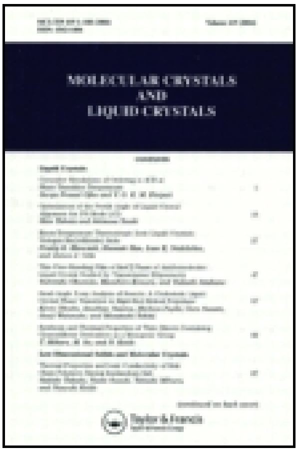

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Study of Birefringence and Dielectric Properties and Determination of Dipole Moment of the Mesogen: 4-Cyano-4′-n-Octylbiphenyl as a Function of Temperature

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Study of Birefringence and Dielectric Properties and Determination of Dipole Moment of the Mesogen: 4-Cyano-4′-n-Octylbiphenyl as a Function of Temperature

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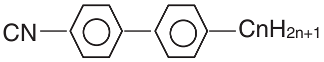
Optical and dielectric studies have been performed on one of the members of mesogenic series 4-cyano-4′-n-alkyl biphenyl. The structural formula of the mesogen 4-cyano-4′-n-octyl biphenyl (code name K24) is given below:

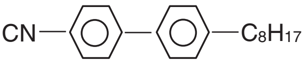


Texture studies have been conducted on the above mesogen to confirm the transition temperatures and the various mesophases. Optical studies using He–Ne laser beam have been performed and refractive indices have been determined as a function of temperature by the application of Chatelain Wedge principle. From this principle, polarizability and orientational order parameter have been determined. The experimentally determined orientational order parameter is compared with theoretical Maier–Saupe values. To study the dielectric property, we have determined the parallel and perpendicular components of dielectric permittivities, i.e., $\varepsilon_{\parallel}$ *and* $\varepsilon_{\perp}$ *in the presence of magnetic field, and from dielectric anisotropy, polarizability, and order parameter, we have calculated effective dipole moment* μ_{eff} *and angle of inclination* β *of the axis of molecule with the director direction as a function of temperature. Dielectric studies of the sample have also been performed in the solution at various concentrations, and by extrapolating the values at infinite dilution, we have obtained isolated molecular dipole moment* μ_{iso} *. We have compared the values of* μ_{eff} *and* μ_{iso} *and have calculated correlation factor "g" that throws a light on nature of bonding of the molecules.*

Keywords Birefringence; dielectric constant; dipole moment; mesogen; order parameter; PACS No. 61.30

Introduction

The compound 4-cyano-4′-n-octyl biphenyl is a member of the homologous series 4-cyano-4′-n-alkyl biphenyl having the structural formula:



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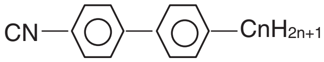
In case of K24, $n = 8$ and the structural formula is:



and its chemical formula is $C_{21}H_{25}N$. It is known to undergo the following phase transitions (Merck Ltd.)

$$\text{Solid} \xrightarrow{21.5^\circ\text{C}} \text{Smectic A} \xrightarrow{33.5^\circ\text{C}} \text{Nematic} \xrightarrow{40.5^\circ\text{C}} \text{isotropic}$$

