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Dielectric studies of binary liquid-crystalline mixtures

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Dielectric studies of binary liquid-crystalline mixtures

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Six binary liquid-crystalline mixtures have been studied by means of dielectric, microscopic and refractometric measurements. Induced smectic phases appear for four of them. The effective values of the components $p_\perp$ and $p_\parallel$ of the dipole moment per one molecule of the mixtures have been calculated from values of $\varepsilon_\perp$ and $\varepsilon_\parallel$. It has been established that the heterocomplexes formed in the mixtures are weak so that they do not cause any changes in the distribution of molecular charges. The observed deviations from linearity of the dielectric constants of the mixtures are caused either by dissociation of the cyanomesogen dimers or by a non-additive behaviour of the mixture density.

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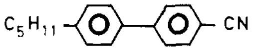
1. Introduction

Since the discovery of an induced smectic phase a variety of experiments have been performed in order to understand the nature of this phase [1–11]. In a number of cases such a phase is observed within some concentration range of the mixture when one of the components has a strongly polar cyano, nitro or isothiocyanato group, while the other has no group of this kind. On the other hand in some cases induced smectic phases appear when neither of the compounds has a strongly polar group, but both of them have an electron-donor character [12]. Until now the kind of molecular interactions and the mechanism responsible for induced smectic phase formation have not been known accurately. Park *et al.* [1, 2], Sharma *et al.* [8] and Strikanta and Madhusudana [11] suggest that an induced smectic phase appears when charge transfer complex formation takes place between the two kinds of molecules, namely the highly polar component acting as an acceptor while the other component acts as a donor. These interactions appear to lead to the formation of a layered arrangement typical of smectic phases. Oh [6] has proposed a lamellar model to account for smectic phase formation. Wacławek *et al.* [13] and Sadowska *et al.* [14] suggest that 1 : 1 complexes, which occur during induced smectic phase formation, have a complexing energy which is smaller than that for complexes usually encountered with hydrogen bonds or charge transfer. Hence, they may be caused by van der Waals forces. Griffin *et al.* [5, 15, 16] find that mixing two mesogens, one component of which has a tendency to form a bimolecular smectic phase and the other a monolayer smectic phase, leads to the induction of smectic mesomorphism.

To learn about the role of a strongly polar group, the effects of substituting a phenyl ring by a cyclohexyl one and the influence of the alkyl chain length in the process of induced smectic phase formation, six binary mixtures were investigated by means of dielectric, refractometric and microscopic measurements. The mixtures were as follows:

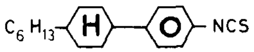
Mixture 1

4-*n*-pentyl-4′-cyanobiphenyl



5CB A

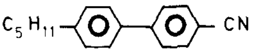
with 4-trans-4′-*n*-hexylcyclohexyl isothiocyanatobenzene



6CHBT B

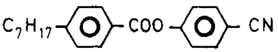
Mixture 2

4-*n*-pentyl-4′-cyanobiphenyl



5CB A

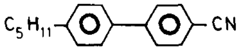
with 4′-cyanophenyl-4-*n*-heptylbenzoate



7BCP B

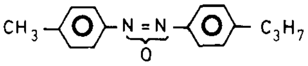
Mixture 3

4-*n*-pentyl-4′-cyanobiphenyl



5CB A

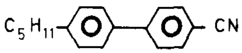
with 4-*n*-methyl-4′-propylazoxybenzene



MPAB B

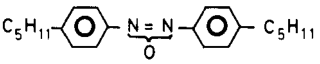
Mixture 4

4-*n*-pentyl-4′-cyanobiphenyl



5CB A

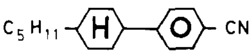
with 4,4′-dipentylazoxybenzene



DPAB B

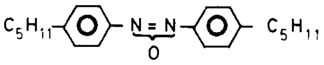
Mixture 5

4-*n*-pentyl-4′-cyanophenyl cyclohexane



PCH A

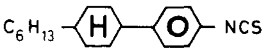
with 4,4′-dipentylazoxybenzene



DPAB B

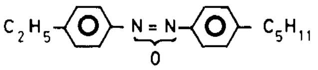
Mixture 6

4-trans-4′-*n*-hexyl-cyclohexyl isothiocyanatobenzene



6CHBT A

with 4-*n*-ethyl-4′-pentylazoxybenzene



EPAB B

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2. Experimental

The components of binary systems investigated have been synthesized and described earlier [17–20, 27, 35]. The mixtures were prepared by weighing and mixing thoroughly in their isotropic state. The phase diagrams were obtained and phase textures were characterized by using a Reichert Thermovar hot stage polarizing microscope. The isotropic n_i, ordinary n_o and extraordinary n_e refractive indices were measured with an Abbé refractometer using the yellow sodium line $\lambda = 589{\cdot}3$ nm. The density ϱ of all the pure compounds and of mixtures 5 and 6 were determined with a pycnometer. The temperature of the refractometer prism was kept constant within $\pm 0{\cdot}2$ K. The surface of the prism was rubbed to align the nematic phase.

