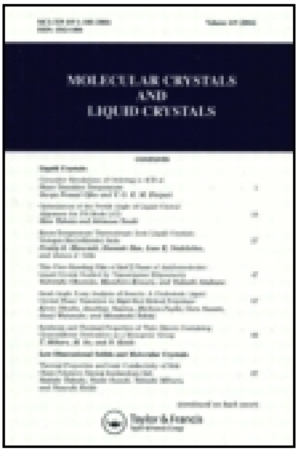


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Thermal Dependence of the Dielectric Behavior of Two Mesogens: A Comparative Study

Molly Dutta Gupta [a], Anuradha Mukhopadhyay [a] & Krzysztof Czuprynski [b]

[a] Department of Physics, Jadavpur University, Kolkata, India

[b] Department of Advanced Technologies and Chemistry, Military University of Technology, Warsaw, Poland

To cite this article: Molly Dutta Gupta, Anuradha Mukhopadhyay & Krzysztof Czuprynski (2012): Thermal Dependence of the Dielectric Behavior of Two Mesogens: A Comparative Study, Molecular Crystals and Liquid Crystals, 557:1, 240-250

To link to this article: http://dx.doi.org/10.1080/15421406.2011.654059

Mol. Cryst. Liq. Cryst., Vol. 557: pp. 240–250, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.654059

Thermal Dependence of the Dielectric Behavior of Two Mesogens: A Comparative Study

MOLLY DUTTA GUPTA,[1] ANURADHA MUKHOPADHYAY,[1,*]
AND KRZYSZTOF CZUPRYNSKI[2]

[1]Department of Physics, Jadavpur University, Kolkata, India
[2]Department of Advanced Technologies and Chemistry, Military University of Technology, Warsaw, Poland

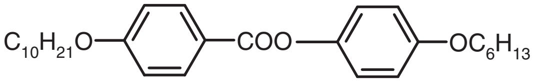
The temperature dependence of the dielectric properties of two thermotropic liquid crystalline mesogens has been investigated to provide a comparison of the OC_6H_{13} *and isothiocyanato (–NCS) groups. A comparative study of the variation of dielectric permittivities of the two compounds has been made and the effective molecular dipole moment* μ_{eff} *determined as a function of temperature. From the present study and previous optical studies [1], a comparison of the temperature variation of the angle of inclination* β *of the molecular dipole moment with the director for both mesogens could be determined and compared. In order to determine the nature of the molecular association in the mesophase, the molecular correlation factors* (g) *have been estimated from measurements of dipole moments of the compounds in solution.*

Keywords Angle of inclination; correlation factor; dielectric permittivity; effective molecular dipole moment

Introduction

The mesogenic compounds S4 and S5 are similar in their structural formula except for their terminal group (OC_6H_{13} in S4 and isothiocyanato [–NCS] group for S5). S5 is a member of the homologous series 4-isothiocyanatophenyl-4'-n-alkyloxybenzoate [2] with $n = 10$. The synthesis of these and some related compounds has been reported previously by Czuprynski [3, 4], and some preliminary X-ray work and phase transition temperatures reported [2, 5] on some members of the series. The present study is a continuation of our work [1] and is concerned with the dielectric properties of S4 and S5. The compounds S4 and S5 have the following structures and transition temperatures.

1. S4

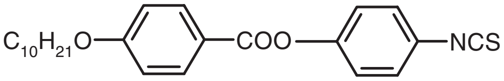


$$\text{Cr} \xrightarrow{62^\circ\text{C}} \text{SmC} \xrightarrow{78.2^\circ\text{C}} \text{SmA} \xrightarrow{83.6^\circ\text{C}} \text{N} \xrightarrow{89.5^\circ\text{C}} \text{I}$$

---

[*] Address correspondence to Anuradha Mukhopadhyay, Department of Physics, Jadavpur University, Kolkata, India. Tel: +919831195750. E-mail: anuradha_mukhopadhyay@yahoo.com

2. S5



$$\mathrm{Cr} \xrightarrow{77^{\circ}\mathrm{C}} \mathrm{SmA} \xrightarrow{97^{\circ}\mathrm{C}} \mathrm{I}$$

