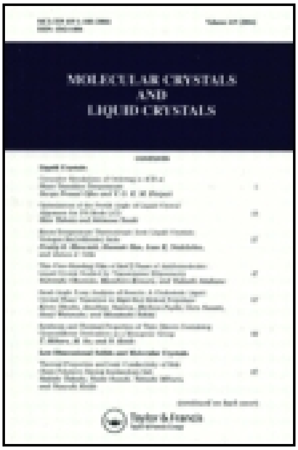

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Effect of the Polar Substituents on the Optical Parameters of Binary Mixtures of 4-Substituted-phenyl-4-hexyloxybenzoates

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Effect of the Polar Substituents on the Optical Parameters of Binary Mixtures of 4-Substituted-phenyl-4-hexyloxybenzoates

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The refractive indices as a function of temperature were measured for the individual components of 4-substituted-phenyl-4-hexyloxybenzoates as well as their binary mixtures. In these components one terminal substitution is $C_6H_{13}O$ *and the other terminal is either the methoxy (*CH_3O*), methyl (*CH_3*), cyano (*CN*), or nitro (*NO_2*) group. Refractive index data were used to estimate the molecular order parameter (*S*) and the length-to-breadth ratio (k) for all samples investigated. The entropy change (*Δs_c*) at the nematic–isotropic transition temperatures (*T_c*) was also calculated from differential scanning calorimetry data (*DSC*). The results were thoroughly analyzed and compared.*

Keywords: binary mixtures; index of refraction; liquid crystals; optical properties

1. INTRODUCTION

Efforts are always made to improve the gain of liquid crystal devices, especially liquid crystal displays and switches. This necessitates, on one hand, the extension of the thermal stability of a liquid-crystalline mesophase and/or the mesomorphic temperature range, and on the other hand, it necessitates the increase of the degree of ordering (anisotropy) of their molecules within such a phase.

With respect to the first aim, some trends were developed to establish more thermally stable mesophases. One of these trends is the study of the effect of various terminal substituents and linking central groups, within the molecules of liquid-crystalline compounds, on their mesophase thermal behavior [1–3]. Another alternative trend is to mix two or more liquid-crystalline compounds to get binary, ternary, or

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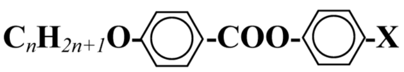

I*n*(*a-d*)

SCHEME 1 $a, = \mathbf{X} = CH_3O$; $b, \mathbf{X} = CH_3$; $c, \mathbf{X} = CN$; $d, \mathbf{X} = NO_2, n = 6-16$ carbon atoms.

multicomponent mixtures, which helps in promoting the thermal stability of their mesophases [4–7]. In this respect, a more recent and systematic study has been carried out [8] using ester compounds Scheme 1.

Although the studies [1–8] of such effects have effectively thrown light on the thermal stability of the mesophases, they feel nothing about these effects on the degree of molecular ordering within these phases.

The effect of the chain length, n, of the alkoxy group as well as the polar group, X, on the degree of ordering has been investigated by the author [9] using single components of the type I(*na–d*), mentioned previously. Many other studies [10–15] using birefringence data were done concerning binary mixtures bearing only different chain lengths while the polar terminal group was mostly fixed. In these studies, the order parameter was found to be sensitive at concentration near the eutectic composition, recording a value that is higher than those of the mixed single components.

The objective of the present work is to investigate the effect of admixing two components with different polar groups, while keeping their chain length fixed, on the enhancement of the order parameter in mixed systems, especially at concentrations near that at the eutectic mixture. For this purpose, systems of the type I6(*a–d*), of similar electron-releasing or electron-withdrawing (I6*a*/I6*b* or I6*c*/I6*d*) or different electron-releasing/electron-withdrawing (I6*a*/I6*b*) substituted molecules,which form only the nematic mesophase, seemed to be suitable. Differences in the mutual conjugation between the terminal polar substituent, X, and the remainder of the molecule will have different effects on the final polarity of the individual ester molecules and, consequently, on their optical properties.

2. EXPERIMENTAL

2.1. Materials

The pure components I6(*a–d*)used in the preparation of the investigated mixtures were kindly supplied by M. M. Naoum, Chemistry

Department, Faculty of Science, University of Cairo. The method of preparation of the compounds was described elsewhere [16].

2.2. Preparation of the Mixtures

Binary mixtures, of each of the systems I*6a*/I*6b*, I*6a*/I*6c*, or I*6c*/I*6d* that cover the whole range of composition, were prepared by mixing the individual components at a temperature higher than their clearing temperatures. Mixtures of any two components in known proportions were prepared by weighing the appropriate amounts of components, intimate mixing, and then cooling in air to room temperature.

2.3. Refractive Index Measurements

Measurements of the refractive index as a function of temperature were performed using an Abbe 60 refractometer attached to an ultra-thermostat. The respective accuracy in refractive index and temperature measurements were ±0.0005 and ±0.2°C. The investigated samples were used without any external aligning aids.

The refractive indices were measured during cooling from the isotropic phase into the nematic one, because all the individual components exhibit monotropic nematic phase except I*6c*, which exhibits enantiotropic nematic phase.