The isotropic ε_I, perpendicular $\varepsilon_\perp$ and parallel $\varepsilon_\parallel$ components of the permittivity tensor, as well as the isotropic σ_I, perpendicular $\sigma_\perp$ and parallel $\sigma_\parallel$ components of the conductivity tensor were measured with a Tesla bridge BM 484 at 1592 Hz, and with a measuring voltage of 3 V. The samples were studied in a double plane capacitor with silver electrodes. The thicknesses of liquid crystal layers were varied from 0·2 mm to 2·0 mm, and so the estimated accuracies for the dielectric constants and conductivities were better than 2·0–0·1 per cent and 5–1 per cent, respectively. To orient the samples a magnetic field of 1 T was used. The temperature was stable to within $\pm 0{\cdot}2$ K.

3. Results

The phase diagrams of all the mixtures investigated are plotted in figures 1–5. We can see that mixtures 1 and 2 for which induced smectic phases do not appear display a negative deviation from the linear dependence of T_{NI} on composition, while mixtures 3–6 with an induced smectic phase show a positive deviation. All of the phase diagrams with an induced smectic phase are very similar in character. Each of them

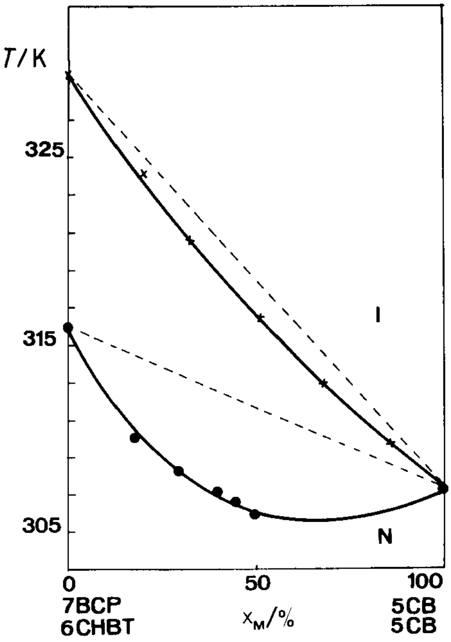

Figure 1. The phase diagrams for the 7BCP–5CB mixture (×) and the 6CHBT–5CB mixture (●).

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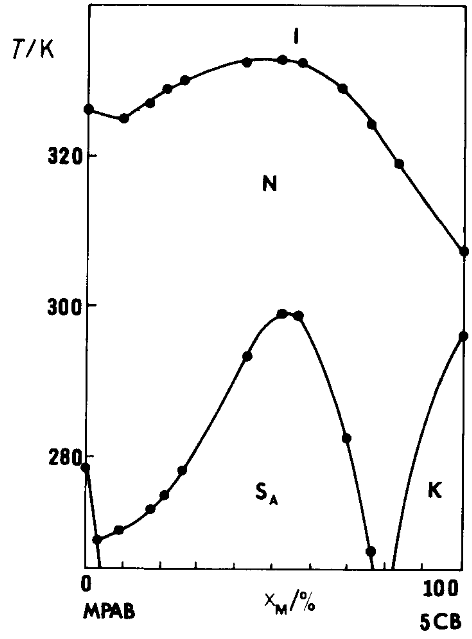

Figure 2. The phase diagram for the MPAB–5CB mixture.

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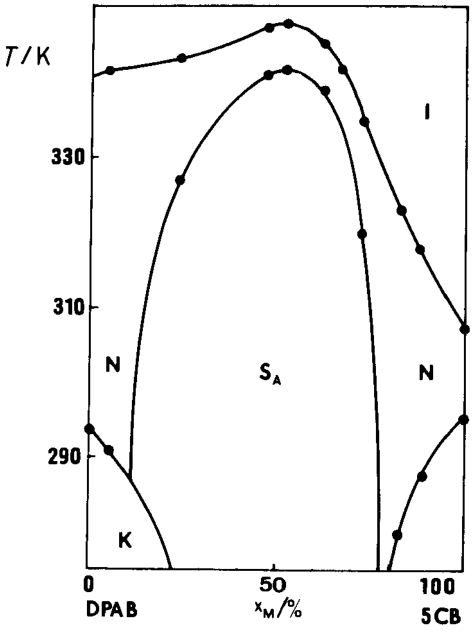

Figure 3. The phase diagram for the DPAB–5CB mixture.

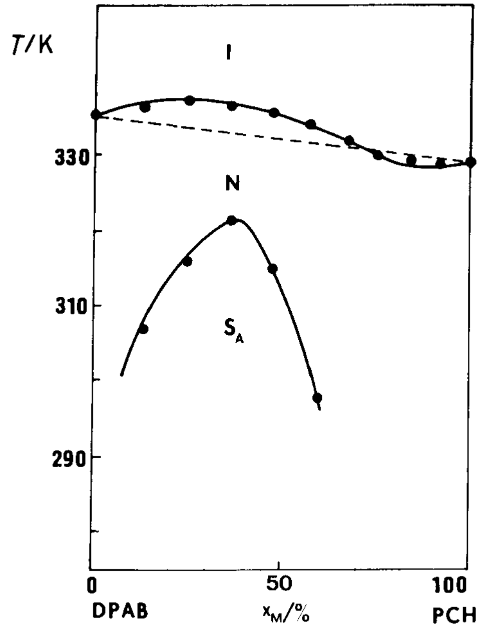

Figure 4. The phase diagram for the DPAB–PCH mixture.

