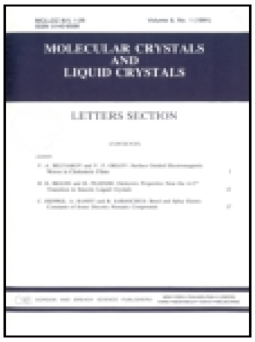

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Electro-Optical Behavior of a High Birefringence Mesogenic Mixture

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Liquid crystal mixtures tailored to possess high birefringence ($\Delta n \geq 0.30$) are being currently used extensively in photonic devices. The present work entails the study of electro-optical properties of such a high birefringence mixture (code name: 1770-2). The multicomponent thermotropic mixture, composed of compounds belonging to families of alkylfluoroisothiocyanatotolanes and alkylphenylfluoroisothiocyanatotolanes, exhibits only the nematic mesophase. The thermal variation of electric permittivities ($\varepsilon_{|}$ and $\varepsilon_{\perp}$) at different frequencies has been determined. Using the birefringence data, thermal variation of polarizability has been determined. The variation of the effective average molecular dipole moment μ_{sol} of the set-up molecules in solutions of varying concentrations (in%wt) at a particular temperature has been determined and the average molecular dipole moment μ_{iso} of the set-up molecules has been obtained. With a view to determine the nature of the molecular association in the mesophase, the molecular correlation factors "g" has been estimated from measurement of average dipole moment of the set-up molecules.

Keywords Correlation factor; dipole moment; electric permittivity; liquid crystal mixture; polarizability

1. Introduction

Liquid crystal mixtures with high birefringence are being formulated especially for use in infrared and THz range of radiation [1,2] devices to improve the electro-optical response. Polar compounds commonly used for increasing the birefringence of mixtures are isothiocyanatotolanes and isothiocyanato phenyltolanes. Isothiocyanates (compounds with terminal NCS group) seem to be more suitable than cyano polar compounds because of lower viscosity [3–5]. A number of different isothiocyanato compounds have been prepared and described recently [3–9]. Fluorine atoms have been joined to molecules to yield large dielectric anisotropies [10]. This is also because fluorine-substituted tolane-based liquid crystals exhibit higher nematogenity and electric permittivity and still low viscosity and good chemical and thermal stability [11]. One drawback is that unsubstituted

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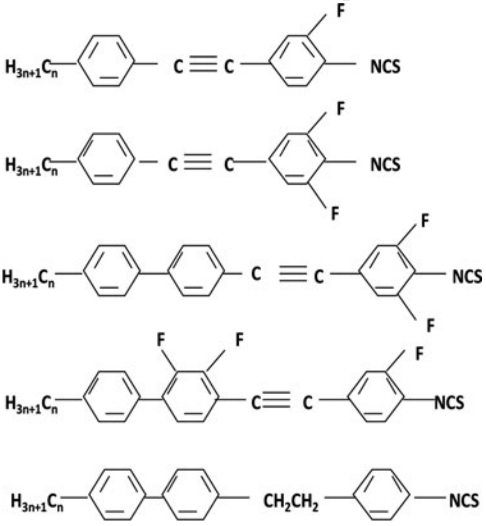
isothiocyanato-tolanes exhibit the crystal E phase. The polar NCS group coupled with lateral substitutes like F atoms in different combinations creates higher dipole moments which give rise to dielectric permittivity tensor component values that are more useful for some applications [12]. These compounds are characterized by good chemical stability, lower ionic conductivity and higher optical anisotropy than the cyano compounds [5,13]. The LC medium presented under study is a multicomponent mixture of linear molecules having a NCS group in one terminal position of the rigid core of the molecules and alkyl group at the other end with laterally substituted F atoms. Its composition and phase transition temperatures are given below. The mixture has been formulated by R. Dabrowski and co-workers.