Although the ordinary refractive index, n_o, in the nematic phase has been directly measured the extraordinary refractive index, n_e, was too high to be measured by the available refractometer. Thus, it was calculated from the relation

$$n^2 = \left(\frac{1}{3}\right)\left(n_e^2 + 2n_o^2\right) \qquad (1)$$

where n is the extrapolated average refractive index (within the nematic phase) as obtained by the extrapolation of n_{iso} to lower temperatures.

3. CALCULATIONS

3.1. The Order Parameter

Different methods are generally used to evaluate the order parameter, S. These are the methods of Neugebauer [17], Saupe and Maier [18], Palffy-Mahoray *et al.* [19], and Vuks [20]. Vuks' method is based on the isotropic internal field model, whereas the other methods are based on the anisotropic internal field model. However, the S-values calculated by all these methods were found to be almost the same [21,22].

In the present work, the S-values for the investigated mixtures have been evaluated using the isotropic internal field model of Vuks [20]. In this model, S is given by

$$S = \frac{\alpha}{\alpha_{II} - \alpha_{\perp}} \times \left[\frac{n_e^2 - n_o^2}{n^2 - 1}\right] \tag{2}$$

where α is the mean polarizability, and α_{II} and $\alpha_{\perp}$ are the principal polarizabilities parallel and perpendicular to the optic axis. To simplify Eq. (2), let

$$\delta = \frac{1}{3}\left(\frac{\alpha_{II} - \alpha_{\perp}}{\alpha}\right). \tag{3}$$

Multiplying Eq. (2) by Eq. (3), one gets

$$\delta.S = \frac{1}{3}\left(\frac{n_e^2 - n_o^2}{n^2 - 1}\right). \tag{4}$$

Using the refractive index data, δ.S could be calculated. To get δ, the Haller extrapolation method [23] of extrapolating to zero temperature a linear fit to the plots ln(δ.S) and ln($1 - T/T_c$) was used. The intersection at zero temperature, *i.e.*, at $S = 1$, gave the δ-value. The order parameter S could, thus, be evaluated at different temperatures.

3.2. The Length-to-Breadth Ratio

Palffy-Mahoray *et al.* [19] have found that the local field η_{zz} for molecules in the nematic phase is nearly proportional to the order parameter S with a slope $= [-4(k - 1)]/[5(k + 2)]$, where k is the length-to-breadth ratio. The local field, η_{zz}, as deduced by Palffy-Mahoray *et al.* [19], is adapted to give

$$\eta_{zz} = \frac{1}{3}\left[\frac{n^2 + 2}{(n^2 - 1)(1 + 2\delta S)} - \left(\frac{n_e^2 + 2}{n_e^2 - 1}\right)\right]. \tag{5}$$

3.3. The Change in Entropy

The entropy change, Δs_c, due to transition from the nematic phase to the isotropic one, is calculated from the relation

$$\Delta s_c = \frac{\Delta H_c}{T_c} \tag{6}$$

where ΔH_c is the heat change, accompanying the transformation from the nematic to the isotropic phase, and T_c the clearing temperature (in Kelvins). The values of ΔH_c and T_c (Tables 1–3) for the different

TABLE 1 System I*6a*/I*6b*

Mol % (I*6b*)	00.00	25.23	43.57	62.44	79.77	89.07	100.00
T_c°C	74.5	70.8	64.3	60.1	54.2	52.0	—
ΔH_c (KJ/mol)	0.50	0.62	0.66	0.61	0.50	—	—

TABLE 2 System I*6a*/I*6c*

Mol % (I*6c*)	00.00	22.49	40.37	59.66	77.02	100.0
T_c°C	74.5	72.7	74.4	76.4	78.4	80.5
ΔH_c (KJ/mol)	0.50	0.63	0.79	0.73	0.72	0.63

TABLE 3 System I*6c*/I*6d*

Mol % (I*6d*)	00.00	23.21	39.84	57.98	80.50	100.00
T_c°C	80.5	77.5	70.8	66.4	61.8	56.1
ΔH_c (KJ/mol)	0.63	0.14	0.12	0.04	0.11	0.19

samples are compiled from differential scanning calorimetry (DSC) data in Ref. [11].

4. RESULTS AND DISCUSSION

The refractive indices were measured for pure and mixed compounds at various temperatures for the three systems investigated, and the data are plotted in Fig. 1a–c. The obtained graphs were used to select a temperature at which all compositions of each mixed system exist safely within the considered phase to compare the different compositions in each system with each other. Clearing temperature values, T_c (in°C), for pure and mixed systems, abstracted from Fig. 1a–c, were compared with those found in [11] and collected in Tables 1–3. It may be noticed from the tables that, for the system of electronically dissimilar substituted components I*6a*/I*6c* (Fig. 1b), T_c is reduced only by 6 degrees, *i.e.*, from 80.5°C for (100 mol.% I*6c*) to 74.5°C for (100 mol.%I*6a*), which makes the comparison possible. Conversely, for the systems of electronically similar substituted components I*6a*/I*6b* (Fig. 1a), and I*6c*/I*6d* (Fig. 1c), as the concentration of the component I*6b* in the first or I*6d* in the second system is increased, the corresponding T_c of the mixture is remarkably reduced. For example, T_c is reduced from 74.5°C for (100 mol% I*6a*) to 52°C for (89.07 mol% I*6b*) and from 80.5°C for (100 mol% I*6c*) to 55°C for (100 mol% I*6d*),