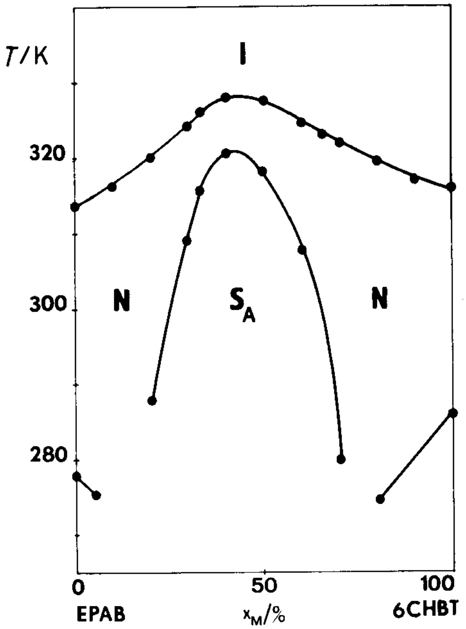

Figure 5. The phase diagram for the 6CHBT–EPAB mixture.

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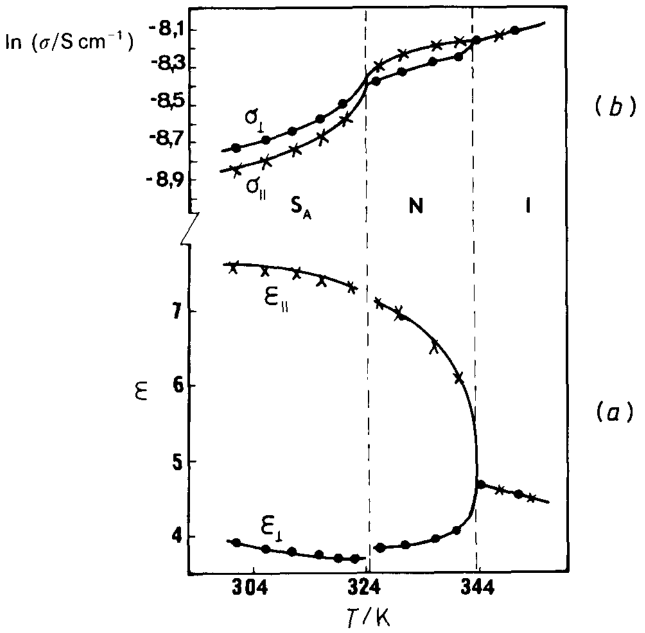

Figure 6. (*a*) The dielectric constants $\varepsilon_\parallel$ (×), $\varepsilon_\perp$ (●) for a mixture of 25 per cent PCH with 75 per cent DPAB as a function of temperature. (*b*) The principal conductivities $\sigma_\parallel$ (×) and $\sigma_\perp$ (●) as a function of temperature for the same mixture.

shows a maximum nematic–isotropic transition temperature at a concentration which also produces a maximum in the smectic–nematic transition temperature. When a phenyl ring is replaced by a cyclohexyl one (i.e. mixture 4 becomes mixture 5), the maxima in the transition temperatures are moved from a molar concentration of 50 per cent of 5CB in mixture 4 to a lower concentration of the highly polar component, namely 36 per cent of PCH in mixture 5. We see the same situation in figure 5, where the phase diagram of the 6CHBT-EPAB mixture is very similar to that of the 5CB-DPAB mixture, but the maximum deviation does not occur at the equimolar concentration, as the transition maxima are moved to a lower composition in 6CHBT. When the alkyl chain lengths are increased (i.e. mixture 3 becomes mixture 4) the tendence to form induced smectic phases in mixture 4 is much stronger than in mixture 3. Optical microscopic observations of the texture indicate that the induced phase seems to be smectic A.

All of the thermal characteristics for the perpendicular $\varepsilon_\perp$ and parallel $\varepsilon_\parallel$ components of the electric permittivities in the smectic, nematic and isotropic states, obtained for mixtures with an induced smectic phase, may be classified into two groups. The dielectric characteristics of mixtures 3, 4 and 5 belong to the first group and these characteristics of mixture 6 belong to the second. Figure 6 presents the temperature dependence of the dielectric constant for a mixture of 25 per cent PCH with 75 per cent DPAB which is typical for mixtures of the first group. It is interesting to note that $\varepsilon_\parallel$ shows an increase, but $\varepsilon_\perp$ shows a decrease at T_{S_AN} when the sample is cooled, and $\varepsilon_\perp$ increases with a decrease in the temperature within the smectic A phase. Figure 7 presents such characteristic of a mixture of 33 per cent 6CHBT with 67 per cent EPAB which is typical for mixtures of the second group. In this case both $\varepsilon_\parallel$ and $\varepsilon_\perp$ show a decrease at T_{S_AN} when the sample is cooled. The principal conductivities of these