It is evident from the phase transition data given above that the introduction of the highly polar NCS moiety in S5 has caused the disappearance of the smectic C (SmC) phase and the nematic phase exhibited by S4. Also the melting temperature has increased considerably from 62°C (S4) to 77°C (S5) and the clearing point has been extended to 97°C in S5. We are thus interested in studying the differences in behavior of these compounds and the present work focuses on the dielectric aspects of these differences. The thermal dependence of the effective molecular dipole moment μ_{eff} of these compounds in the mesophase has been determined from dielectric studies. From the present study and previous optical studies [1], a comparison of the temperature variation of the angle of inclination β of the molecular dipole moment with the director for both mesogens has been determined and compared. The variation of the dipole moments μ_{sol} of the mixtures in solutions of varying concentrations (%wt) at a particular temperature have been investigated and the molecular dipole moment μ_{iso} of the isolated molecules have been determined. In order to determine the nature of the molecular association in the mesophase, the molecular correlation factors (g) have been estimated from measurements of dipole moments of the compounds in solution.

Experimental Methods

Routine optical microscopic studies were conducted to confirm the phase transition temperatures as mentioned in [1]. Each sample was introduced into a hot stage (Mettler FP 82 HT) and the temperature was raised at the rate of 1°C min^{-1} during heating and the texture viewed through a polarizing microscope (Leitz) having a magnification of 150×. Phase transition temperatures were noted during heating and cooling.

A. Dielectric Studies

In order to perform dielectric studies a pair of indium tin oxide (ITO) coated conducting glass plates, separated by thin cover slips on three sides were used to prepare the sample cells (or capacitor). The sample cells have an effective size of 4.0 cm × 2.5 cm × 0.5 cm and its capacitance (air) is ~21 μF. 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). Each sample 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 of a temperature 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 dielectric permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were evaluated from the capacitance values by standard procedure of calibration. The bridge voltage across the sample was maintained sufficiently low (∼0.3 V) so as not to produce any electric-field-induced instability. The effect of electrode polarization or any other parasitic phenomena is canceled out during the process of standardization of the cell using standard liquids.

B. Measurement of Dipole Moment of Isolated Molecule

Different concentrations of the solutions of each compound in *p*-xylene (a nonpolar solvent) were prepared. Each solution was introduced into the sample cell (a fresh, standardized sample cell was used for each sample) and dielectric studies were performed at 10 kHz to obtain the dielectric permittivities ε_{12} of the solutions at a particular temperature (80°C). The dielectric permittivity ε_1 of the solvent was likewise determined at the same temperature.

Birefringence studies of the solutions were carried out with a He-Ne laser source ($\lambda = 633$ nm) using the Chatelain – Wedge [6] method. Details of the experimental arrangement and procedure are given in [7]. The solutions of different concentrations (by %wt) were introduced in a glass prism (angle ∼1–2°), which was inserted in a sample holder of a temperature regulated with an accuracy of ±0.5°C. The prism was prepared with glass slides whose inner surfaces were treated with polyvinyl alcohol for surface alignment. The sample holder was placed in an aligning magnetic field of ∼8 kGauss to further ensure an aligned monodomain sample. The sample was heated to the required temperature (80°C) in the aligning field and the He-Ne beam was made incident on the prism. From the deviations of the refracted beam, the refractive indices of the solutions could be calculated. The refractive index of all solvents was likewise determined at the same temperature. The above data were used in obtaining the molecular dipole moment from the following relation [8].

$$\mu_{\text{sol}}^2 = \frac{27K_{\text{B}}T\left\{\left(\varepsilon_{12} - n_{12}^2\right) - \left(\varepsilon_1 - n_1^2\right)\right\}}{4\pi N(\varepsilon_1 + 2)\left(n_1^2 + 2\right)c} \tag{1}$$

Where the numbers 1 and 12 refer to the solvent and solution parameters respectively, c is the concentration (mol/cc) at temperature T (K), N is the Avogadro number and K_{B} is the Boltzmann constant.

The dipole moment μ_{iso} of the isolated molecule was obtained by extrapolating the curve of μ_{sol} versus concentration (c) to infinite dilution. The values obtained in esu cm obtained may be converted to a Coulomb-meter or Debye using the factor of 3.3356×10^{-12}.

Results and Discussions

The phase transition temperatures recorded and reported in [1], were reconfirmed and are given below for completeness and easy reference.