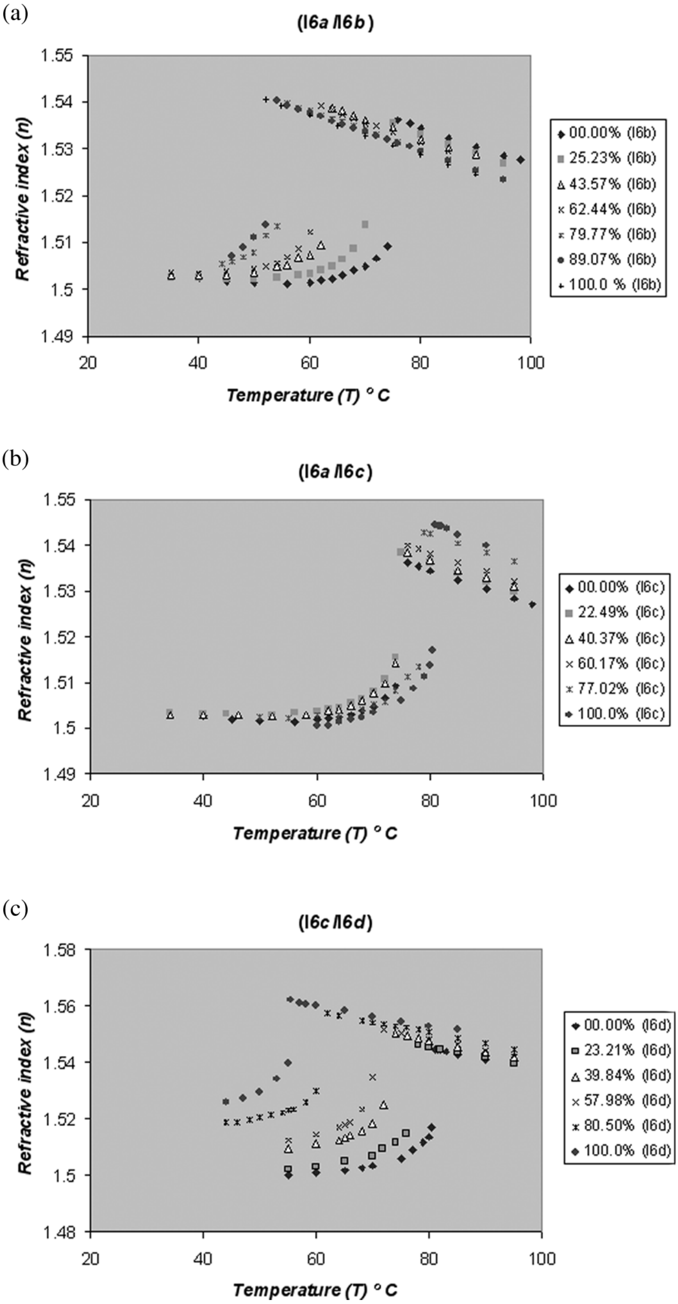

FIGURE 1 Temperature dependence of the measured refractive index for various compositions of the binary systems, (a) I*6a*/I*6b*, (b) I*6a*/I*6c*, (c) I*6c*/I*6d*.

respectively. This makes the interpolation at a common temperature for all systems, for sake of comparison, impossible. For this reason, in nematic phase a reduced temperature T' ($=T_c - T$) is used for comparison rather than a normal temperature T.

4.1. Isotropic Phase, Refractive Index

To investigate the effect of the polar terminal substituents, X, on the refractive index in the isotropic phase, n_{iso}, the composition dependence of n_{iso}, at 85°C, for the three investigated systems is plotted in Fig. 2. As seen from the figure, n_{iso} is found to vary more or less linearly with composition from its value of one component to the value of the other one in the mixture. These findings may be taken as evidence for the compatibility of all these molecules in their isotropic phase. The dependence of n_{iso} values on the substituents CH_3O, CH_3, CN, or NO_2 in the pure components is argued to the variation of the electronic nature of these substituents. To clarify this, n_{iso} at 85°C for the individual components is plotted as a function of Hammett's substituent constants, σ, in Fig. 3. The values of σ used in such correlation were taken from the compilation of Ritchie and Sagar [24]. The data show that n_{iso} increases as the magnitude of σ increases and it seems to have its minimum value at $\sigma = 0$, *i.e.*, for the unsubstituted analogue (X = H).

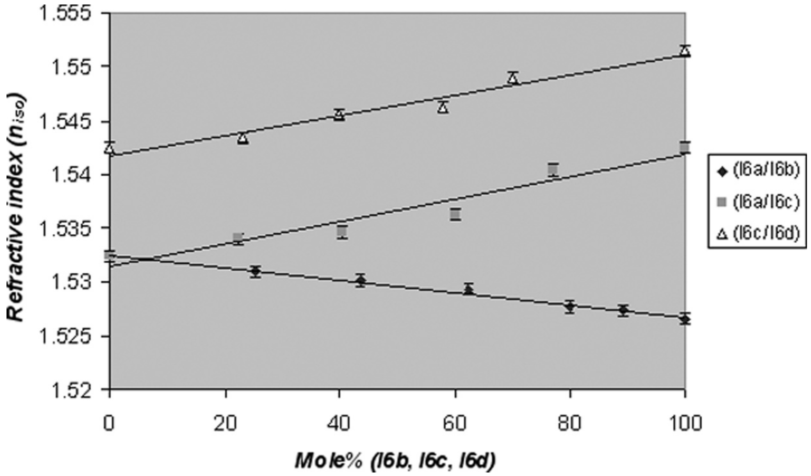

FIGURE 2 Composition dependence of the refractive index in the isotropic phase at 85°C for various systems I6*a*/I6*b*, I6*a*/I6*c*, and I6*c*/I6*d*.

