → 135°C nematic isotropic molecular weight 258.28

p,p'-di-*n*-hexyloxyazoxybenzene (PHAB)



82°C crystalline to nematic → 130°C nematic to isotropic molecular weight 398.55

The nematogen PAA was obtained from Riedel Co. (Hannover, Germany), while the nematogen PHAB was obtained from Frinton Labs. (Frinton, N.J.). Both nematogens were recrystallized twice from water-ethanol mixtures and dried under vacuum before their use. The mixtures were made by weighing desired amounts of each nematogen to an accuracy ±0.0001 gm. and mixing them while in the isotropic state.

B Transition temperature measurements

The transition temperatures were determined by microscopic observation with a Reichert heating-stage microscope using a Mettler TM 16 thermometer. The accuracy of these temperature measurements was ±0.1°C.

C Dilatometric measurements

The densities of the liquid crystals at various temperatures were measured using a capillary dilatometer. The height changes were observed by a cathetometer with a precision of 0.001 cm. With a 0.002 cm^2 cross sectional capillary and one gram sample, the accuracy of the density measurements was estimated to be ±0.0005 gm/cm^3. The temperatures of the samples were maintained by a Poly Science Corp. Model 80 constant temperature circulator with a temperatures stability of ±0.1° C.

D Refractive indices measurements

The refractive indices for the 5893 Å sodium line were measured using the minimum deviation method of Pellet and Chatelain.[22] The values of the prism angle and minimum deviation angles were measured with 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

The nematic isotropic phase boundary for the *p*-azoxyanisole/*p,p'*-di-*n*-hexyloxyazoxybenzene system is shown in Figure 1. It is very similar to the phase boundary of the same system obtained by Hsu and Johnson[15] and Demus *et al.*[16] As we pointed out in the introduction, Humphries and Luckhurst[20] have developed a statistical theory for liquid crystal mixtures which might be capable of explaining the shape of the nematic isotropic phase boundary of binary liquid crystal mixtures. Using the densities of the PAA/PHAB mixtures obtained in this study, we find that a best fit of the experimental data to the theory could be achieved with a deviation in ϵ_{12} (the interaction parameter between the different types of molecules in the mixture) of 4% from the geometric mean approximation. With incorrect molar volume data, Humphries and Luckhurst found that the best fit was achieved with a deviation of 5% in ϵ_{12}.

In Table I, we have listed the densities of PAA, PHAB and their mixtures in the nematic and isotropic phases. From the density data, we have calculated the coefficient of thermal expansion for PAA, PHAB and their mixtures and have listed them in Table I, also. After converting the densities into molar volumes, we find that all the mixture exhibit a drop in the molar volumes as they make a transition from the isotropic to the nematic phase. This clearly indicates that the nematic-isotropic transitions of the PAA/PHAB are all first order transitions. We also find that pretransitional effects exist in all the mixtures on the nematic side. Away from the transition region, we find that the molar volumes of the mixtures nearly obey the additive rule (the excess volume of mixing is less than 0.6%). The fractional volume changes at the nematic-isotropic transition do not appear to follow the additive rule.

From the molar volumes of PAA and PHAB, we find that the contributions to the molar volumes due to a single methylene group are 17.12 cm^3/mole and 18.21 cm^3/mole at the relative temperature of 9.5° C into the nematic and isotropic phases, respectively. These values are close to the values 16.89 cm^3/mole and 17.17 cm^3/mole obtained for the molar volumes of HBT and OBT.[23] The isotropic phase data of the *n*-alkanes, alkylbenzenes and alkylbiphenyls indicate that the methylene group contribution to the isotropic molar volumes of these three series are 16.4, 16.6 and 17.1 cm^3/mole. The solid state data of the *n*-alkanes[24] indicate that the methylene group contribution to the solid phase molar volumes is 14.5 cm^3/mole. Thus it appears that the packing