The phase transition temperatures are:
13°C 82°C
Solid → Nematic → Isotropic



The optical properties and orientational order parameter have been investigated recently by the present authors [14]. Physical and electro-optical properties of some mixtures of this kind are given in Ref. [15]. The effects of conducting polymer, poly-(3, 4-dioxythiophenyl) - ethylene nanotubes and carbon nanotubes on the electro-optical properties of the above mixture (1770-2) have been studied [16].

In the present work, we have investigated the nature of variation of electric permittivities with temperature at frequencies of 1, 10, and 100 kHz. Since in our present study, the effective average molecular weight (M) is known (334.57), we were able to determine the effective average polarizabilities (α_e and α_o) from our optical studies reported earlier [14]. The average dipole moment of the effective molecule in isolate state and in the mesophase has been ascertained and molecular-molecular correlation has been determined.

2. Experimental Methods

2.1. Determination of Polarizabilities and Order Parameter

The polarizabilities α_e and α_o and thereby the order parameter of known mixture have been determined from optical data as a function of temperature from the measurement of the densities of the mixture. The densities of the sample at various temperatures were determined by introducing the weighed sample into a dilatometer, which was then placed in a heat bath. The length of the sample column in the dilatometer tube was measured with a traveling microscope at intervals of 1°C and the density of the sample was calculated. The polarizabilities were determined using Vuks formula [17] viz.:

$$\frac{\mathrm{n}_{\gamma}^{2}-1}{\mathrm{n}^{2}+2}=\frac{4\pi}{3}N\alpha_{\gamma} \tag{1}$$

(n_γ is the refractive index, n_e or n_o, $n = n_{ave} = [n_e + 2n_o]/3$, N is the number of molecules per cc and is given by $N = N_A d/M$, N_A is the Avogadro number, d the density of the sample, and M the average molecular weight). From the data of n_e and n_o obtained from our previous work [14] and known value of the average molecular weight ($M = 334.57$) of the set-up molecule in mixture the polarizabilities were calculated using the density values. The orientational order parameter $<P_2>$ was obtained from the macroscopic property of the polarization anisotropy using de Gennes expression [18] in the form:

$$< P_2 >= \frac{(\alpha_e-\alpha_o)}{(\alpha_{\mathrm{II}}-\alpha_{\perp})} \tag{2}$$

where $\alpha_{\|}$ and $\alpha_{\perp}$ are the values of α_e and α_o in the perfectly ordered state when all the molecules are expected to be perfectly aligned along the director axis. $\alpha_{\|}$ and $\alpha_{\perp}$ are usually ascertained using Haller's extrapolation procedure [19] by plotting $\ln(\alpha_e - \alpha_o)$ versus $\ln(T_C - T)$ and extrapolating the straight line thus obtained to $T = 0$ (i.e., $\ln T_c$) corresponding to the perfectly ordered state.

2.2. Dielectric Studies

A pair of indium tin oxide (ITO)-coated conducting glass plates, separated by thin cover slips on three sides has been used to prepare the sample cell (or capacitor). The sample cell has an effective size of 4.0 cm × 2.5 cm × 0.5 cm and its capacitance (air) is (∼21pF). The sample cell has been calibrated using standard liquids (benzene and p-xylene) with the help of an LCR meter (6471 Forbes Tinsley) at different operating frequencies (1, 10, and 100 kHz). The mixture was introduced into the cell as an isotropic liquid through the open end which was subsequently sealed. The sample cell encapsulated within a sample holder whose temperature may be regulated by a temperature controller by (±1°C), was taken through a number of temperature cycles in presence of an aligning magnetic field of approximately 8 kGauss to obtain an aligned monodomain sample. Readings for the parallel and perpendicular components of the capacitance were taken at temperature intervals of 2°C from room temperature to beyond the nematic-isotropic transition temperature at frequencies of 1, 10, and 100 kHz. The values of the parallel and perpendicular components of the electric permittivities $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ were evaluated from the capacitance values by standard procedure of calibration. The bridge voltage across the sample was maintained sufficiently low (∼0.3V) so as not to produce any electric-field-induced instability.