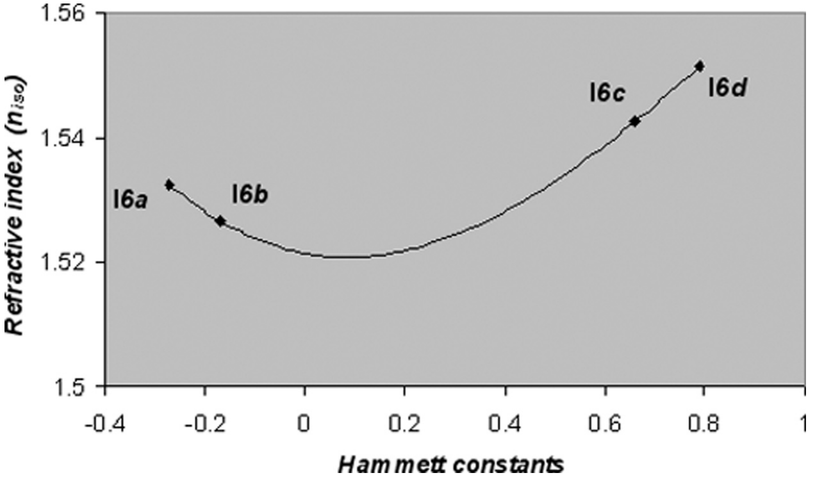

FIGURE 3 Hammet's correlations of the refractive index, n_{iso}, in the isotropic phase at 85°C for variously substituted derivatives I*6*(*a–d*).

4.2. Nematic Phase

4.2.1. Binary Mixtures of Electron-Releasing Substituted Compounds (I6a/I6b)

Composition Dependence of the Order Parameter. Substituting for the refractive index data at different temperatures (T) in Eq. (4) and applying the Haller extrapolation method [21], the order parameter (S) could be evaluated and plotted in Fig. 4 against the reduced temperature ($T' = T_c - T$) for various samples investigated. The figure is used to extract the S-values at different compositions for the system (I*6a*/I*6b*) at any common reduced temperature, ($T' = 6°C$) for instance, at which all the considered mixtures exist, safely, in the nematic phase. These data are presented as a function of composition in Fig. 5. It is seen from the figure that S passes through a minimum value nearby the eutectic composition (43.57 mol% I*6b*).

Composition Dependence of the Entropy Change at the Clearing Temperature. From the DSC data, apart from the refractive index data, the entropy change Δs_c at the nematic–isotropic transition temperature (T_c) is calculated and plotted as a function of composition (Fig. 6.) It is seen from the figure that Δs_c increases by the addition of one component to the other, passing a maximum (*i.e.*, minimum ordering) at the eutectic composition. This is in accordance with the composition dependence of S that is shown in the previous section.

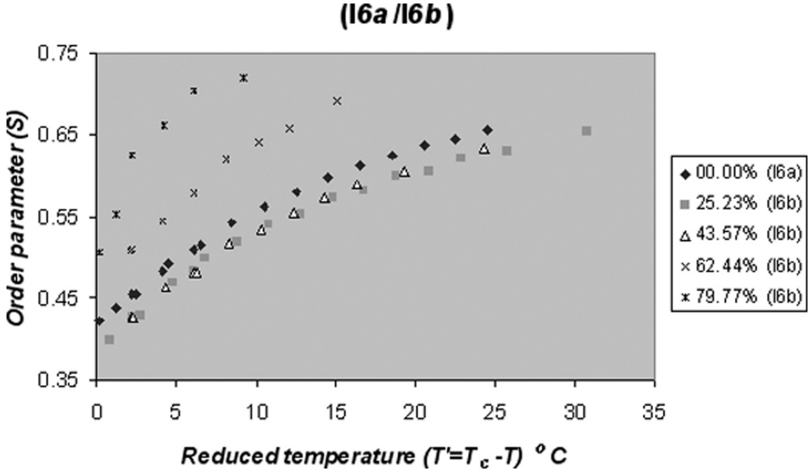

FIGURE 4 Reduced temperature T′ dependence of the order parameter, S, for various compositions of the binary system I*6a*/I*6b*.