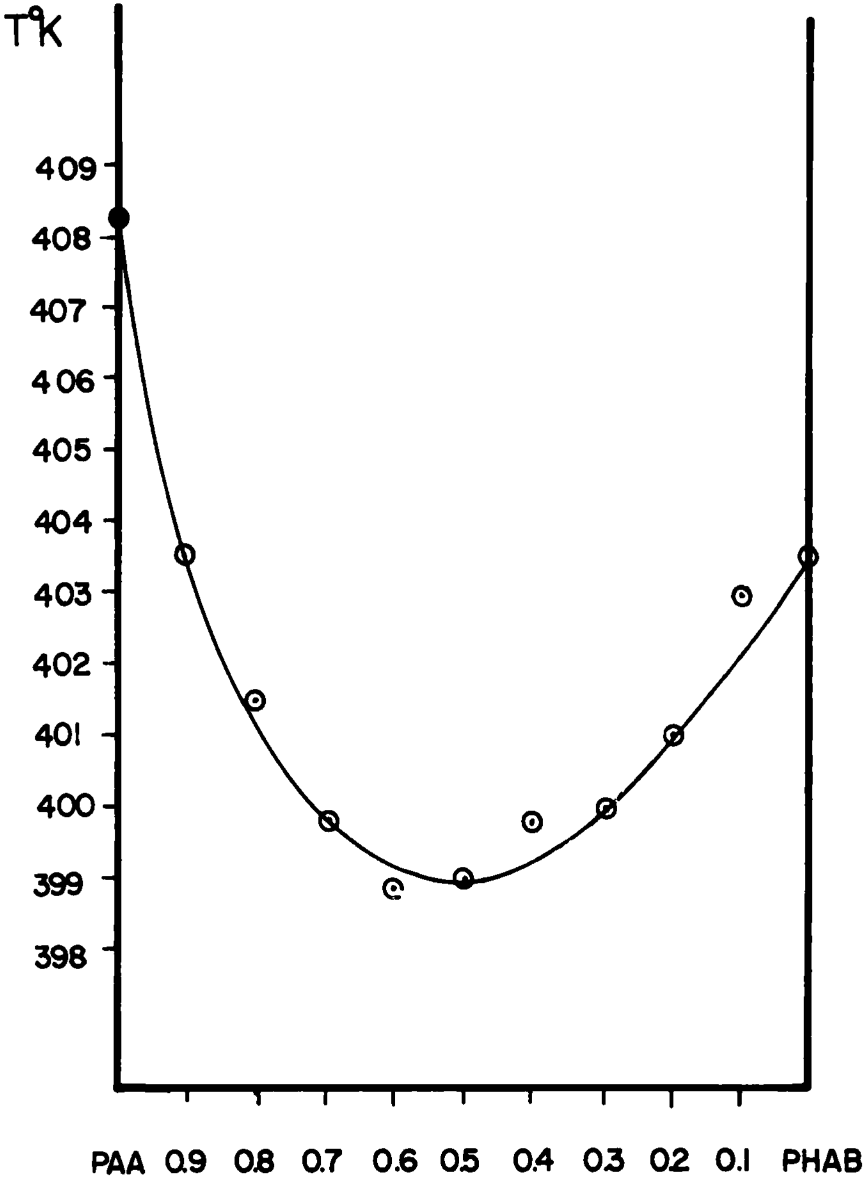


FIGURE 1 Nematic isotropic phase boundary of the PAA/PHAB system. The solid line is the best least square fit of the experimental points to the theory of mixtures proposed by Humphries and Luckhurst.[20]

TABLE I

The densities and expansion coefficients of some mixtures of PAA and PHAB. τ is the mole fraction of PAA in the mixture. The units of T are °C; of the densities ρ, gm/cm, and of the expansion coefficients β, 10^{-4} °C^{-1}.