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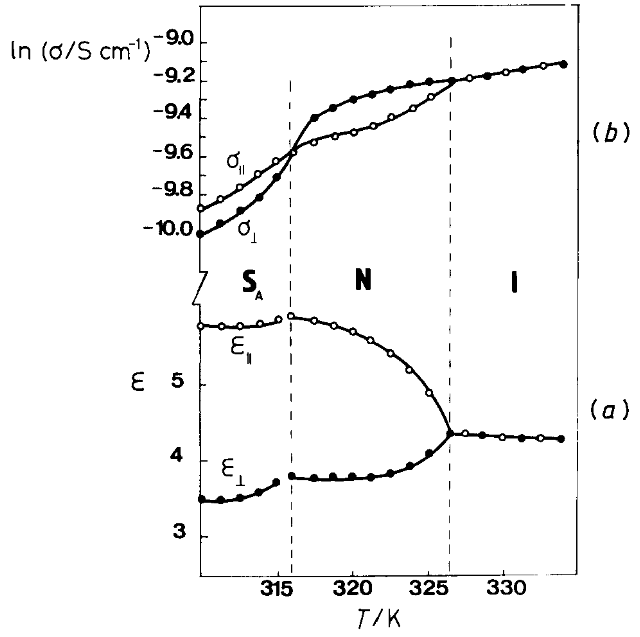

Figure 7. (*a*) The dielectric constants $\varepsilon_{\parallel}$ (○) and $\varepsilon_{\perp}$ (●) for a mixture of 33 per cent 6CHBT with 67 per cent EPAB as a function of temperature. (*b*) The principal conductivities $\sigma_{\parallel}$ (○) and $\sigma_{\perp}$ (●) for the same mixture as a function of temperature.

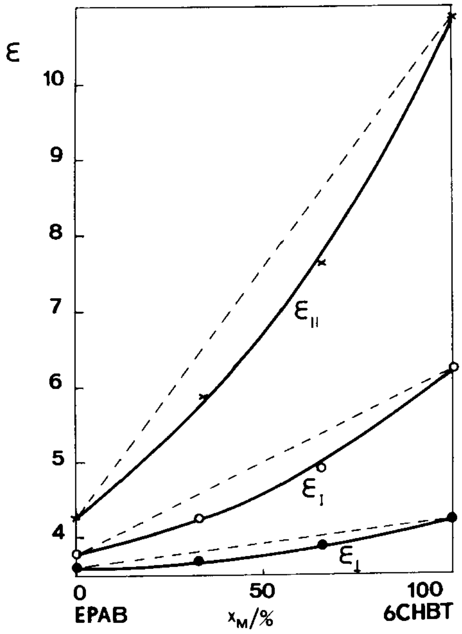

Figure 8. The concentration dependence of the dielectric constants $\varepsilon_{\parallel}$ (×), $\varepsilon_{\perp}$ (●) and ε_{I} (○) for the 6CHBT–EPAB mixture; all of the values are taken for $T = T_{\mathrm{NI}} - 10\,\mathrm{K}$.

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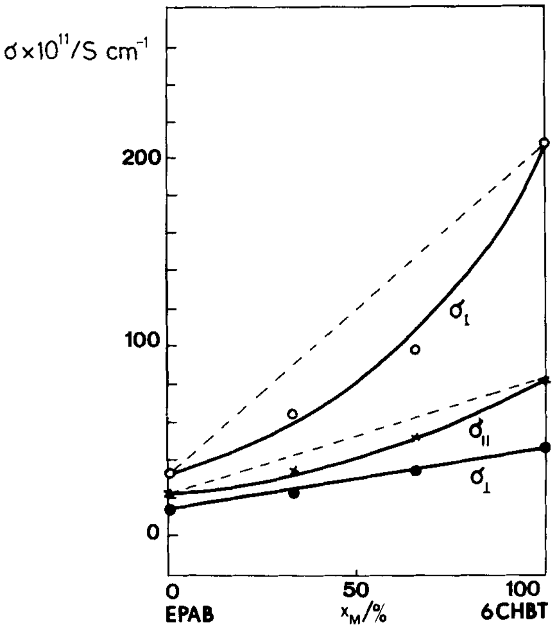

Figure 9. The concentration dependence of the conductivities $\sigma_{\parallel}$ (×), $\sigma_{\perp}$ (●) and σ_{I} (○) of the 6CHBT–EPAB mixture; all of the values are taken for $T = T_{\mathrm{NI}} - 10\,\mathrm{K}$.

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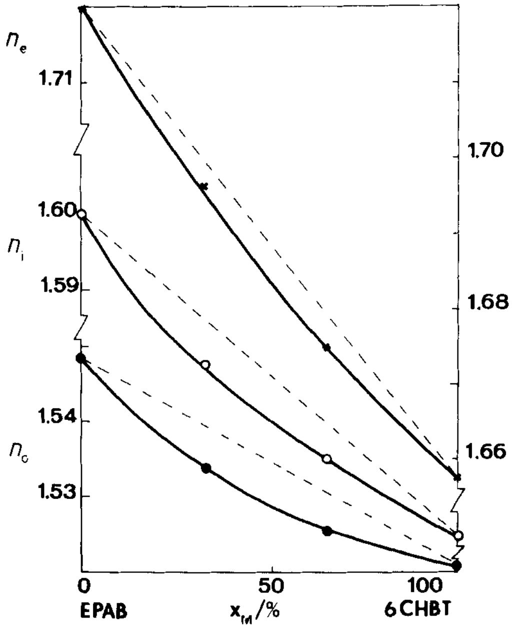