Composition Dependence of the Length-to-Breadth Ratio. The dependence of k on the composition is represented graphically in Fig. 7. From the figure, k is found to pass through a maximum value at the eutectic composition. An increase in k may generally be ascribed

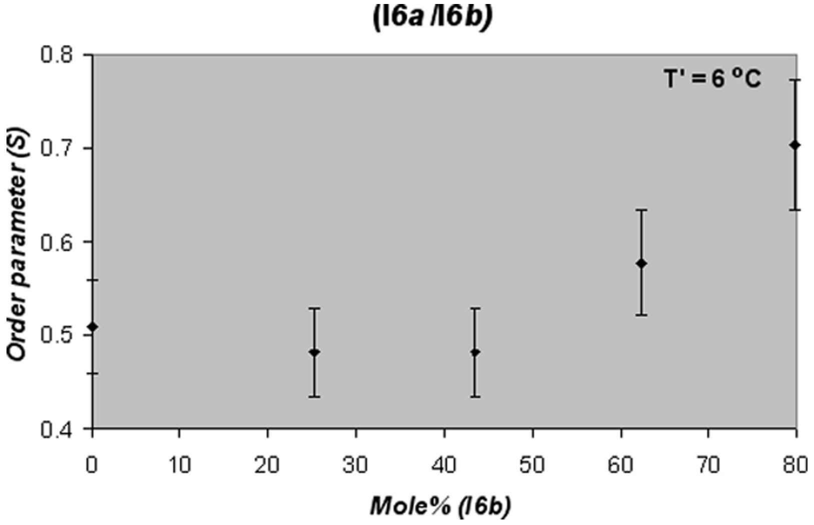

FIGURE 5 Composition dependence of the order parameter, S, for the binary system I*6a*/I*6b* at T′ = 6°C.

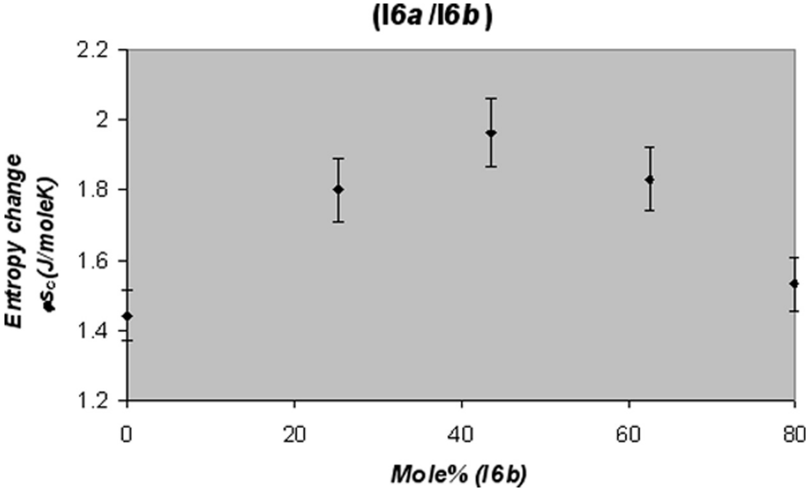

FIGURE 6 Composition dependence of the entropy change, Δs_c, at the nematic-isotropic transition temperature for the binary system I*6a*/I*6b*.

either to an increase in the length of molecules upon mixing or to a decrease in breadth. The first possibility can never be realized. Thus, the second possibility is the only probable. This can be explained in terms of the formation of swarms of molecules rather than their

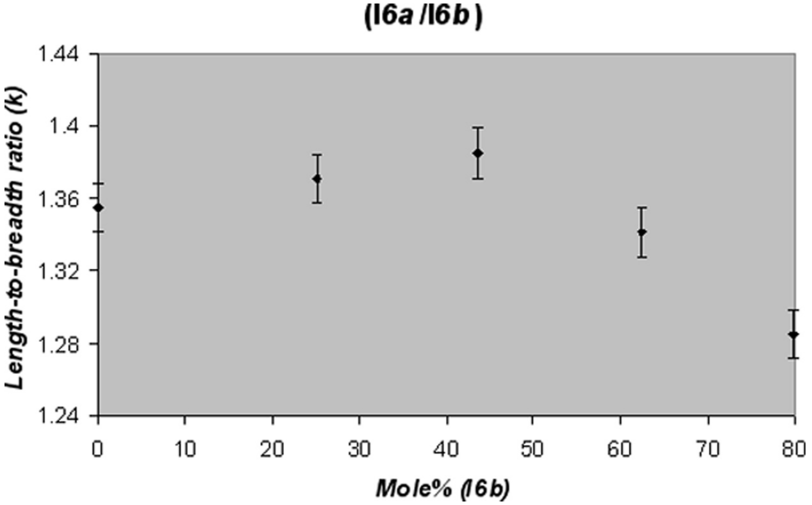

FIGURE 7 Composition dependence of the length-to-breadth ratio, k, for the binary system I*6a*/I*6b*.

existence in single separated molecules. A decrease in the breadth, *i.e.,* an increase in k, upon addition of either component to the other can be attributed to the destruction of the wide swarms to narrower swarms. Swarm narrowing is compatible with the decrease of S.

4.2.2. Binary Mixtures of Electron-Withdrawing Substituted Compounds (I6c/I6d)

Composition Dependence of the Order Parameter. The calculated order parameter, S, for the binary mixture of electron-withdrawing substituted compounds (I*6c*/I*6d*) was plotted as a function of reduced temperature T′ in Fig. 8. From the figure, the S-values as function of composition was deduced, at the same reduced temperature (T′ = 6°C), and plotted as a function of composition in Fig. 9. It is seen from the figure that adding either component to the other S is, unexpectedly, found to increase passing through maximum nearby the eutectic composition (57.98 mol% I*6d*), taking into consideration that the two components of the system have polar terminal groups of similar electronic nature like those described in the previous sections. Such discrepancies may be attributed to a steric effect rather than an electronic one. The methoxy group, which is angular, in molecules of I*6a* forces the molecules of I*6b* (bearing the linear methyl group) apart and hence disturbs the molecular ordering within the phase, consequently lowering the value of S.