Pure PAA			$\tau = 0.80$			$\tau = 0.30$			Pure PHAB		
T	ρ	β	T	ρ	β	T	ρ	β	T	ρ	β
129	1.1623	8.0	122	1.1103	9.7	122	1.0255	9.4	120	0.9949	9.3
131.2	1.1601	9.8	124	1.1083	10.4	124	1.0235	10.4	125	0.9902	11.2
133.5	1.1575	10.6	126	1.1059	10.9	126	1.0210	12.3	127	0.9880	11.7
134.5	1.1562	11.6	126.5	1.1053	13.6	126.8	1.0201	12.9	129.1	0.9857	13.3
135.4	1.1550	12.1		two phases coexist		127.2	1.0195	17.7	130	0.9842	14.7
136	1.1541	14.4	126.8	1.1047	17.9		two phases coexist		130.2	0.9836	18.3
	two phases coexist		127.3	1.1036	19.1	127.3	1.0192	19.6		two phases coexist	
136.3	1.1536	45.1	127.9	1.1025	21.2	127.5	1.0189	32.7	130.5	0.9833	36.6
136.5	1.1515	82.5	128.5	1.1011	24.9	127.6	1.0182	78.6	130.7	0.9821	66.2
	isotropic phase		129.1	1.0996	13.6	127.7	1.0173	73.7	130.9	0.9807	45.9
136.7	1.1498	45.7		isotropic phase		127.9	1.0167	39.3		isotropic phase	
137.1	1.1491	11.6	129.2	1.0995	9.1		isotropic phase		131.1	0.9803	15.3
137.6	1.1486	7.3	131	1.0979	8.4	127.9	1.0165	14.8	132	0.9794	11.2
138.3	1.1481	6.5	133	1.0960	7.3	129	1.0155	8.3	133	0.9786	7.7
140	1.1466	7.8	135	1.0944	7.0	131	1.0137	8.5	134.1	0.9766	8.1

of the methylene groups in the nematic phase is closer in the isotropic phase than in the solid state phase.

In Figure 2, we have plotted the temperature dependence of n_0 (the ordinary refractive index), n_e (the extra ordinary refractive index), $\bar{n}(\bar{n}^2 = (n_e^2 + 2n_0^2)/3)$ and n_i (the isotropic phase refractive index) for PAA, PHAB and some of their mixtures. Using the data of Figure 2 and of Table I, we have calculated the mean polarizabilities of PAA, PHAB and their mixtures according to the