2.3. Measurement of Average Dipole Moment of Set-Up Molecules

Solutions of different concentrations (by%wt) of the mixture were prepared in a nonpolar solvent, viz., p-xylene. The solution was introduced into a fresh sample cell prepared and standardized as before and the electric permittivities ε_{12} of the solution were determined at 100 kHz for each of the concentrations of the solution at a fixed temperature(40°C), using an LCR bridge (6471 Forbes Tinsley). The dielectric permittivity ε_1 of the solvent has likewise been determined at the same temperature.

The refractive indices n_{12} of the solution were also obtained for each concentration with the Chatelain–Wedge [20] method using He-Ne laser beam (wave length $\lambda = 633$ nm). The solutions of different concentrations (by%wt) were introduced into a glass prism (angle $\sim 1°–2°$) at room temperature (25°C). The prism was formed with glass slides whose inner surfaces were treated with polyvinyl alcohol for planar surface alignment. The prism, encapsulated in a sample holder whose temperature was controlled up to ± 1°C with the help of a temperature controller was placed in an aligning magnetic field of ~8 kGauss. The He-Ne beam was made incident on the solution through a hole in the sample holder and the refracted beam projected on a screen several meters away (~5.0 m). From measurements on the screen, the refractive index n_{12} of the solution could be determined at a particular temperature with knowledge of the prism angle. Details of the experimental arrangements and procedures are described in Ref. [21]. The refractive index of the solvent n_1 was likewise determined at the same temperature.

The dipole moments μ_{sol} of the molecules in a solution of concentration c (mole/cc) at a fixed temperature (40°C) were obtained from the following relation [22]:

$$\mu_{\text{sol}}^2 = \frac{27\ K_B T\{\left(\varepsilon_{12} - n_{12}^2\right) - \left(\varepsilon_1 - n_1^2\right)\}}{4\pi N(\varepsilon_1 + 2)\left(n_1^2 + 2\right)\text{c}} \tag{3}$$

(the suffices 1 and 12 refer to the solvent and solution parameters, respectively, N is the Avogadro number, and K the Boltzmann constant.)

The variation of the dipole moments μ_{sol} with the solution concentration (in%wt) was fitted to a polynomial and the curve extrapolated to infinite dilution to obtain the dipole moment μ_{iso} of the isolated effective molecule for the mixture. The values in esu cm obtained above might be converted to Coulomb meter using the factor of 3.3356×10^{-12}.

3. Results and Discussions

3.1. Average Polarizabilities and Order Parameter

The thermal variation of the polarizabilities α_e, α_o of the mixture has been depicted in the Fig. 1. The average polarizability $\alpha_{\text{ave}} = (\alpha_e + 2\alpha_o)/3$ is almost constant throughout the nematic range and continuous with the respective α_{iso} values at T_{NI}. The average polarizability α_{ave} of the mixture is $\sim 30.21 \times 10^{-24}\text{cm}^{-3}$ (40°C). The polarizability variation shows trends similar to thermal variation of refractive indices as obtained from our optical studies [14] performed earlier. The estimated error in determination of polarizability is about 2–3%.

Figure 2 shows the variation of the orientational order parameter $<P_2>_{\text{expt}}$ as a function of temperature. The variations of theoretically computed order parameter $<P_2>_{\text{MS}}$ on the basis of Maier–Saupe theory [23] and experimental order parameter (obtained without the knowledge of average molecular weight M, computed from our optical studies reported earlier [14]) have also been depicted in Fig. 2. Both the experimental order parameters $<P_2>_{\text{expt}}$ (M known and unknown) match quite satisfactorily. The variations of $<P_2>_{\text{expt}}$ show more or less similar trends till 60°C with $<P_2>_{\text{MS}}$ whereupon the fall in experimental values is less gradual as the isotropic temperature is approached. The estimated error in determination of order parameter is about 2%.