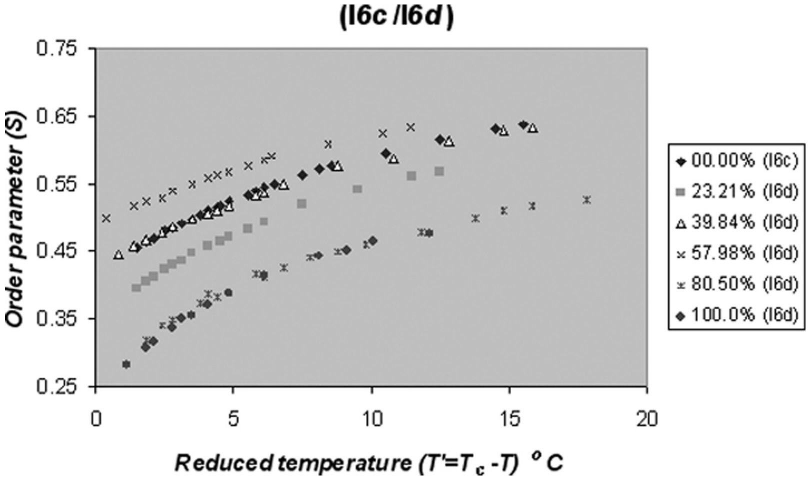

FIGURE 8 Reduced temperature T′ dependence of the order parameter, S, for various compositions of the binary system I*6c*/I*6d*.

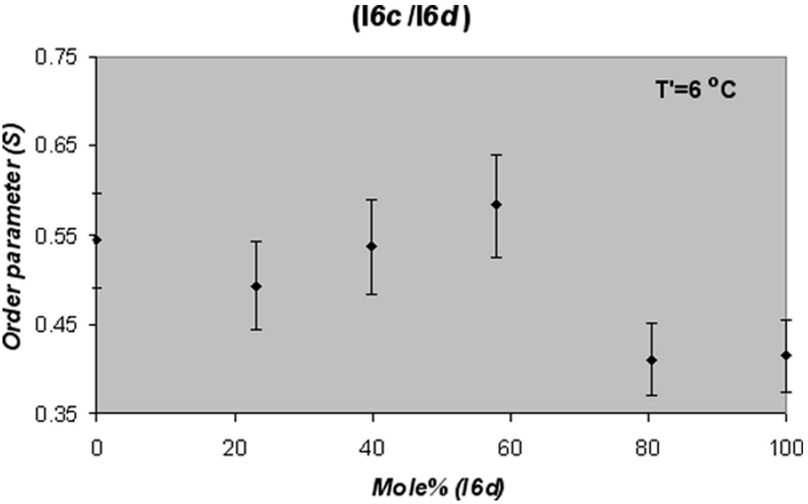

FIGURE 9 Composition dependence of the order parameter, S, for the binary system I*6c*/I*6d* at T′ = 6°C.

The reverse trend, the positive deviation from linear composition dependence of S, observed in the other electronically similar substituted components (bearing the cyano and nitro groups) can be attributed to a strong dipole–dipole association because both components possess high dipole moments compared with those of the components of the other system I*6a*/I*6b*.

Composition Dependence of the Entropy Change at the Clearing Temperature. The composition dependence of the entropy change, Δs_c, at the clearing temperature T_c is represented in Fig. 10. It is found from the figure that Δs_c has a minimum value near the eutectic composition, a trend that supports the behavior of S with composition, observed in the previous section.

Composition Dependence of the Length-to-Breadth Ratio. As should be expected, k should have a minimum value at the eutectic composition when plotted as a function of mixture composition. This is found to be the case, as observed from Fig. 11, which represents this relation.

4.2.3. Binary Mixtures of Electron-Releasing/Electron-Withdrawing Substituted Compounds (I6a/I6c)

Composition Dependence of the Order Parameter, Entropy Change, and Breadth-to-Width Ratio. This binary mixture system,

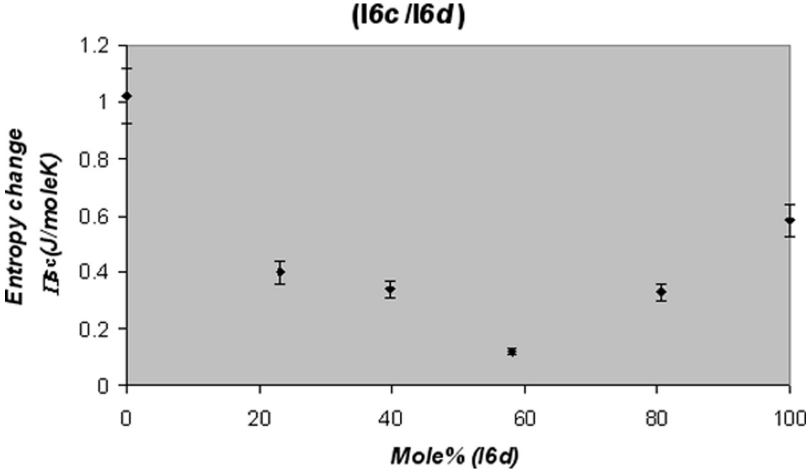

FIGURE 10 Composition dependence of the entropy change, Δs_c, at the nematic–isotropic transition temperature for the binary systems (I6*c*/I6*d*).