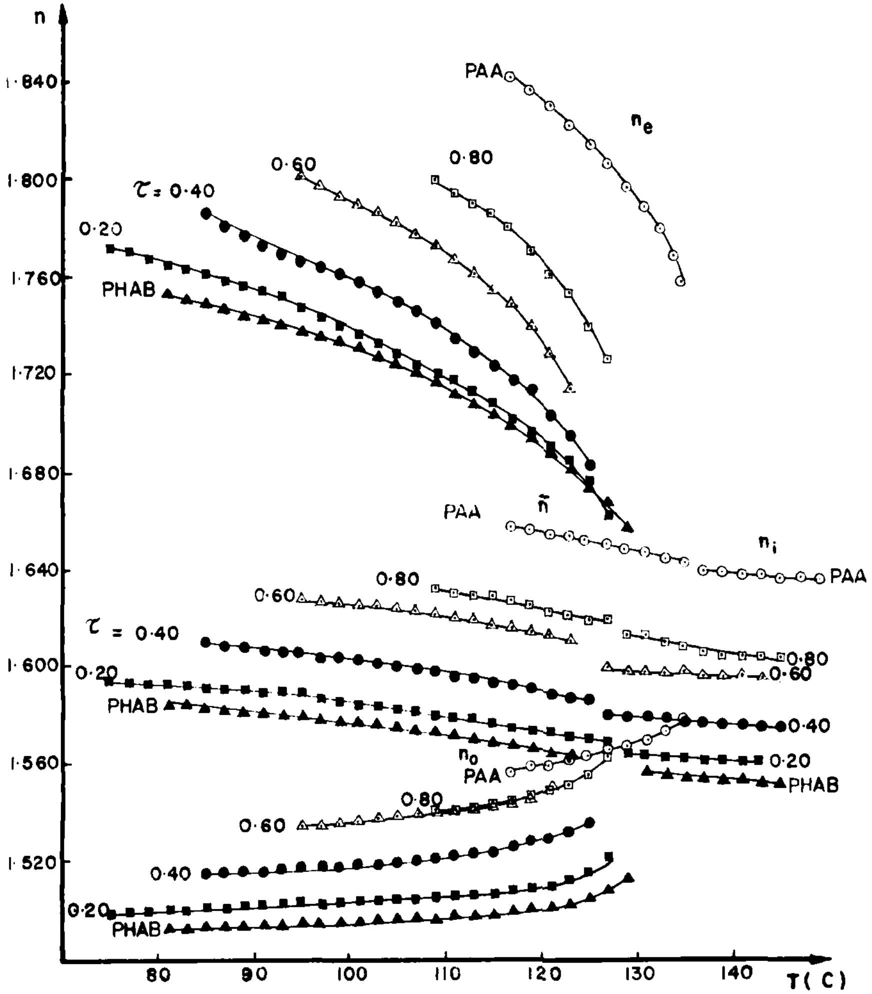


FIGURE 2 Refractive indices of PAA, PHAB and several of their mixtures. n_0 is the ordinary refractive index. n_e is the extra ordinary refractive index $\bar{n}^2 = (n_e^2 + 2n_o^2)/3$. n_i is the refractive index the isotropic phase.

Lorentz-Lorenz equation for the isotropic phase and the Born relation for the nematic phase

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

where N_0 is Avogadro's number; M is the molecular weight and ρ is the densities in the respective phases. The results of these calculations are shown in Figure 3. As we can clearly see, the mean polarizabilities of the mixtures follow the additive rule. We find that the mean polarizability of PAA is 32.24×10^{-24} cm^3 and that of PHAB is 52.4×10^{-24} cm^3. These values are close to those obtained by Hansen and Shen[3] (31.9×10^{-24} cm^3 and 51.0×10^{-24} cm^3). Our values indicate that the mean polarizability of each methylene group is 2.02×10^{-24} cm^3 in comparison with Hansen and Shen's 1.91×10^{-24} cm^3.

The refractive index and density data may also be used to determine the 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. The order parameter S is related to the polarizabilities through the relation[1]

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

where α_e and α_0 are the effective polarizabilities and $\Delta\alpha$ is the polarizability anisotropy. The connections between the effective polarizabilities and the refractive indices depend on the model used to describe the local field inside the liquid crystal. In the Vuks model,[25] which assumes that the local field is isotropic even in a highly anisotropic liquid, the differences between the effective polarizabilities $(\alpha_e - \alpha_0)$ can be calculated from the refractive measurements via