1. S4: Phase transition temperatures.

$$\text{Crystal} \underset{62.0 \circ \text{C}}{\overset{62.1 \circ \text{C}}{\underset{<\,-\,-\,-}{-\,-\,->}}} \text{Smectic C} \underset{79.2 \circ \text{C}}{\overset{79.4 \circ \text{C}}{\underset{<\,-\,-\,-}{-\,-\,->}}} \text{Smectic A} \underset{83.1 \circ \text{C}}{\overset{84.0 \circ \text{C}}{\underset{<\,-\,-\,-}{-\,-\,->}}} \text{Nematic} \underset{87.1 \circ \text{C}}{\overset{88.3 \circ \text{C}}{\underset{<\,-\,-\,-}{-\,-\,->}}} \text{Isotropic}$$

2. S5: Phase transition temperatures.

$$\text{Crystal}\ \underset{77.0\circ\text{C}}{\overset{77.2\circ\text{C}}{\rightleftarrows}}\ \text{Smectic A}\ \underset{95.5\circ\text{C}}{\overset{96.4\circ\text{C}}{\rightleftarrows}}\ \text{Isotropic}$$

Dielectric Studies

The nature of thermal variation of dielectric permittivities ($\varepsilon_{\|}$ and $\varepsilon_{\perp}$) for both compounds at frequencies 1, 10, and 100 kHz are depicted in Figs. 1 and 2. From the figures, it is evident that the average dielectric permittivity ε_{ave} is higher for S5 than S4 at all frequencies. The average values being 6.32, 6.76, and 7.42 at 1, 10, and 100 kHz, respectively for S5 (80°C), the corresponding values for S4 being 4.57, 4.83, and 4.89. This is compatible with the optical data where the average refractive index $n_{\text{ave}} = ({n_{\text{e}}}^2 + 2{n_{\text{o}}}^2)/3$ was found to be greater for S5 (1.58 at 80°C) compared to S4 (1.51 at 80°C) [1].

It is observed that for both the compounds $\varepsilon_{\|}$ decreases with increase in frequency but the increase in $\varepsilon_{\perp}$ more than compensates for this decrease, contributing to the increase in ε_{ave}. Consequently the dielectric anisotropy $\Delta\varepsilon$ also decreases with frequency for both the compounds. This point is discussed later in more detail.

In case of S4, ε_{ave} is more or less constant in the SmC phase, but increases slightly in the smectic A (SmA) and nematic phases. The discrepancy of ε_{ave} with ε_{iso} at T_{NI} is just discernable at 1 kHz but becomes more significant with increase in operating frequency. This feature is also observed in the optical behavior [1], where n_{ave} shows a discontinuity with n_{iso} at the N-I transition. This behavior is attributed to molecules with relatively high or moderate molecular dipole moment [9]. For S5, the average ε_{ave} remains more or less constant throughout the SmA range and its discontinuity with ε_{iso} at $T_{\text{SmA-I}}$ is hardly perceptible. This behavior is also in agreement with the optical behavior of S5 where discrepancy between n_{ave} and n_{iso} at $T_{\text{SmA-I}}$ is hardly discernable. Though in nematic-isotropic transitions this is generally attributed to nonpolar compounds [10], the same may possibly not be inferred for SmA-I transition as it is expected that S5 having a terminal isothiocyanato group (-NCS) will have a strong molecular dipole moment.

Dielectric anisotropy $\Delta\varepsilon$ is greater for S5 (2.76 at 1 kHz) than for S4 (2.57 at 1 kHz) at 80°C as in the case with optical anisotropy Δn [1]. This is as per our expectation since polar terminal isothiocyanato group is commonly employed to increase the birefringence by elongating the molecular conjugation [11]. However at higher frequencies of 10 and 100 kHz, $\Delta\varepsilon$ for S4 is greater than for S5 having values of 2.0 and 1.67 (at 10 and 100 kHz respectively), corresponding values for S5 being 1.79 and 1.42. It is evident that $\Delta\varepsilon$ for both S4 And S5 declines with frequency the effect being more marked for S4 than S5. This behavior may be a pointer to the crossover effect exhibited in the megahertz frequency range especially by compounds with carboxylic bridges where at a certain frequency the sign of dielectric anisotropy changes [12]. The estimated error in determination of the dielectric permittivity is about 2%.