in contrast to the previous two systems (I6*a*/I6*b* and I6*c*/I6*d*), consists of two components bearing substituents of dissimilar electronic nature. Consequently, the decomposition dependence of this system is expected to behave in a manner opposite to that of the system of

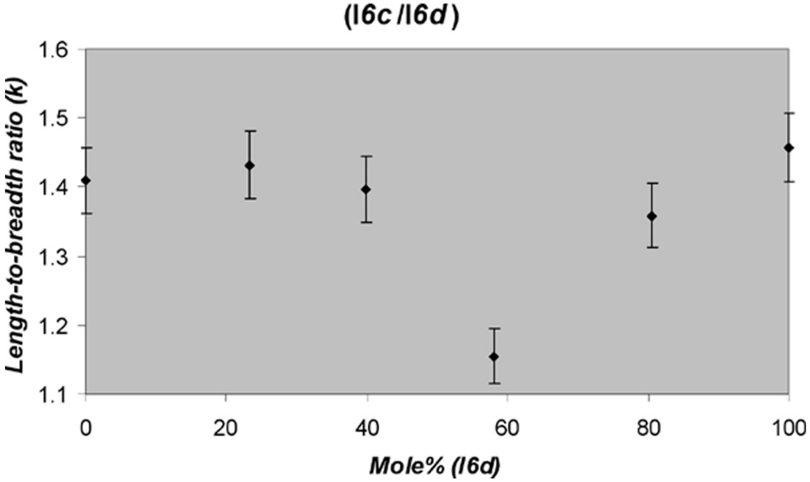

FIGURE 11 Composition dependence of the length-to-breadth ratio, k, for the binary system I6*c*/I6*d*.

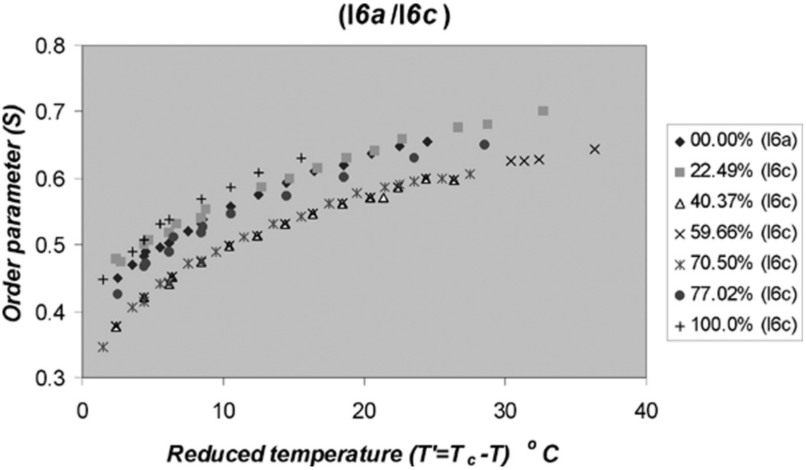

FIGURE 12 Reduced temperature T′ dependence of the order parameter, S, for various compositions of the binary system I*6a*/I*6c*.

electronically similar substituted components, I*6a*/I*6b*. Inversely, as shown from Fig. 13, the composition dependence of S at T′ = 6°C for the dissimilar system I*6a*/I*6c* gave a trend parallel to that of the system I*6a*/I*6b* (Fig. 5); *i.e.,* S exhibits its minimum value near the

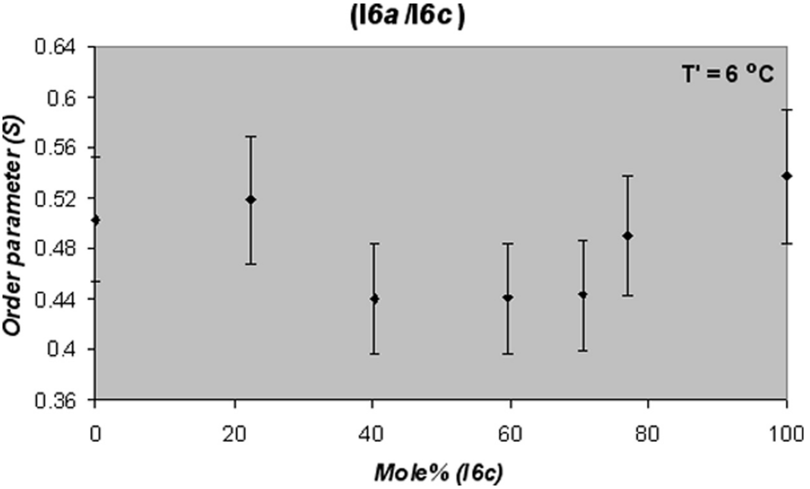

FIGURE 13 Composition-dependence of the order parameter, S, for the binary system I*6a*/I*6c* at T′ = 6°C.