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

and

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

which can be combined to give

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

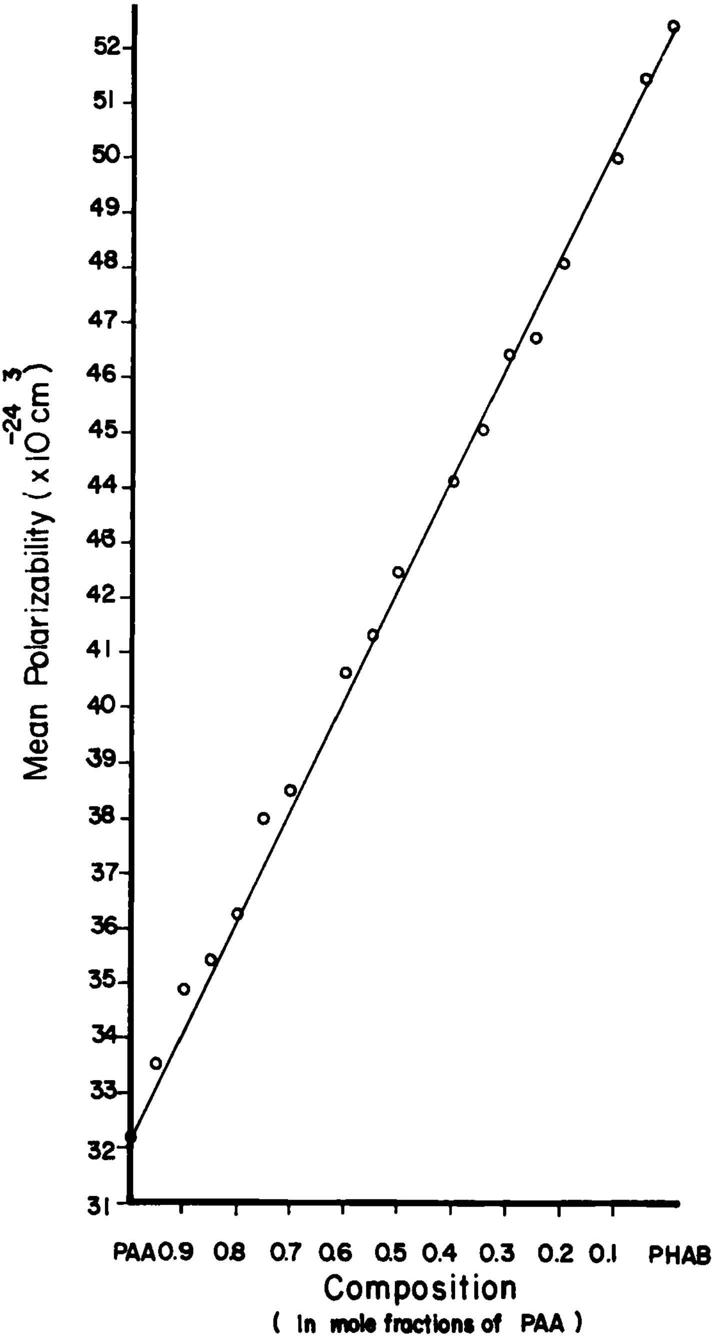


FIGURE 3 Compositional dependence of the mean polarizability of the PAA/PHAB system. The points were obtained by applying equation 2 to all the data taken in the study.

In the Neugebauer model,[26] the local field is taken to be anisotropic and the differences between the effective polarizabilities can be calculated by Horn's equation[27]

$$\alpha_e - \alpha_0 = \alpha \frac{9}{4} B\left[\left(B^2 - \frac{10}{3} B + 1\right)^{1/2} + \frac{B}{3} - 1\right] \qquad [7]$$

where

$$B = \frac{n_i^2 - 1}{n_i^2 + 2}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2(n_0^2 + 2)}{n_0^2 - 1}\right] \qquad (8)$$

The results of these calculations are listed in Table II.

The order parameters of PAA, PHAB and their mixtures can be calculated from a knowledge of $\alpha_e - \alpha_0$ only if the polarizability anisotropies of PAA, PHAB and their mixtures are known. Chandrasekhar and Madhusudana[17] obtained values for the anisotropies of the PAA / PAP systems from the solid state data.[6] In the absence of solid state data or of other means of measuring the anisotropies, reasonable assumptions about the values of the anisotropies have to be made. Chang *et al.*,[28] in their studies of the homologous series *p*-alkoxybenzylidene butylaniline, assumed that the polarizability anisotropies of all the members of the series have approximately the same value as the first member of the series. Their assumption was based on the belief that the small variations in the chain lengths of the alkoxy ($CH_3(CH_2)_{n-1}O$) end groups in their liquid crystals do not cause an appreciable variation in the anisotropies of the members of the series. Karat and Madhusudana[29] have calculated, however, that the addition of an extra methylene (CH_2) group in the end chains leads to an increase in the polarizability anisotropy of $+0.27 \times 10^{-24}$ cm^3 if the additional C—C bond is along the molecular axis and is -0.1×10^{-24} cm^3 if the C—C bond is at a large angle. According to this scheme, the calculated polarizability anisotropy for PAP (35.24×10^{-24} cm^3) is very close to the solid state optically determined value[17] (35.1×10^{-24} cm^3). The above scheme gives as the polarizability anisotropy of *p,p′*-di-*n*-hexyloazoxybenzene a value 35.92×10^{-24} cm^3.