A calorimetric investigation has been carried out on the above compound to study the temperature dependence of the heat capacity as well as for the enthalpy [1]. Dielectric and static Kerr constant of the compound in highly diluted cyclohexane solution has been determined, and from it, dipole moment at infinite dilution at 25°C has been reported [2]. Dipole moment of the whole cyano biphenyl (CB) series (0CB to 12CB) in four solvents has also been reported by [3]. From it, they have also calculated isolated molecular dipole moment using a different procedure than ours but which agrees well with our calculated values. They have compared these experimental values with those calculated by theoretical molecular mechanics methods. A pretransitional effect in the electric permittivities of the compound in nematic-isotropic transition was found by Brandshaw and Raynes [4]. They concluded that for polar molecules at NI transition, $\varepsilon_{\text{average}}$ and ε_{iso} curves will be discontinuous for this effect, which is a fact similar to our experiment. Dielectric permittivities at N-S_A phase transition of some member of CB series (including K24) were carried out by Buka and Bata [5]. From this, they have also calculated the orientational order parameter. Dynamic Kerr effect behavior and transient molecular reorientation have been investigated in nematic phase of the three members of the series including K24 [6]. They have also reported dipole moment in cyclohexane solution at a particular temperature in a different method [7]. In our present work, we have determined refractive indices as a function of temperature by Chatlain Wedge principle using a He–Ne laser beam ($\lambda = 633$ nm). From it, polarizability and order parameter as a function of temperature were determined. So far, no work has been reported to determine refractive indices, and from it, polarizability and order parameter of this sample using our method. In dielectric studies, we have determined dielectric constant as a function of temperature, and from it, molecular dipole moment μ_{eff} and angle of inclination β between the molecular axis and director direction have been calculated. We have also determined the dipole moment in p-xylene solution at different concentrations and extrapolated it at an infinite dilution, and we have calculated isolated molecular dipole moment, which agrees well with the work by Megnassan and Proutiere [3] and Ghanadzadeh and Beevas [7].

Experimental Methods

Texture Studies

Texture studies were performed using a polarizing microscope (Leitz) having a hot stage (Mettler FP 82 HT) to confirm the different phases and also to determine phase transition temperatures. The powdered sample was heated beyond the isotropic temperature and placed as a thin film on a glass slide and a cover slip was placed on it. Observations were performed under crossed polarizer with a magnification of 150×. One and two temperature cycles were performed at a rate of 1° per minute. Then, photographs of the sample were taken at different temperatures.

Optical Studies

Optical studies were performed using Chatelien Wedge principle. The powdered sample was placed on a 1°–2° glass prism made by the author; the prism angle was determined by the reflected beams from two sides of it. Details of the experimental arrangement are given in the paper by Bhowmick et al. [8]. The inner surfaces of the prism were treated by polyvinyle alcohol for alignment of the sample. Then, the prism with the sample was placed in a sample holder (fabricated in house) whose temperature may be regulated up to ±1°C with the help of a temperature controller. The sample holder with sample was then placed in a magnetic field of strength ~8K gauss for alignment. A He–Ne laser beam ($\lambda = 633$ nm) was passed through the sample by a hole on the sample holder. The refracted beams (extraordinary and ordinary) emerge out and project on a screen approximately 4 m away. By measuring the distances and applying simple geometry, the angular deviations and corresponding refractive indices n_e and n_o were determined.

The density of the sample was determined at various temperatures. In melted form, the sample was introduced in a dilatometer, which was placed in a heat bath. The sample height was measured by a traveling microscope. The polarizabilities could be determined as a function of temperature from birefringence studies and density measurements.

Dielectric Studies

A pair of indium tin oxide (ITO)-coated conducting glass plates separated by thin cover slips by its three sides was used to form the sample cell (capacitor). The cell was calibrated by standard liquids benzene and p-xylene with the help of an *LCR* meter (6471 Forbes Tinsley). The sample was introduced into the cell as an isotropic liquid and the open end sealed. Then, it is placed in a sample holder (designed and fabricated in house) that is connected to a temperature controller so that the temperature of the sample can be regulated (±1°C). The sample was taken through a number of temperature cycles at the rate of 1°C per minute in the presence of a magnetic field of approximately 8K gauss to get an aligned monodomain sample. Readings for the parallel and perpendicular components of capacitance were taken at various temperatures during cooling at frequencies of 1, 10, and 100 kHz. The values of the parallel and perpendicular components of the dielectric constant $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were obtained from the capacitance values by a standard procedure. The bridge voltage across the sample was maintained low enough (~0.3 V) so as not to produce any electric-field-induced instabilities.