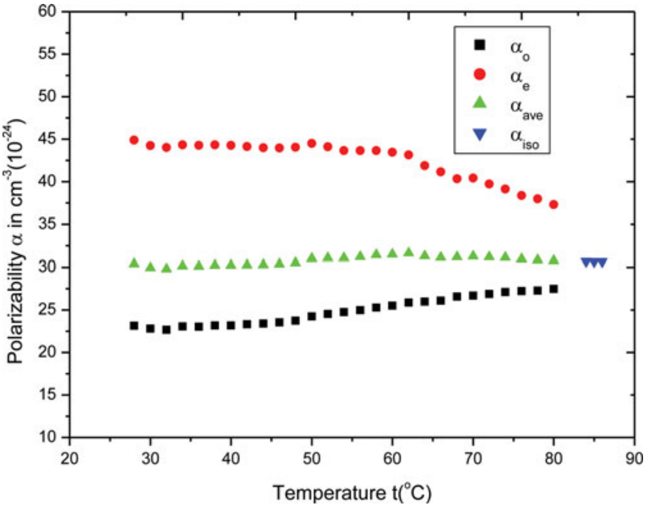


Figure 1. Thermal variation of polarizabilities of 1770-2.

3.2. Dielectric Studies

Figures 3(a)–(c)show the thermal variations of electric permittivities ($\varepsilon_\parallel$ and $\varepsilon_\perp$) for the mixture at frequencies of 1, 10, and 100 kHz. One at once notices the significantly large value of dielectric anisotropy $\Delta\varepsilon$: 16.78 (1 kHz), 15.44 (10 kHz), and 14.96 (100 kHz), respectively, at a temperature of 40°C. Keeping in mind the very large value of birefringence $\Delta n \sim 0.34$ (40°C) reported earlier in our optical studies [14], $\Delta\varepsilon$ values are as per our expectation. The corresponding values of average dielectric permittivities are 11.56, 10.74, and 10.31 at 1, 10, and 100 kHz (40°C), respectively. The average dielectric permittivity ε_{ave} is almost constant throughout the nematic range and continuous with the respective

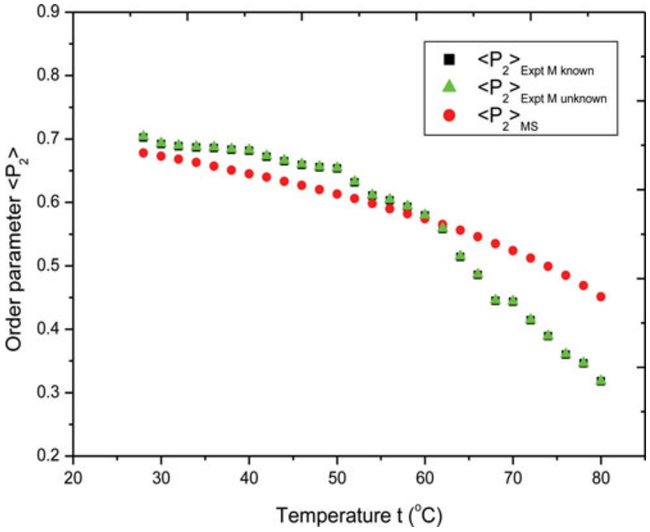


Figure 2. Thermal variation of order parameter of 1770-2.