Haller *et al.*[30] proposed that the extrapolation of the calculated $S\Delta\alpha$ values down to $t = -1$ (where t is the reduced temperature $(T - T_{IN})/T_{IN}$) and, by assuming that $S = 1$ at $T = 0°$ K, would yield a value of $\Delta\alpha$. This procedure has been used extensively to obtain the polarizability anisotropy of individual liquid crystals.[31] However its application to the refractive index data of homologous series of liquid crystals produces a set of anisotropy values for the series which does not exhibit any general pattern as the number of methylene groups is increased.[8,32] de Jeu *et al.*[8] discarded this method because of the lack of a general trend in the extrapolated anisotropies. Determination of the polarizability anisotropies through d.c. Kerr measurements[9] and optical measurements[3,4] of the *p,p′*-di-*n*-alkoxy azoxybenzenes indicate that a systematic

TABLE II

Effective polarizability anisotropies of PAA, PHAB and their mixtures. $(S\Delta\alpha)_V$ are calculated from the Vuks approach, Eq. (6). $(S\Delta\alpha)_N$ are calculated from the Neugebauer approach, Eq. (7). The values are presented in units of 10^{-24} cm^3.

	Pure PAA			$\tau = 0.90$	
$T_{IN} - T$	$(S\Delta\alpha)_V$	$(S\Delta\alpha)_N$	$T_{IN} - T$	$(S\Delta\alpha)_V$	$(S\Delta\alpha)_N$
1.5	11.54	9.67	1.5	12.14	10.99
3.5	13.02	10.56	3.5	14.07	11.57
5.5	13.89	11.25	5.5	14.95	11.84
7.5	14.51	11.77	7.5	15.54	12.05
9.5	15.19	12.10	9.5	15.92	12.45
11.5	15.80	12.49	11.5	16.59	12.55
	$\tau = 0.80$			$\tau = 0.70$	
1.5	11.89	8.88	1.3	11.76	8.90
3.5	13.51	10.56	3.3	13.55	10.46
5.5	14.81	11.81	5.3	14.88	11.34
7.5	15.52	12.29	7.3	16.28	11.99
9.5	16.31	12.68	9.3	16.80	12.74
			11.3	17.34	13.47
	$\tau = 0.60$			$\tau = 0.50$	
0.8	11.16	8.99	3	13.83	11.32
2.8	13.17	10.83	5	15.59	12.64
4.8	15.09	12.24	7	16.73	13.96
6.8	16.07	13.35	9	17.59	14.55
8.8	16.97	13.78	11	18.36	14.84
10.8	17.53	14.15	13	19.04	15.23
	$\tau = 0.40$			$\tau = 0.30$	
$T_{IN} - T$	$(S\Delta\alpha)_V$	$(S\Delta\alpha)_N$	$T_{IN} - T$	$(S\Delta\alpha)_V$	$(S\Delta\alpha)_N$
1.8	13.76	11.09	2	14.74	12.17
3.8	15.34	12.19	4	17.05	13.65
5.8	16.35	13.30	6	17.88	14.45
7.8	17.15	13.52	8	18.69	15.32
9.8	17.88	14.34	10	19.41	15.65
11.8	18.51	15.27	12	19.97	16.12
	$\tau = 0.20$			$\tau = 0.10$	
1.5	14.54	11.70	1	14.64	12.09
3.5	16.82	13.31	3	17.45	13.78
5.5	17.96	14.60	5	19.12	15.68
7.5	18.98	15.84	7	20.08	16.62
9.5	19.58	16.40	9	20.70	17.28
11.5	20.28	16.80	11	21.11	17.60
	Pure PHAB				
1.5	16.53	12.35			
3.5	18.35	14.70			
5.5	19.47	16.21			
7.5	20.48	17.11			
9.5	21.26	17.56			
11.5	22.02	18.02			