Figure 10. The concentration dependence of the refractive indices n_e (×), n_o (●) and n_i (○) for the 6CHBT–EPAB mixture; all of the values are taken for $T = T_{\mathrm{NI}} - 10\,\mathrm{K}$.

mixtures are plotted in parts (*b*) of figures 6 and 7. As in other cases [11, 21], the anisotropy of the conductivity changes its sign, becoming negative a few degrees above T_{S_AN}. The parallel component, $\sigma_\parallel$, shows a jump at T_{NS}, while the perpendicular component, $\sigma_\perp$, is continuous. This behaviour can be easily understood, because the formation of smectic layers in liquid crystals strongly disturbs the movement of ions in a direction perpendicular to smectic layers. For ions, moving along a direction parallel to the layers, the smectic state appears to be like a nematic structure.

After analysing all of the results it can be stated that mixture 1 displays a positive deviation from the linearity for $\varepsilon_\parallel$, ε_I, $\sigma_\parallel$, $\sigma_\perp$, σ_I, n_e, n_i, n_o and ϱ and no deviations for $\varepsilon_\perp$, whereas mixture 2 exhibits a positive deviation from linearity for n_e, n_i, n_o and ϱ but negative ones for $\varepsilon_\parallel$, ε_I, $\sigma_\parallel$, $\sigma_\perp$, σ_I, and in practice no deviation for $\varepsilon_\perp$ [22]. Mixtures 3, 4 and 5 are very similar in that all of the parameters investigated (versus the compositions) change. These mixtures display positive deviation from linearity for $\varepsilon_\parallel$, ε_I, n_e, n_i, n_o and ϱ, negative deviations for $\sigma_\parallel$, $\sigma_\perp$ and σ_I and no deviation for $\varepsilon_\perp$ [23]. Mixture 6 displays negative deviations for n_e, n_i, n_o, ϱ, $\varepsilon_\parallel$, $\varepsilon_\perp$, ε_I, $\sigma_\parallel$, $\sigma_\perp$ and in practice no deviations for $\sigma_\perp$ [29].

The dielectric constants $\varepsilon_\parallel$, $\varepsilon_\perp$ and ε_I for the 6CHBT-EPAB mixture are plotted versus compositions in figure 8. Principal conductivities $\sigma_\parallel$, $\sigma_\perp$ and σ_I, the refractive indices n_e, n_o and n_i for the same mixture are plotted versus the compositions in figures 9 and 10, respectively. All of the results in figures 8, 9 and 10 are taken for $T = T_{NI} \pm 10\,\text{K}$.

4. Calculations

Effective values of the components $p_\parallel$ and $p_\perp$ of the molecular dipole moments **p** of the mixture were calculated from the values of $\varepsilon_\parallel$, $\varepsilon_\perp$ and ε_I [24, 25] using the equations obtained from the work by Maier and Meier [26];

$$p_\parallel^2 = \left\{\left[\frac{3N}{\varepsilon_o(2\bar{\varepsilon}+1)}\right]^{-1}\frac{\Phi}{\bar{\varepsilon}}\left(\bar{\varepsilon}-1-\frac{2\Delta\varepsilon}{3S}\right)-\alpha_l\right\}kT\Phi,$$

$$p_\perp^2 = \left\{\left[\frac{3N}{\varepsilon_o(2\bar{\varepsilon}+1)}\right]^{-1}\frac{\Phi}{\bar{\varepsilon}}\left(\bar{\varepsilon}-1-\frac{\Delta\varepsilon}{3S}\right)-\alpha_t\right\}kT\Phi,$$

where

$$\Phi = \left[1-\frac{3N}{\varepsilon_o(2\bar{\varepsilon}+1)}\frac{2\bar{\alpha}(\bar{\varepsilon}-1)}{9}\right],$$

$$\bar{\varepsilon} = \frac{\varepsilon_\parallel+2\varepsilon_\perp}{3},$$

$$\bar{\alpha} = \frac{\alpha_l+\alpha_t}{3}.$$

Here N is the number of molecules in 1 m^3 of the mixture, α_l is the longitudinal and α_t is the transverse molecular polarizability. In these calculations the molecular parameters, such as the transverse and longitudinal polarizabilities, as well as temperature dependence of the nematic order parameter $S(T)$ for the pure compounds of all the mixtures, were calculated from their refractive indices $n_o(T)$, $n_e(T)$, $n_i(T)$ and densities. In these cases Neugebauer's equations combined with the Haller

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extrapolation procedure were used. For the mixture of A and B compounds the polarizabilities α'_l and α'_t were calculated from

$$\alpha'_l = \alpha_l^A N_A + \alpha_l^B N_B,$$

$$\alpha'_t = \alpha_t^A N_A + \alpha_t^B N_B.$$

where N_A and N_B are the numbers of molecules of A and B in 1 m^3 of the mixture. N_A and N_B were calculated from the Lorentz–Lorenz equation

$$N_A = 3\varepsilon_o \left(\frac{n^2 - 1}{n^2 + 2}\right)\left(\alpha_A + \alpha_B \frac{M_A}{M_B}\frac{1 - X_W}{X_W}\right)^{-1},$$

and

$$N_B = \frac{1 - X_W}{X_W}\frac{M_A}{M_B} N_A,$$

with

$$N = N_A + N_B,$$

where X_W is the weight concentration of compound A and M_A and M_B are the molar weights. The mean polarizabilities are

$$\alpha_A = \frac{\alpha_l^A + 2\alpha_t^A}{3},$$

$$\alpha_B = \frac{\alpha_l^B + 2\alpha_t^B}{3},$$

and

$$n^2 = \frac{n_e^2 + 2n_o^2}{3}$$

is the mean square of the refractive index for the mixture.