Molecular Dipole Moment Measurement

Solutions of the sample at different concentrations (by wt%) were made in a nonpolar solvent, namely, p-xylene. The solution was introduced into a fresh sample cell prepared and standardized as before and the dielectric permittivities ε of the solution were determined at 1 kHz for each of the concentrations of the solution at a fixed temperature (34°C) using the *LCR* bridge (6471 Forbes Tinsley). The refractive indices n of the solution were obtained for each concentration using a He–Ne laser beam and the Chatelain Wedge method described in detail in the paper by Bhowmick et al. [8]. The dipole moment μ of the molecule in a solution of concentration c (mole/cc) at a fixed temperature (K) was calculated using the following relation [9]:

$$\mu^2 = \frac{27\mathrm{kT}\left(\varepsilon_{12} - \mathrm{n^2}_{12}\right) - \left(\varepsilon_1 - \mathrm{n}_1^2\right)}{4\pi \mathrm{N}(\varepsilon_1 + 2)\left(\mathrm{n}_1^2 + 2\right)\mathrm{c},} \tag{1}$$

where the suffixes 1 and 12 refer to the solvent and solution parameters, respectively, N is the Avogadro number, and *k* is the Boltzman constant. The variation of the dipole moment μ with solution concentration (in wt%) was fitted to a polynomial and the curve extrapolated to an infinite dilution to obtain the dipole moment μ_{iso} of the isolated molecule. The values in esu.cm. obtained from the above relation might be converted to cm. using the factor 3.3356×10^{-12}.

Results and Discussion

Texture Studies

The transition temperatures as observed from texture studies are as follows:

$$\text{Solid} \rightarrow \text{Smectic A} \underset{21.5^\circ\mathrm{C}}{\overset{33^\circ\mathrm{C}}{\rightleftarrows}} \text{Nematic} \underset{39.4^\circ\mathrm{C}}{\overset{39.8^\circ\mathrm{C}}{\rightleftarrows}} \text{isotropic}$$

The transition temperatures from smectic A to nematic and nematic to isotropic are in a close agreement with the quoted value supplied by Merck Ltd. We had no provision to cool the sample. So, we could not take the photographs below 32°C, and thus could not verify the transition temperature of solid to smectic A. Representative texture photographs of nematic and smectic A phases are shown in Figs. 1 and 2. Figure 1 is a typical photograph of nematic phase. Figure 2 is a fan-like structure of smectic A phase.

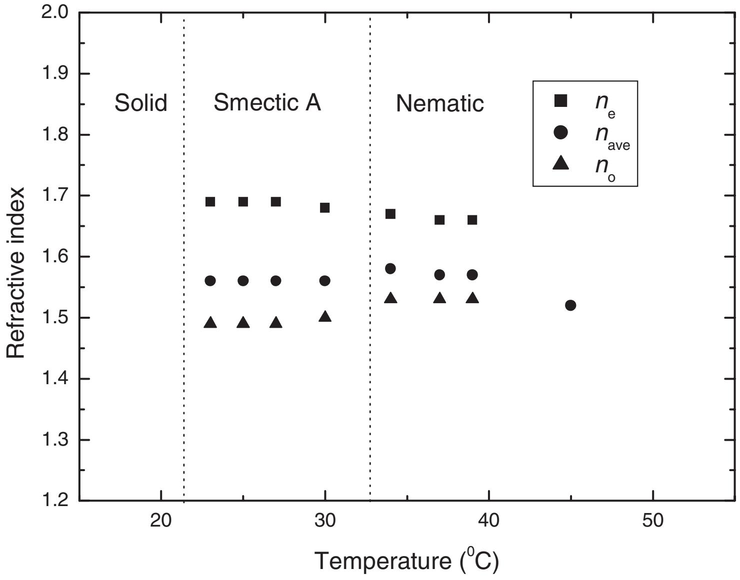


Figure 1. Variation of refractive indices with temperature.