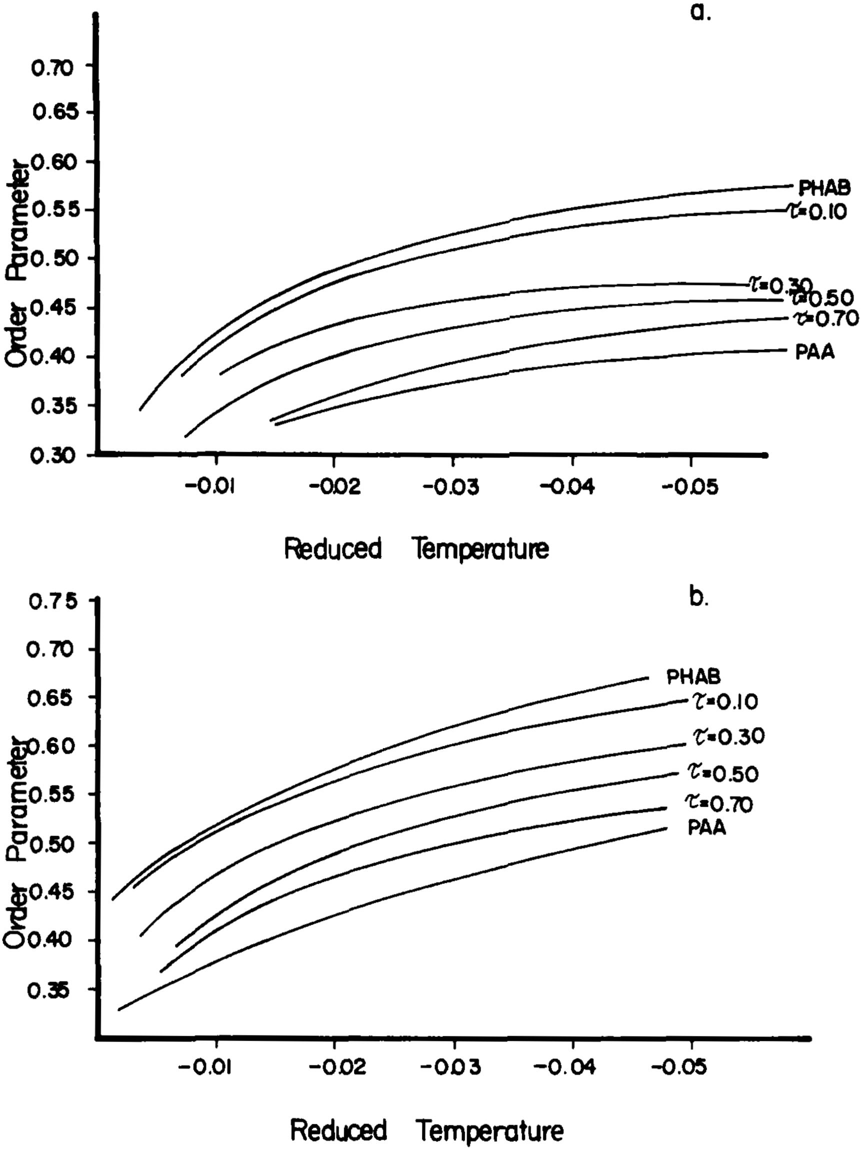


FIGURE 4 Temperature dependence of the order parameters of PAA, PHAB and several of their mixtures. 4a. Results obtained using the Neugebauer approach. 4b. Results obtained using the Vuks approach.

pattern in the polarizability anisotropies of the homologous does exist. In addition, Van Heckle *et al.*,[32] finds that the extrapolation method when applied to $\alpha_e - \alpha_0$ values calculated by the Vuks model and the Neugebauer model produces a different set of values for the two models. This is surprising since there can be only one polarizability anisotropy per compound (or mixture).