The order parameters, S, for the mixtures were calculated from the Neugebauer–Maier–Saupe equation

$$S = \frac{3}{\alpha_l - \alpha_t}\frac{(R\alpha - 3) + \{[3(R\alpha + 1)]^2 - 48\, R\alpha\}^{1/2}}{4R},$$

where

$$R = \frac{N}{3\varepsilon_o}\left(\frac{n_e^2 + 2}{n_e^2 - 1} + 2\frac{n_o^2 + 2}{n_o^2 - 1}\right)$$

and

$$\alpha = \frac{\alpha'_l + 2\alpha'_t}{3}.$$

The results of the calculations are summarized in tables 1–6.

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Table 1. Characteristics of mixture 1; all of the values taken for $T = T_{\mathrm{NI}} - 10\,\mathrm{K}$.

	6CHBT							5CB
X_{M}/per cent	0	8·1	17·8	29·6	39·2	45·4	50·6	100
T/K	306·1	303·0	300·1	298·5	297·3	296·7	295·9	297·4
$\varepsilon_{\perp}$	4·25	4·35	4·50	5·00	5·20	5·35	5·50	6·56
$\varepsilon_{\parallel}$	10·90	11·30	12·40	14·15	15·15	15·85	16·25	18·80
$p_{\perp} \times 10^{30}/\mathrm{C\,m}$	3·00	2·82	2·30	2·59	2·21	1·77	1·46	0·26
$p_{\parallel} \times 10^{30}/\mathrm{C\,m}$	8·41	8·55	8·98	9·54	9·86	10·14	10·36	10·76
$p_{\mathrm{c}} \times 10^{30}/\mathrm{C\,m}$	8·90	9·00	9·26	9·88	10·10	10·29	10·47	10·76

Table 2. Characteristics of mixture 2; all of the values are taken for $T = T_{\mathrm{NI}} - 10\,\mathrm{K}$.

	7BCP				5CB
X_{M}/ per cent	0	40·1	58·5	73·2	100
T/K	319·8	300·5	306·5	303·6	297·4
$\varepsilon_{\perp}$	9·0	8·0	7·3	7·2	6·56
$\varepsilon_{\parallel}$	24·3	21·0	19·7	18·80	18·80
$p_{\perp} \times 10^{30}/\mathrm{C\,m}$	5·1	3·95	3·01	2·95	0·26
$p_{\parallel} \times 10^{30}/\mathrm{C\,m}$	14·7	12·6	11·8	11·19	10·76
$p_{\mathrm{c}} \times 10^{30}/\mathrm{C\,m}$	15·44	13·6	12·10	11·63	10·76

Table 3. Characteristics of mixture 3; all of the values are taken for $T = T_{\mathrm{NI}} - 10\,\mathrm{K}$.

	MPAB						5CB
X_{M}/ per cent	0	9·2	21·3	42·5	51·5	83.3	100
T/K	316·0	315·0	318·5	321·5	322·5	309·0	297·4
$\varepsilon_{\perp}$	4·15	4·4	4·7	5·1	5·4	6·1	6·56
$\varepsilon_{\parallel}$	4·65	6·9	9·8	12·2	13·5	17·0	18·80
$p_{\parallel} \times 10^{30}/\mathrm{C\,m}$	3·40	5·40	7·17	8·41	9·03	10·29	10·76
$p_{\perp} \times 10^{30}/\mathrm{C\,m}$	4·41	4·01	3·43	2·94	2·72	1·40	0·26
$p_{\mathrm{c}} \times 10^{30}/\mathrm{C\,m}$	5·50	6·72	7·92	8·91	9·43	10·39	10·76

Table 4. Characteristics of mixture 4; all of the values are taken for $T = T_{\mathrm{NI}} - 10\,\mathrm{K}$.

	DPAB					5CB
X_{M}/ per cent	0	5·4	24·2	67·1	83·6	100
T/K	331·0	332·0	333·5	332·5	313·1	297·4
$\varepsilon_{\perp}$	3·55	3·70	4·2	5·4	5·9	6·56
$\varepsilon_{\parallel}$	3·80	4·76	7·5	14·0	16·3	18·80
$p_{\parallel} \times 10^{30}/\mathrm{C\,m}$	2·52	4·37	7·07	10·19	10·51	10·76
$p_{\perp} \times 10^{30}/\mathrm{C\,m}$	5·00	4·69	4·02	2·02	1·14	0·26
$p_{\mathrm{c}} \times 10^{30}/\mathrm{C\,m}$	5·60	6·41	8·13	10·39	10·58	10·76

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Table 5. Characteristics of mixture 5; all of the values are taken for $T = T_{NI} - 10$ K.