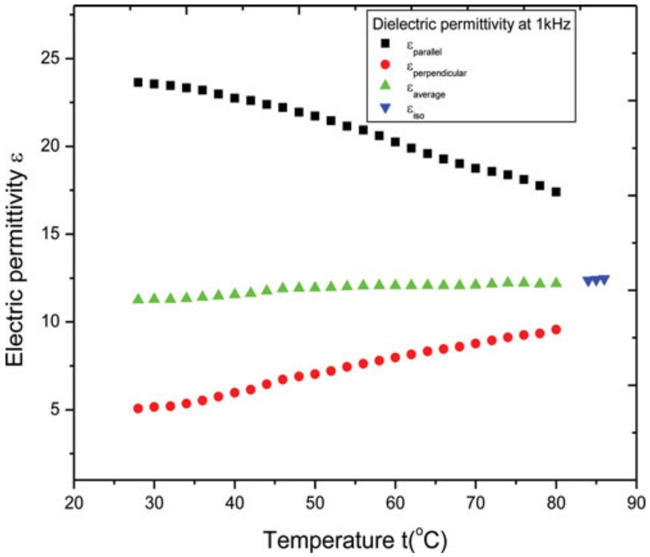


Figure 3a. Thermal variation of electric permittivity of 1770-2 at 1 kHz.

ε_{iso} at T_{NI}. This behavior is also exhibited by n_{ave} as obtained from our optical studies [14] performed earlier. The estimated error in determination of the dielectric permittivity is about 1%.

In the present study, the average polarizabilities of the set up molecules were determined with the knowledge of average molecular weight M of the set-up molecules (as described in the earlier section) and hence effective average molecular dipole moment μ_{eff} of the

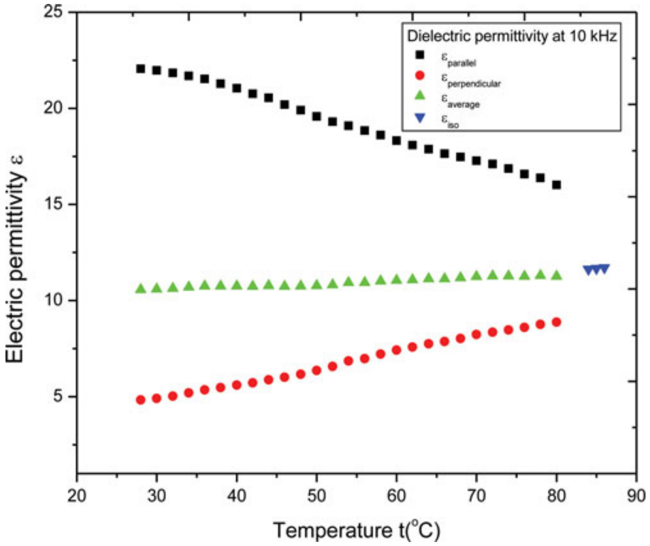


Figure 3b. Thermal variation of electric permittivity of 1770-2 at 10 kHz.

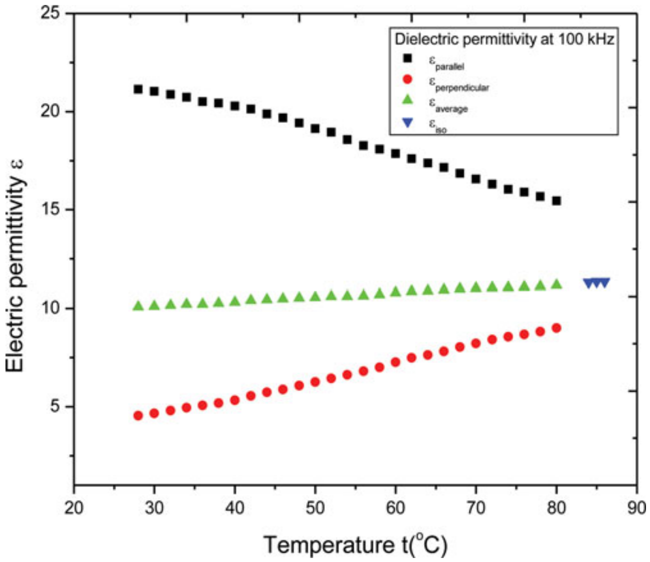


Figure 3c. Thermal variation of electric permittivity of 1770-2 at 100 kHz

mixture could be obtained from the following expression of Maier and Meier [24], viz.:

$$\varepsilon_{ave} = 1 + 4\pi NhF[\alpha_{ave} + F\mu_{eff}^2/3KT] \tag{4}$$

$$[\mathrm{h} = 3\ \varepsilon_{\mathrm{ave}}/(2\ \varepsilon_{\mathrm{ave}} + 1)$$

$$f = 4\pi N(2\ \varepsilon_{\mathrm{ave}} - 2)/3(2\ \varepsilon_{\mathrm{ave}} + 1)$$

$$\varepsilon_{\mathrm{ave}} = (\varepsilon_{||} + 2\ \varepsilon_{\perp})/3, \alpha_{\mathrm{ave}} = (\alpha_{\mathrm{e}} + 2\alpha_0)/3,\ F = 1/(1 - \alpha_{\mathrm{ave}}\ f)]$$

The average angle of inclination β of the set-up molecules was obtained from the following expression of Maier and Meier [24]:

$$\Delta\varepsilon = 4\pi NhF\left[\Delta\alpha - \frac{F\mu_{\mathrm{eff}}^2(1 - 3\cos^2\beta)}{2KT}\right]\langle P_2\rangle \tag{5}$$

average angle of inclination β of the set-up molecules with temperature at frequencies of 1, 10, and 100 kHz. At 60°C, the β values are found to be 29.99°, 30.88°, and 30.96° at 1, 10, and 100 kHz, respectively, showing a slight increase of β values with the increase in frequency. The variations of β with temperature exhibit the same trend for the different frequencies and show a marked increase till about 60°C, whereupon the behavior is altered. As the isotropic temperature is approached, this trend is disturbed and β values show fluctuations, the behavior at 100 kHz being decidedly different from that at 1 and 10 kHz behavior. The fluctuation may be ascribed to vigorous vibration of the molecules as the nematic–isotropic phase transition is approached. The estimated error in determination of the angle of inclination is about 3%.

3.3. Dipole Moment in Solution and Determination of Correlation Factor

The variation of the dipole moment in solution μ_{sol} with concentration c (% wt) at a temperature of 40°C and operating frequency of 100 kHz is depicted in Fig. 5. By extrapolating

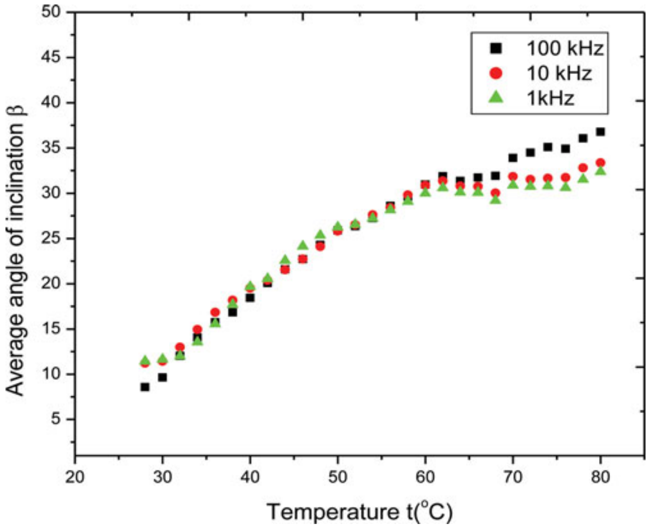


Figure 4. Thermal variation of angle of inclination β of 1770-2.

the curve to infinite dilution, the isolated or free molecular dipole moments μ_{iso} of the set-up molecules is found to be 3.75D. It is a little higher as expected than in unsubstituted molecule of 6CHBT (3.35) Ref. [25]. Comparing the above value of μ_{iso} with the corresponding value of μ_{eff} (at 40°C and 100 kHz) which is 2.97D, we note that there is a difference between them, indicating some antiparallel correlation between neighboring molecules. The Kirkwood theory [26] based on a short-range molecular correlation has been extended by Frolich [27] to include the deformation polarizability of the molecules. This has led to the Kirkwood–Frolich theory [28] from which the Kirkwood correlation factor