For the polarizability anisotropies of the PAA/PHAB mixtures, we shall assume that the anisotropies follow the additive rule,

$$\Delta\alpha_{\text{mixture}} = \tau\Delta\alpha_{\text{PAA}} + (1-\tau)\Delta\alpha_{\text{PHAB}} \tag{9}$$

where $\Delta\alpha_{\text{PAA}}$ and $\Delta\alpha_{\text{PHAB}}$ are the polarizability anisotropies for PAA and PHAB which are obtained in the case of PAA from the solid state data (34.7×10^{-27} cm^3) and in the case of PHAB from Karat and Madhusudana[29] method of calculating the anisotropy (35.38×10^{-24} cm^3). The assumption regarding the additive nature of the anisotropy has been shown to be true for the PAA/PAP system.[17] We believe that the polarizability anisotropies for the PAA/PHAB will deviate from the additive rule by a few percent at most (Note

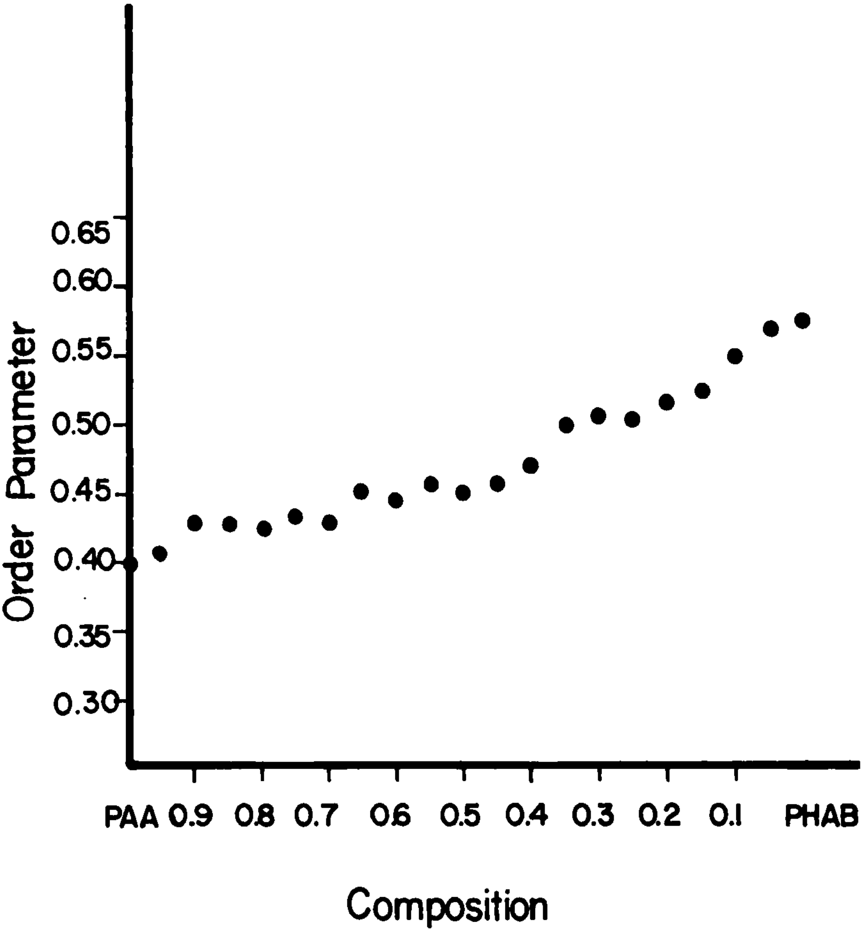


FIGURE 5 Compositional dependence of the Vuks determined order parameters at the reduced temperature $t_{\text{red}} = 0.013$. The points are the results of applying the Vuks analysis to all the data taken in the study.

the additive or nearly additive nature of the mean polarizabilities and molar volumes for this system).

We have plotted in Figure 4 the temperature dependence of the order parameters of several mixtures of *p*-azoxyanisole and *p,p*-di-*n*-hexlooxyazoxybenzene using the Neugebauer model (Figure 4a) and the Vuks model (Figure 4b). As we see, the order parameters of the mixtures decrease at all reduced temperatures as the concentration of *p*-azoxyanisole in the mixture is increased. In Figure 5, we have plotted the compositional dependence of the Vuks order parameter at the reduced temperature of $t_{\rm red} = 0.013$. It is possible to fit the points to a straight line. We conclude that the order parameters of the PAA/PHAB mixtures appear to obey the additive rule.

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