The effective dipole moment μ_{eff} and the angle of inclination β have been computed using the following relations (2 and 3), which have been obtained from the expressions for $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ [13].

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

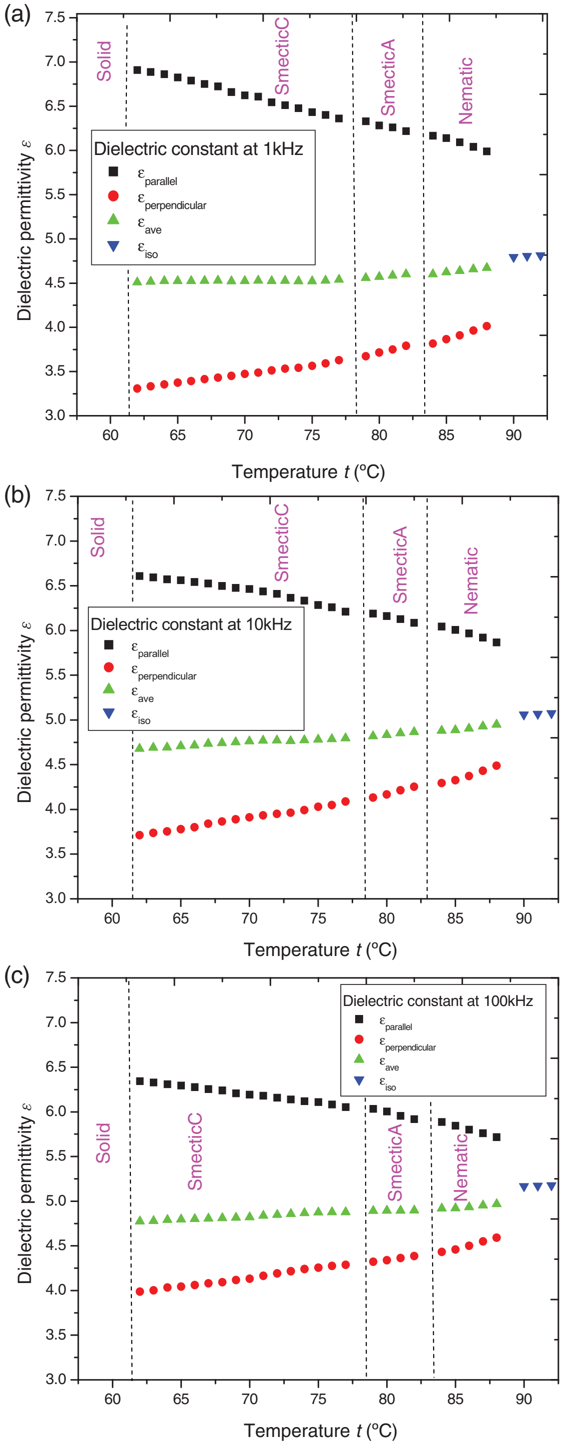


Figure 1. Thermal variation of dielectric permittivity of S4 at (a) 1 kHz, (b) 10 kHz, (c) 100 kHz.