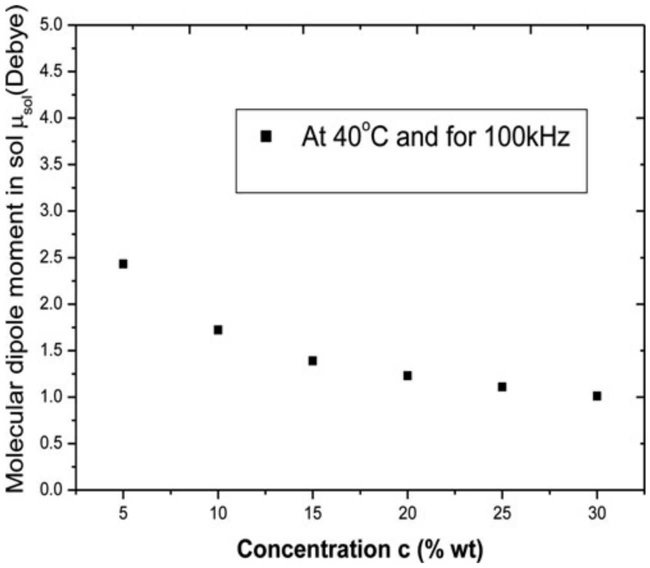


Figure 5. Variation of molecular dipole moment of 1770-2 in solution with concentration.

g may be obtained. "g" gives a measure of the molecular association between a reference molecule and its nearest neighbors and a departure of g from unity is indicative of molecular association. For no association between molecules $g = 1$ and the Kirkwood–Frolich equation is reduced to the Onsagar equation [29,30]; $g > 1$ indicates a parallel orientation of dipoles of neighboring molecules, while $g < 1$ results from an antiparallel orientation. We have obtained an estimate of the molecular association for the sample from the Kirkwood factor g using the expression $g = {\mu_{\mathrm{eff}}}^2/{\mu_{\mathrm{iso}}}^2$. At 40°C, the value of g obtained at a frequency of 100 kHz is 0.627, indicating an antiparallel correlation between neighboring molecules in the sample.

4. Conclusion

The present study is a continuation of our work on the above mixture and provides a befitting example of how dielectric behavior may be tuned to advantage in the design and formulation of mixtures. The dielectric anisotropy is desirably high ~14.96 (100 kHz, 40°C) and should be accounted for by the dipole moment of the effective molecule. The effective average dipole moment of the set up of molecule in the isolated state is found to be moderately large ~3.75D and is augmented in the mesophase due to molecular-molecular association ($g = 0.627$). This value of μ_{eff} is only a little larger than it is observed for 6CHBT (4-(4-trans-hexylcyclohexyl benzeneisothiocyanates) ($\mu = 3.4$).

References

[1] Wu, S. T. (1987). *Opt. Eng.*, *26*, 120.

[2] Scherger, B., Reuter, M., Scheller, Altmann K., Vieweg, N., Dabrowski, R., Deibel, J. A., Koch M. (2012) *J. Infrared Millim. Te.*, *33*, 1117.

[3] Gauza, S., Wen, C. H., Wu, B., Wu, S. T., Spadlo, A., Dabrowski, R. (2006). *J. Soc. Inf. Disp.*, *14/3*, 241.

[4] Dabrowski, R., Dziaduszek, J., Ziolek, A., Szczucinski, L., Stolarz, Z., Sasnouski, G., Bezborodov, V., Lapanik, W., Gauza, S., Wu, S. T. (2007), *Opto-Electron. Rev.*, *15*(1), 47.

[5] Dąbrowski, R., Kula, P., and Herman, J. (2013), *Crystals, 3*, 443.