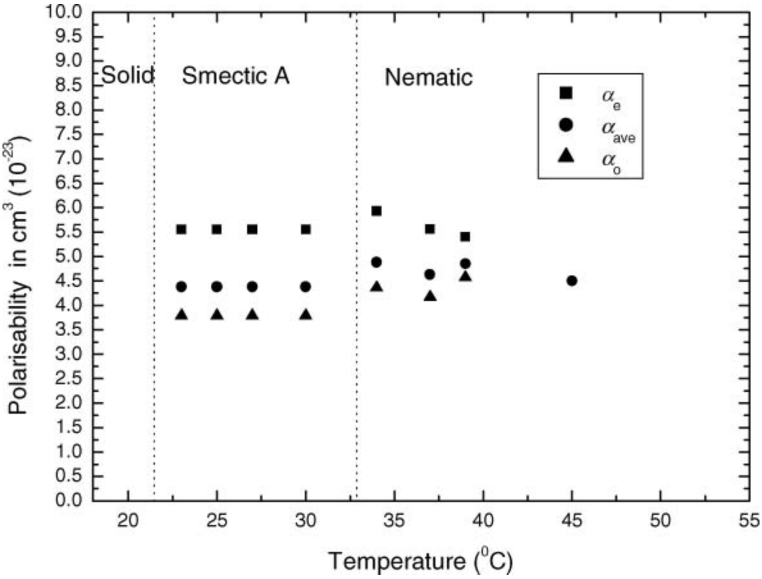


Figure 2. Variation of polarizability with temperature.

Optical Studies

Figures 3 and 4 show the variation of refractive indices n_e and n_o and polarizabilities α_e and α_o with temperature. There is a discontinuity near 33°C for both refractive indices and polarizability graphs. This is because of the smectic to nematic phase transition. The curves are also discontinuous at nematic to isotropic transition, a feature that is also shown by ε_{ave}

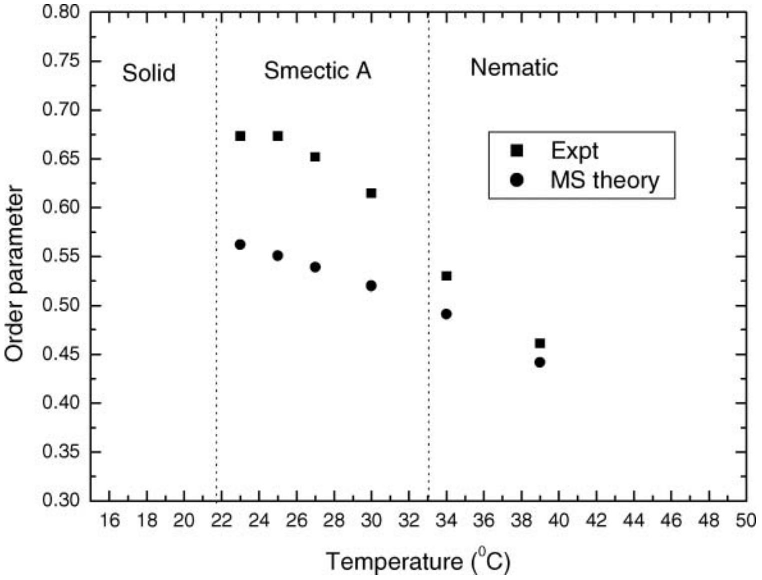
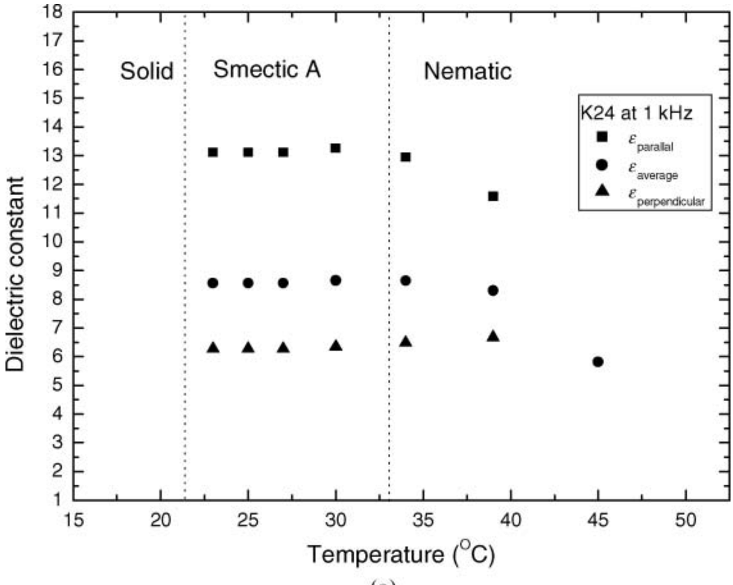
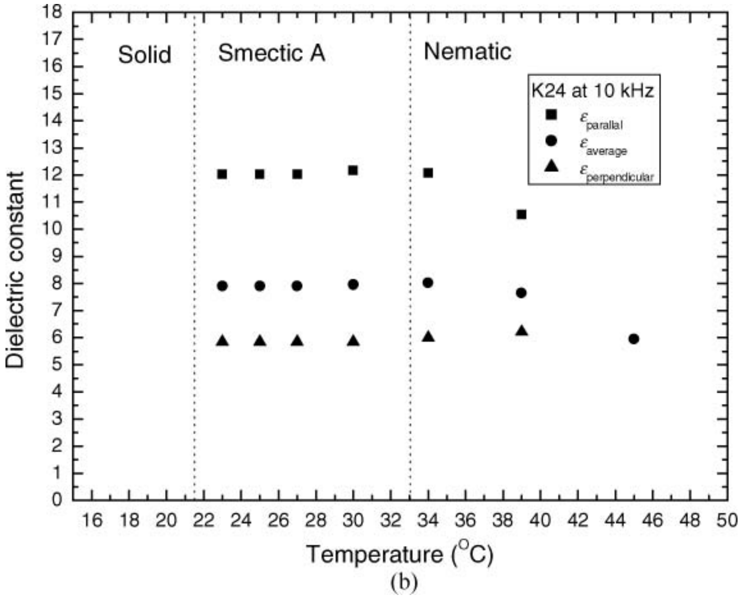