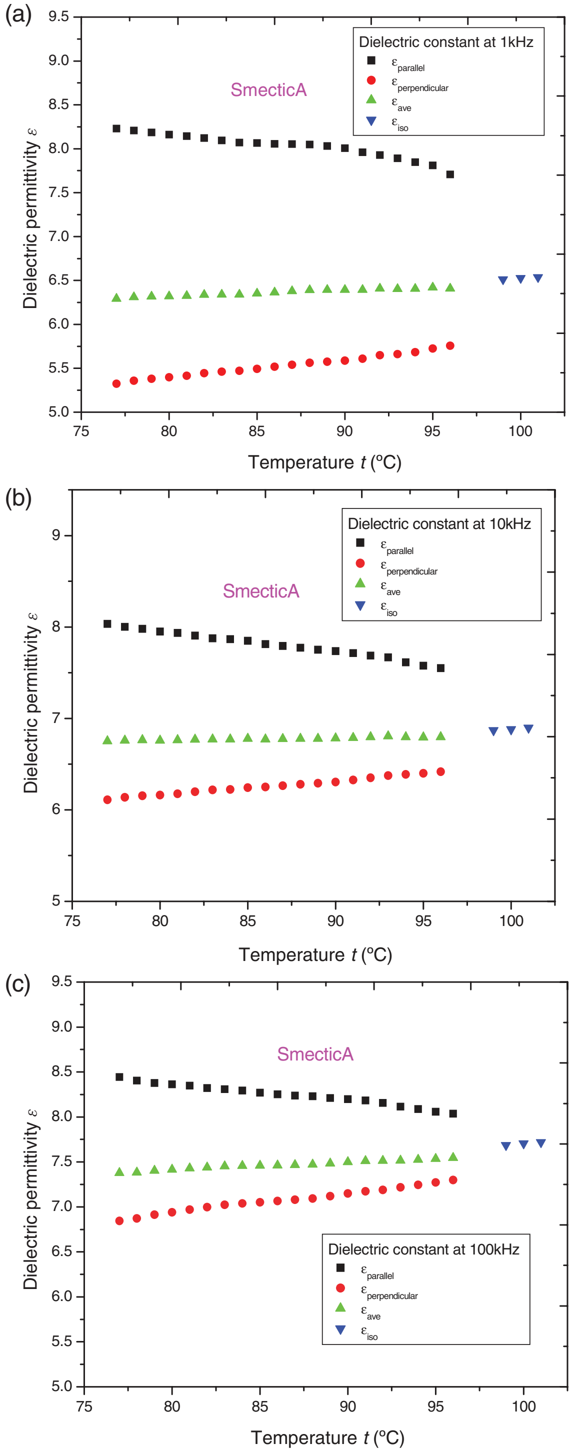


Figure 2. Thermal variation of dielectric permittivity of S5 at (a) 1 kHz, (b) 10 kHz, (c) 100 kHz.

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

Where,

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

The values of polarizability anisotropy $\Delta\alpha$, average molecular polarizability α_{ave}, and orientational order parameter (P_2) at different temperatures have been taken from our optical data [1].

The variation of μ_{eff} with temperature at three frequencies 1, 10, and 100 kHz are shown in Figs. 3 and 4. In case of S5, μ_{eff} increases gradually with temperature in SmA phase at all frequencies and is greater for higher frequency at any particular temperature, values being 2.82, 2.96, and 3.16 Debye at 1, 10, and 100 kHz at 80°C. In case of S4, the increase of μ_{eff} with temperature is more conspicuous, the increase being sharper in the SmA and nematic phases than in the SmC phase. The μ_{eff} values for S4 also increase with operating frequency, though the difference from 10 kHz to 100 kHz is hardly perceptible especially in the nematic phase. At 80°C (SmC phase) μ_{eff} values for S4 are 2.32, 2.44, and 2.46 at 1, 10, and 100 kHz respectively. It is thus evident that the polar terminal isothiocyanato group is responsible for the increased effective molecular dipole moment of S5 as compared to S4.

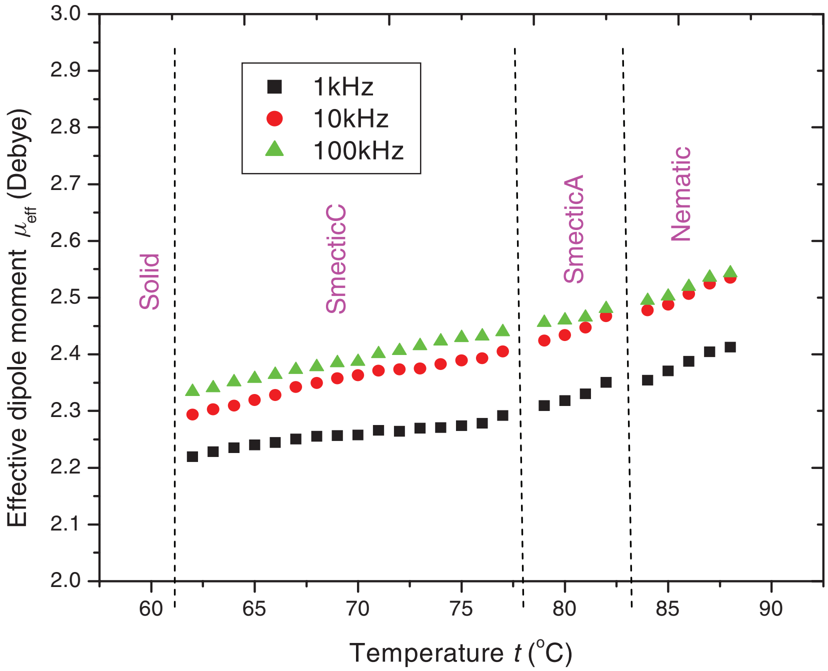


Figure 3. Thermal variation of effective molecular dipole moment μ_{eff} of S4.