	DPAB			PCH
X_M / per cent	0	25·0	66·7	100
T/K	331·0	333·5	325·0	318·0
$\varepsilon_\perp$	3·55	3·88	4·61	5·01
$\varepsilon_\parallel$	3·80	6·72	9·90	11·60
$p_\parallel \times 10^{30}$/C m	2·52	6·49	8·08	8·67
$p_\perp \times 10^{30}$/C m	5·00	3·81	3·90	4·13
$p_c \times 10^{30}$/C m	5·60	7·52	8·97	9·60

Table 6. Characteristics of mixture 6; all of the values are taken for $T = T_{NI} - 10$ K.

	EPAB			6CHBT
X_M / per cent	0	32·6	64·6	100
T/K	304·1	316·5	313·6	306·1
$\varepsilon_\perp$	3·68	3·80	3·90	4·25
$\varepsilon_\parallel$	4·30	5·90	7·55	10·90
$p_\parallel \times 10^{30}$/C m	3·11	5·27	6·65	8·41
$p_\perp \times 10^{30}$/C m	4·05	3·72	3·31	3·00
$p_c \times 10^{30}$/C m	5·11	6·45	7·43	8·90

5. Discussion

When the dipole moment associated with the effective component values $p_\parallel$ and $p_\perp$ have to be calculated from the electric permittivity (cf. the equations in §4) the results of the calculations, at a temperature of $(T - T_{NI})$ is -10 K, do not depend significantly on the order parameters S. For example, with EPAB a change in S from 0·513 to 0·713 causes a change in $p_\parallel$ (from $3{\cdot}28 \times 10^{-30}$ C m to $3{\cdot}00 \times 10^{-30}$ C m) and $p_\perp$ (from $3{\cdot}95 \times 10^{-30}$ C m to $4{\cdot}14 \times 10^{-30}$ C m) smaller than 10 per cent and the total moment p_c remains unchanged, because the total moment is independent of S. The total moment p_I calculated from the isotropic phase is, of course, independent of S. Clearly every component of a mixture has its own order parameter, but the difference in component order parameters should not affect the calculations to any significant extent, as follows from the example of EPAB. Taking these observations into consideration it has been decided to describe the mixture by a single order parameter S as calculated from the Neugebauer–Maier–Saupe equation, because this parameter for $T - T_{NI} = -10$ K is not very important for this calculation. The most important factors in the calculations of $p_\parallel$ and $p_\perp$ are the parameters $\varepsilon_\parallel$, $\varepsilon_\perp$, ε_I, n_o, n_e and n_I which are determined directly by measurement.

The effective dipole moments, particularly the parallel components, are much lower than those for the isolated molecules not only for the pure cyanomesogenes, but also for their solutions. The effect decreases with increasing temperature. This can be regarded as evidence that antiparallel association occurs in all these cases. On the other hand, this effect does not appear in pure 6CHBT [27] and dialkylazoxy compounds [28].

Positive deviation from the linearity of the $p_\parallel$ component of the mean dipole moment (dipole moment per one molecule of the binary mixture) in the 6CHBT–5CB mixture (see figure 11) shows that antiparallel complexes $(5CB)_2$ vanish as the concentration of 6CHBT increases. The negative deviation from linearity of the same

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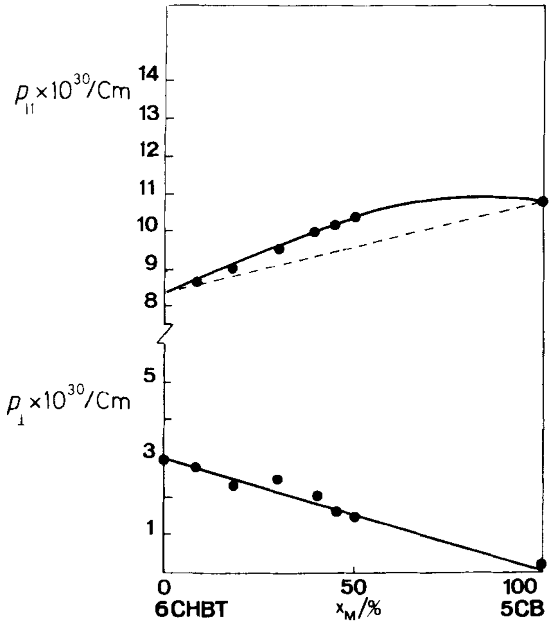

Figure 11. The concentration dependence of the effective values of the parallel $p_{\parallel}$ and perpendicular $p_{\perp}$ components of the molecular dipole moment for the 6CHBT–5CB mixture. All of the values are taken for $T = T_{NI} - 10$ K.

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parameter for the 7BCP–5CB mixture suggests that antiparallel complex formation takes place between molecules of 5CB and 7BCP.

These conclusions are also supported by the concentration dependence of the conductivities, i.e. $\sigma_{\parallel}$, $\sigma_{\perp}$ and σ_{I}. The positive deviation of the conductivities in the 6CHBT–5CB mixtures could be interpreted as an effect of increased mobility of the charge carriers caused by a decrease in the concentration of dimers. Consistently, the opposite behaviour of the conductivities in the 7BCP–5CB mixture could be caused by an increase in the concentration of heterocomplexes.