Figure 3. Variation of order parameter with temperature.

in dielectric curves. Optical anisotropy Δn is found to be 0.2 at 27°C and 0.14 at 37°C, whereas the quoted values are 0.157 at 27°C and 0.137 at 37°C. The orientational order parameter $<P_2>$ was calculated using the relation $<P_2> = (\alpha_e - \alpha_o)/(\alpha_{\|} - \alpha_{\perp})$ [10], where $\alpha_{\|}$ and $\alpha_{\perp}$ are the polarizabilities parallel and perpendicular to the long axis corresponding to the solid phase and have been obtained using Haller et al.'s [11] extrapolation procedure. Variation of $<P_2>_{\text{expt}}$ together with theoretical Maier–Saupe (MS) [12] values of the order parameter are depicted in Fig. 5. Order parameter values gradually decrease with

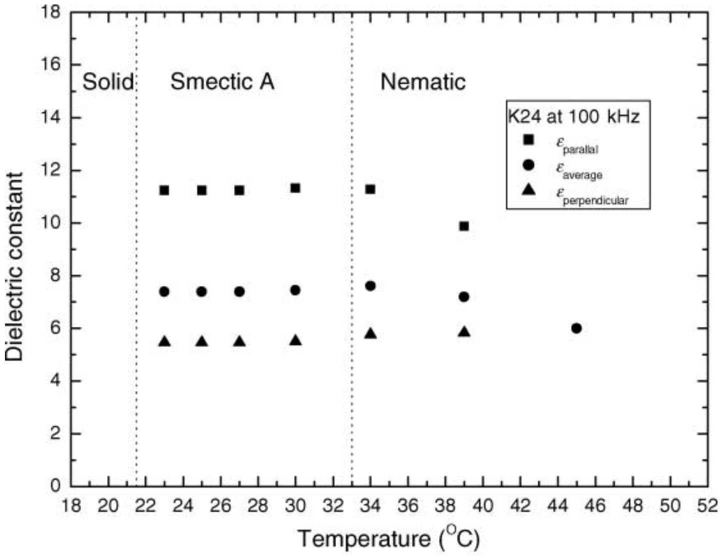


(a)



(b)

Figure 4. Variation of dielectric constant with temperature (a) at 1 kHz, (b) 10 kHz, and (c) 100 kHz.