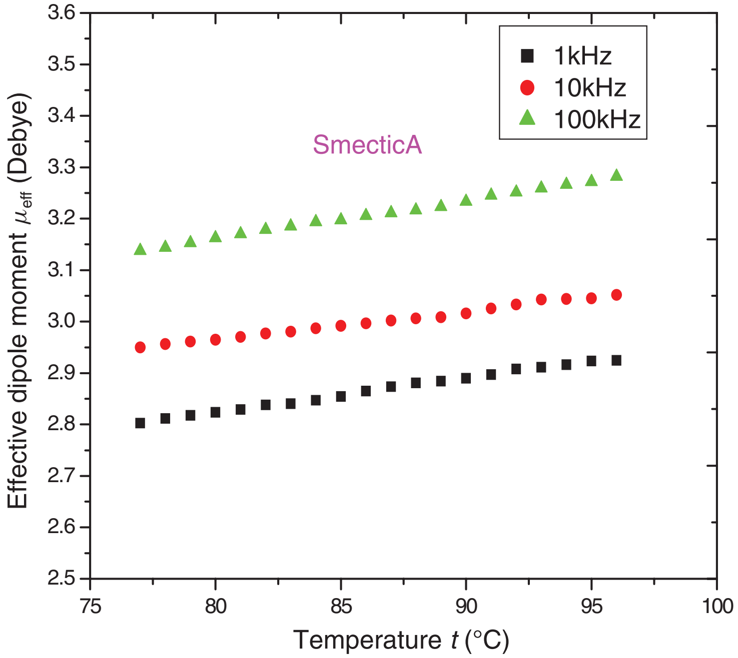


Figure 4. Thermal variation of effective molecular dipole moment μ_{eff} of S5.

The temperature dependence of the angle of inclination β of the two liquid crystalline compounds S4 and S5 at 1, 10, and 100 kHz frequencies are depicted in Figs. 5 and 6 respectively. In general, β values are found to increase with increase in frequency from 1 kHz to 10 kHz and from 10 kHz to 100 kHz, values at 80°C being 25.11°, 35.34°, 39.20° and 41.63°, 47.49°, 49.96° (at 1, 10, and 100 kHz) for S4 and S5 respectively. With temperature, S5 does not show any marked increase of β, in fact a decrease is noted at 1 kHz to 10 kHz near clearing point. In S4, the trends in variation in the three different phases are different. In the SmC phase, β fluctuates about an average where as in SmA and nematic phases there is an overall increase with increase in temperature.

Dipole Moment In Solution

Variations of the dipole moment in solution μ_{sol} with concentration c (%wt) are shown in Figs. 7 and 8 for both the samples at a temperature of 80°C and operating frequency of 10 kHz. By extrapolating the curve to an infinite dilution, the isolated or free molecular dipole moments of S4 and S5 are found to be 2.5D and 3.15D respectively. Therefore, both the molecules possess significant dipole moment in isolation. Comparing the above values of μ_{iso} with the corresponding values of μ_{eff} (at 80°C and 10 kHz), which are 2.43 and 2.96D respectively, we note that there is a difference between them, the difference indicating correlation between neighboring molecules. The Kirkwood theory [14] based on a short-range molecular correlation has been extended by Frolich [15] to include the deformation polarizability of the molecules. This has led to the Kirkwood–Frolich theory [16] from which the Kirkwood correlation factor (g) may be obtained, which gives a measure of the molecular association between a reference molecule and its nearest neighbors and a