[6] Gauza, S., Wang, H., Wen, C. H. Wu, S. T., Seed, A. J. and Dabrowski, R.,(2003). *Jpn. J. Appl. Phys.*, *42*(1), 3463.

[7] Spadlo, A., Dabrowski, R., Filipowicz, M., Stolarz, Z., Przedmojski, J. Gauza, S., Fan C. Y., Wu, S. T. (2003), *Liq. Cryst.*, *30*(2), 191.

[8] Catanescu, C. O., Chien L. C., Wu, S. T. (2004). *Mol. Cryst. Liq. Cryst.*, *411*, 93.

[9] Gauza, S., Wen, C. H., Wu, S. T., Janarthanan, N., Hsu, C. S. (2004), *Jpn. J. Appl. Phys.*, *43*, 7634.

[10] Dabrowski, R. (1990), *Mol. Cryst. Liq. Cryst.*, *191*, 17.

[11] Khoo, I. C., Wu, S. T. (1993). *Optics and Nonlinear Optics of Liquid Crystals*, World Scientific, Singapore.

[12] Czub, J., Dabrowski, R., Dziaduszek., J., Urban, S. (2009). *Phase Transition, 82*(6), 485.

[13] Sarkar, P., Mandal, P., Paul, S., Paul, R., Dabrowski, R., Czuprynski, K. (2003). *Liq. Cryst.*, *30*, 507.

[14] Dutta Gupta, M., Mukhopadhyay, A., Roy, S. K., Dabrowski, R. (2013). *J. Appl. Phys.*, *113*, 0535161.

[15] Nowinowski-Kruszelnicki, E., Kedzierski, J., Raszewski, Z., Jaroszewicz, L., Dabrowski, R., Kojdecki, M., Piecek, W,. Perkowski, P., Garbat, K., Olifierczuk, M., Sutkowski, M., Ogrodnik, K., Morawiak, P., Miszczyk, E. (2012). *Opt. Appl.*, *42*(1), 167.

[16] Ghosh, S., Nayek, P., Roy, S. K., Gangopadhyay, R., Molla, M. R., Dabrowski, R. (2011). *Mol. Cryst. Liq. Cryst.*, *545*, 22.

[17] Vuks, M. F. (1966). *Opt. Spectrosc.*, *20*, 361.
[18] deGennes, P. G. (1971). *Mol. Cryst. Liq. Cryst.*, *12*,193.
[19] Haller, I., Huggins, H. A., Lilienthal, H. R., McGuire, T. R. (1973). *J. Phys. Chem.*, *77*, 950.
[20] deJeu, W. H. (1980). *Physical Properties of Liquid Crystalline Materials*, Gordon & Breach. London.
[21] Bhowmick, K., Mukhopadhyay, A., Mukherjee, C. D. (2003). *Phase Transition*, *76*(7), 671.
[22] Guggenheim, E. A. (1949). *Trans. Faraday Soc.*, *45*, 714.
[23] Maier, W., Saupe, A. (1959). *Z. Naturforsch. 14a*, 882.
[24] Maier, W., Meier, G. (1961). *Z. Naturforsch*, *16a*, 1200.
[25] Puchala, Cz., Waclawek, W. (1991). *Research Papers of Higher Pedagogical School of Czestochowa (Chemistry)*, Poland, 143.
[26] Kirkwood, J. G. (1939). *J. Chem. Phys.*, *7*, 911.
[27] Frohlich, H. (1949). *Theory of Dielectrics*, Oxford University Press, London.
[28] Bottcher, C. J.F. (1973). *Theory of Electric Polarization (2nd edition)*, Elsevier, Amsterdam, Vol. I, sec. 39.
[29] Onsager, L. (1936). *J. Am. Soc.*, *58*, 1486.
[30] Smyth, C. P. (1980). *Molecular Interactions*, Vol. II, John Wiley & Sons, Ltd: London.