(c)

Figure 4. (Continued)

temperature. These values are in close agreement with the values found by Buka and Bata [5] and from dielectric studies.

Dielectric Studies and Dipole Moment

The variation of dielectric constant with temperature is depicted in Fig. 4. Dielectric anisotropy is found to be 6.9 at 1 kHz, 6.1 at 10 kHz, and 5.5 at 100 kHz at 37°C, which

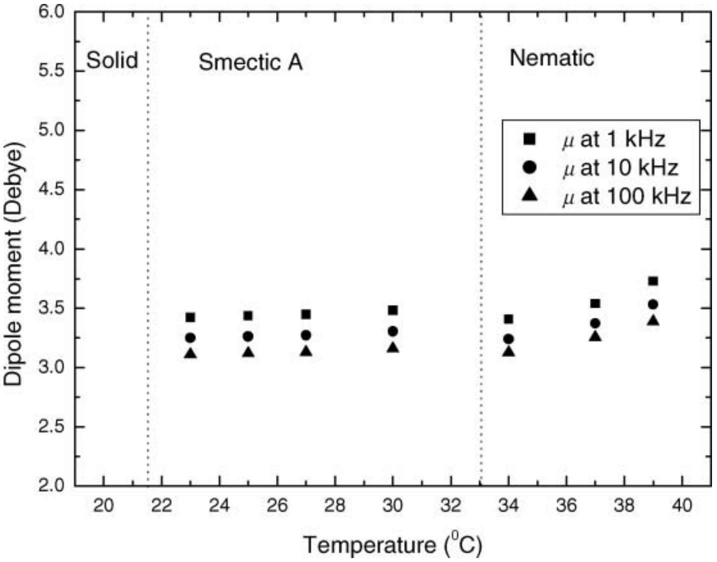


Figure 5. Variation of dipole moment with temperature.

is slightly less than the quoted value 7.7 at 1 kHz. There is a slight discontinuity at 33°C (smectic A to nematic transition) in $\varepsilon_{\mathrm{ave}}$ curve. $\varepsilon_{\mathrm{ave}}$ is also discontinuous with $\varepsilon_{\mathrm{iso}}$ at the nematic-isotropic transition. It is due to a pretransitional effect [4] that occurs in all nematics with strongly polar end groups and can be interpreted as a consequence of the antiparallel local ordering. On approaching from nematic-isotropic transition temperature from the isotropic phase, there is a coupling between the developing short-range nematic ordering and intrinsic antiparallel local ordering, resulting in increased antiparallel correlation, which reduces the molecular dipole moment contribution to $\varepsilon_{\mathrm{iso}}$. Similarly, the increase in $\varepsilon_{\mathrm{ave}}$ observed in nematic phase can be attributed to a decrease in antiparallel correlation resulting from the rapidly reducing long-range nematic ordering.

By using the expressions for $\varepsilon_{||}$ and $\varepsilon_{\perp}$ of Maier and Meier [13], the effective dipole moment μ and the angle of inclination β between the director direction and the molecular axis have been calculated from the following expressions:

$$\varepsilon_{\mathrm{ave}} = 1 + 4\pi \mathrm{NhF}(\alpha_{\mathrm{ave}} + \mathrm{F}\mu^2/3\mathrm{KT}) \tag{2}$$

and

$$\Delta\varepsilon = 4\pi \mathrm{NhF}\{\Delta\alpha - \mathrm{F}\mu^2(1 - 3\mathrm{Cos}^2\beta)/2\mathrm{kT}\} < P_2 > \tag{3}$$