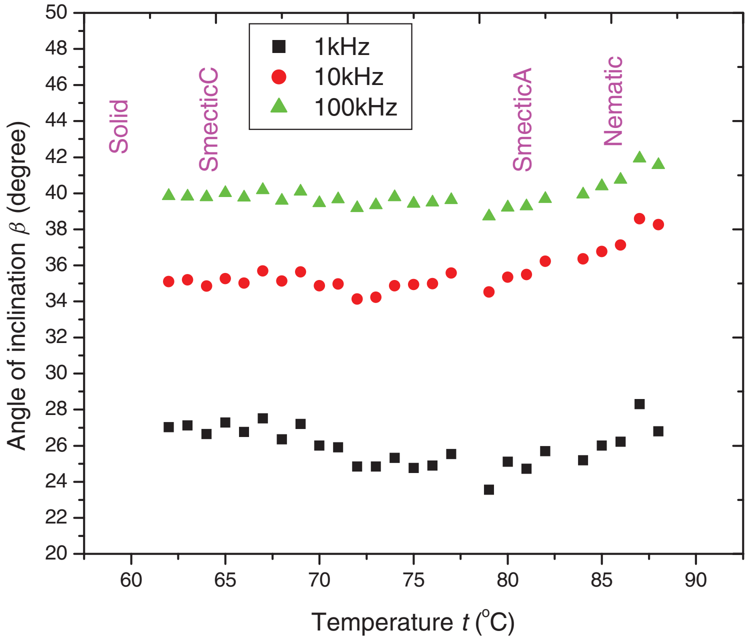


Figure 5. Thermal variation of angle of inclination β of S4.

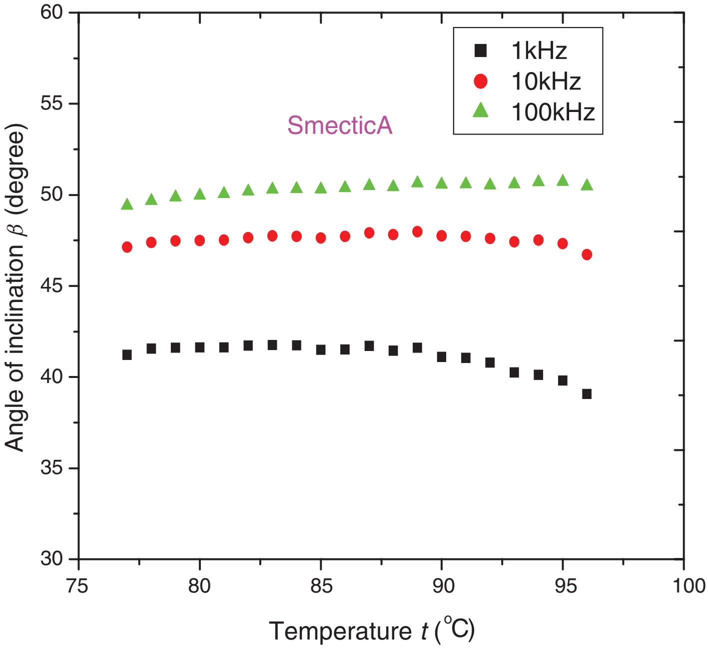


Figure 6. Thermal variation of angle of inclination β of S5.

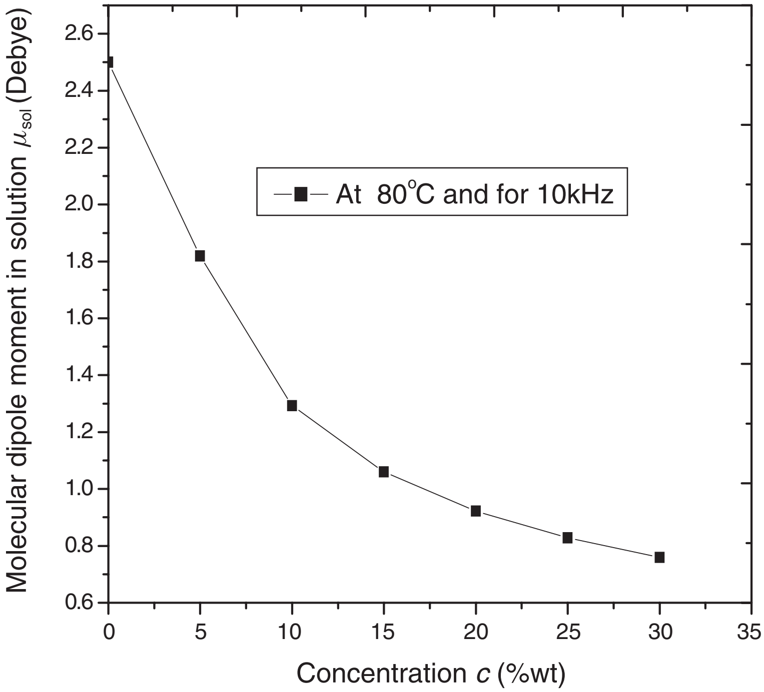


Figure 7. Variation of molecular dipole moment of S4 in solution with concentration.