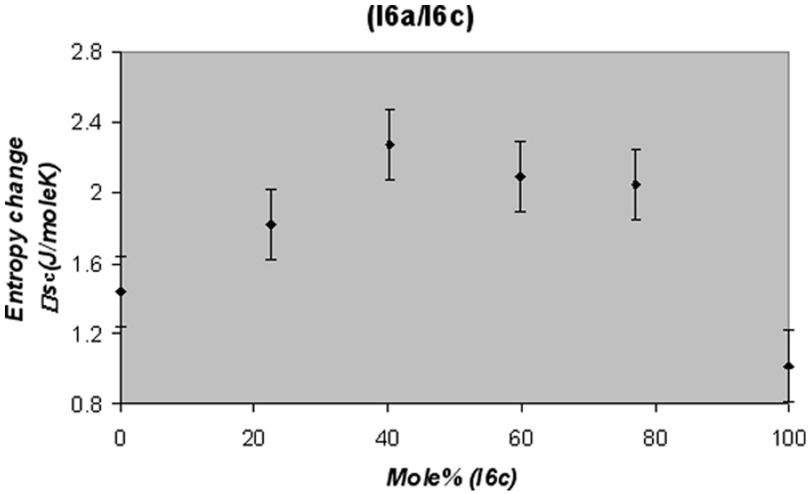

FIGURE 14 Composition dependence of the entropy change, Δs_c, at the nematic–isotropic transition temperature for the binary system I*6a*/I*6c*.

eutectic composition (70.5 mol% I*6c*). Such a negative deviation from the linear plot is supported by a positive deviation either in the composition dependence of Δs (Fig. 14) or of k (Fig. 15). Because a positive deviation may be attributed to a strong dipole–dipole association, a

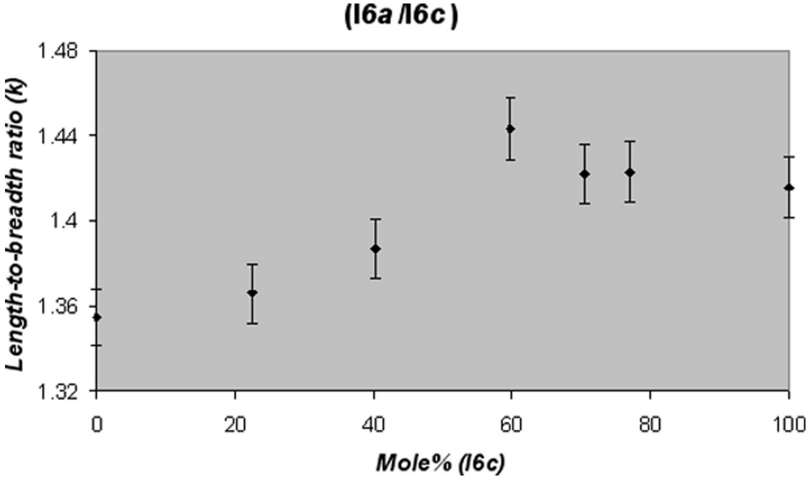

FIGURE 15 Composition dependence of the length-to-breadth ratio, k, for the binary system I*6a*/I*6c*.

steric factor may be pronounced more than a dipole–dipole interaction in our case. The angular methoxy group may play the same role as in I*6a*/I*6b* system; *i.e.,* it would force the molecules of I*6a* from those of I*6c* bearing linear cyano group.

5. CONCLUSION

The refractive indices of three binary systems of compounds of the type 4-$C_6H_{13}OC_6H_4COOC_6H_4X$ were measured for their individual compositions as a function of temperature. Based on the measured data, the order parameter (S) and the length-to-breadth ratio (k) were calculated. The entropy change at the nematic–isotropic transition (Δs_c) was also estimated by differential scanning calorimetry (DSC). Depending upon the difference in polarity and/or steric effect (linearity) of the two substituents (X) on either component of the system, the following conclusions can be drawn:

(1) In the isotropic phase all systems, independent of the polarity or linearity of the substituents, showed compatible mixtures; *i.e.,* all gave more or less linear composition dependences.
(2) The refractive index of the isotropic phase at a given temperature changes linearly upon substitution from one component's value to that of the other depending on the Hammet's constant of the substituent in the molecule.
(3) In the nematic phase, the order parameter (S) exhibits a negative deviation from the linear dependence on composition in the electronically similarly substituted derivatives I*6a*/I*6b*. This may be attributed to the disturbance of molecular ordering of I*6b* bearing the linear CH_3 substituent upon addition of I*6a* bearing the angular CH_3O substituent. The composition dependence of the other parameters (Δs_c and k) is in confirmation with this hypothesis.
(4) The second system (I*6c*/I*6d*), where its components bear the strong polar CN and NO_2 groups, showed a reverse trend in the S-composition dependence. This positive deviation can safely be attributed to a strong dipole–dipole association. The negative deviations in the composition dependence of either Δs_c or k are in accordance with such association.
(5) In the third system (I*6a*/I*6c*), where its components bear substituents of opposite polarity (CH_3O and CN), the main factor affecting the mode of intermolecular interaction is a steric one. The composition dependence of S exhibits a negative deviation from linearity, whereas the other two parameters Δs_c and k exhibit positive deviations.

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