where

$$\varepsilon_{\mathrm{ave}} = (\varepsilon_{||} + 2\varepsilon_{\perp})/3,\ \alpha_{\mathrm{ave}} = (\alpha_{\mathrm{e}} + 2\alpha_{\mathrm{o}})/3,\ \mathrm{f} = 4\pi\mathrm{N}(2\varepsilon_{\mathrm{ave}} - 2)/3(2\varepsilon_{\mathrm{ave}} + 1)$$
$$\mathrm{h} = 3\varepsilon_{\mathrm{ave}}/(2\varepsilon_{\mathrm{ave}} + 1),\ \mathrm{F} = 1/(1 - \alpha_{\mathrm{ave}}\mathrm{f})$$

$<P_2>$ values have been taken from the birefringence studies.

The variation of μ with temperature is depicted in Fig. 5. At frequencies of 1, 10, and 100 kHz, a discontinuity in dipole moment is observed in the smectic A to nematic transition at 33°C. Effective molecular dipole moment slightly decreases with an increase in frequency. Its value is 3.5 Debye at 1 kHz, 3.3D at 10 kHz, and 3.2D at 100 kHz at 34°C, indicating the presence of a polar end group. The value of angle β is almost constant with frequency and it is approximately 26° at 34°C. Variation of dipole moment in solution of the sample with concentration c (wt%) is shown in Fig. 6 at a fixed temperature of 34°C at 1 kHz. Extrapolating the curve to an infinite dilution, the molecular dipole moment of the sample is found to be 4.9 Debye. Thus, the molecules possess significant dipole moments in isolation, as they have a polar end group. The corresponding value of μ_{eff} (at 34°C, 1 kHz) in the nematic phase is 3.5 Debye. The correlation factor "g" may be calculated from the Kirkwood–Frolich theory [14] in which short-range dipole–dipole interaction has been considered explicitly. An estimate of the correlation factor has been obtained using the expression $g = \mu^2{}_{\mathrm{eff}}/\mu^2$, where μ is the molecular dipole moment obtained from the solution at an infinite dilution and μ_{eff} is the effective dipole moment defined in Equation (2). For no association between molecules, $g = 1$ and deviation of g from unity is indicative of molecular association. Positive deviation of g from unity, i.e., $g > 1$, results from parallel orientation of dipoles of neighboring molecules, while $g < 1$ results from antiparallel orientation. At 34°C, "g" is found to be 0.51 for 1 kHz, indicating a strong antiparallel correlation between neighboring molecules of the sample.

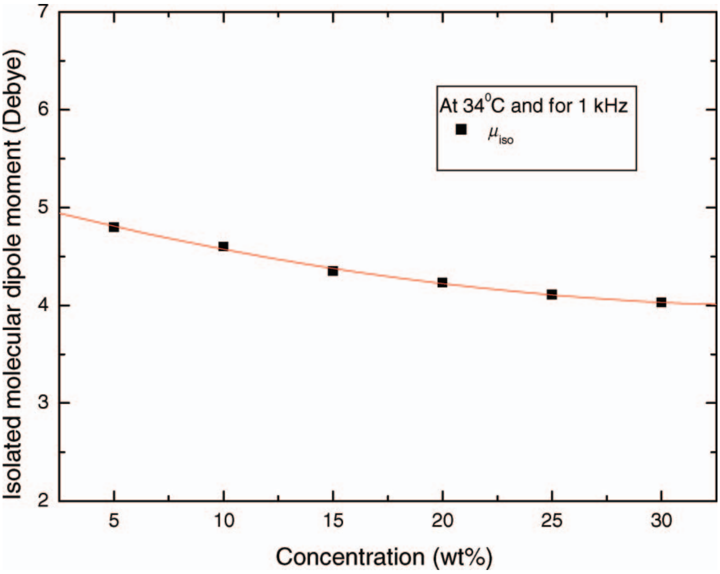


Figure 6. Variation of isolated molecular dipole moment with temperature.

Acknowledgments

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