The positive deviations from linearity of the parallel component of the mean dipole moment of mixtures 3, 4 and 5, with an induced smectic phase (see figure 12), can be understood in terms of an increase in the number of strongly polar–weakly polar molecular pairs while the antiparallel complexes of $(5CB)_2$ or $(PCH)_2$ vanish.

The negative deviation of $p_{\perp}$ for the DPAB–PCH mixture seems to indicate new heterocomplex formation by DPAB and PCH molecules with antiparallel correlation of the dipole moments. The negative deviations of the conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$ of mixtures 3, 4 and 5 are consistent with this supposition. However, it is very difficult in this case (when the mixtures contain cyanomesogens, the mesophases of which in the pure state are built of single molecules mixtures and dimers of antiparallel structure [27–32]) to decide to what extent the changes, observed in the mean dipole moments of the mixture molecules, are induced by the formation of new heterocomplexes and to what extent by dissociation of cyanomesogen dimers.

This problem was solved by studies of the EPAB–6CHBT mixture with an induced smectic phase formed from non-dimerizing compounds [27, 28]. Assuming that charge transfer complexes or complexes with antiparallel dipole moments or other strong complexes are formed in the EPAB–6CHBT mixtures, it is clear that some

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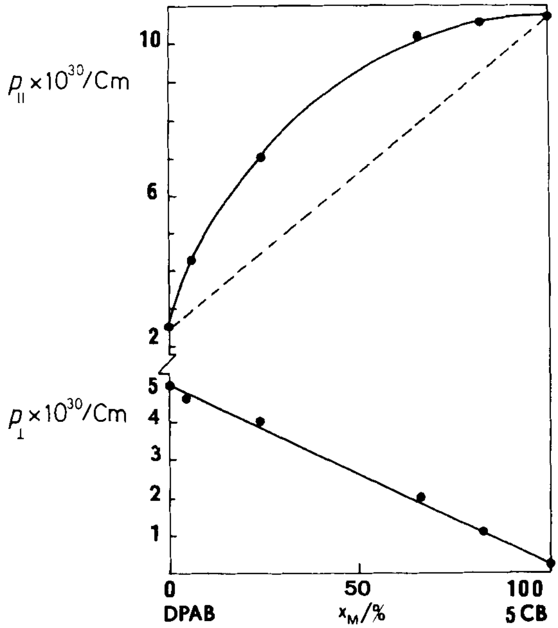

Figure 12. The concentration dependence of the effective values of the parallel $p_{\parallel}$ and perpendicular $p_{\perp}$ components of the molecular dipole moment for the DPA–5CB mixture. All of the values are taken for $T = T_{NI} - 10\,K$.

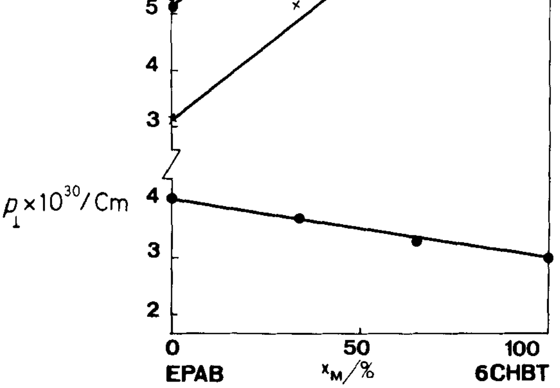

Figure 13. The concentration dependence of the effective values of the parallel $p_{\parallel}$ (×) and perpendicular $p_{\perp}$ (●) components of the molecular dipole moment; the total dipole moment: p_c (●), calculated from nematic phase; p_I (○), calculated from nematic phase for the EPAB–6CHBT mixture. All of the values are taken for $T = T_{NI} - 10\,K$.

extra changes of the dielectric constants of these mixtures should occur. Some negative deviations from linearity for $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and ε_{I} had been observed, but after our calculations we notice that the EPAB–6CHBT mixture presents no deviation from linearity for $p_{\parallel}$, $p_{\perp}$ and p_{c} (calculated from the nematic phase) as well as for p_{I} (calculated from the isotropic phase). The changes in the linear character of the mean dipole moments per one molecule (see figure 13) can be regarded as evidence that neither complex with antiparallel correlation of the dipole moments, nor charge transfer, nor any other strong complexes are being formed. Deviations from additivity for the dielectric constants of the EPAB–6CHBT mixture are caused by a non-additive behaviour of the mixture density only. The negative deviation from linearity of $\sigma_{\parallel}$ and σ_{I} for the EPAB–6CHBT mixture can be interpreted as an effect of the reduced mobility of the charge carriers caused by the appearance of new heterocomplexes. However to be in accord with that which is indicated by the analysis of the calculations, these complexes have to be so weak, that they do not cause any changes in charge distribution of the constituent molecues, at least by dielectric measurements. These suggestions about the weak bonding of the heterocomplex molecules in mixtures displaying an induced smectic phase are in complete agreement with other work [33, 34].

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