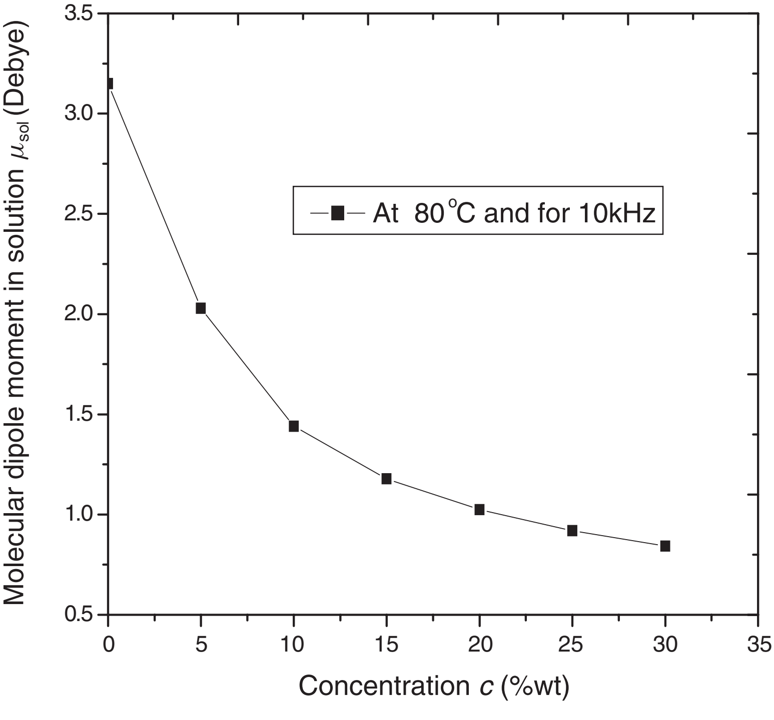


Figure 8. Variation of molecular dipole moment of S5 in solution with concentration.

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 [17, 18]; $g > 1$ 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 both the samples from the Kirkwood factor (g) using the expression $g = {\mu_{\mathrm{eff}}}^2/{\mu_{\mathrm{iso}}}^2$. At 80°C, the values for both the samples were obtained at a frequency of 10 kHz are 0.95 and 0.89 for S4 and S5 respectively, indicating an antiparallel correlation between neighboring molecules in both the compounds, the correlation being greater in S5 than in S4.

Conclusion

The present study reveals that the replacement of the OC_6H_{13} group at the terminal position of S4 by the isothiocyanato group (S5), besides causing changes in the mesogenic range and obliterating the SmA and nematic phases, has caused a significant increase in the molecular dipole moment. The associated increase in $\Delta\varepsilon$ value of S5 compared to S4, though in agreement with increase in Δn observed from our optical studies, is only at the operating frequency of 1 kHz and decreases subsequently at higher operating frequency of 10 kHz to 100 kHz. Whether this observation is a precursor to the cross-over effect exhibited by many systems containing carboxylic bridges can only be concluded from dielectric studies in the dynamic frequency range. The higher dipole moment of S5 when compared to S4 is also reflected in the respective 'g' values, which indicate stronger antiparallel molecular–molecular correlation of S5 than S4.

References

[1] Dutta Gupta, M., Mukhopadhyay, A., & Czuprynski, K. (2010). *Phase Trans.*, *83*(4), 284.

[2] Heppke, G., Pfeiffer, S., Ranft, A., & Shashidhar, R. (1991). *Mol. Cryst. Liq. Cryst.*, *206*, 31.

[3] Dabrowski, R., Dziaduszek, J., Szczucinski, T., Stolarzowa, Z., & Czuprynski, K. (1989). *Liq. Cryst.*, *5*(1), 209.

[4] Dabrowski, R., Dziaduszek, J., Drzewinski, W., Czuprynski, K., & Stolarz, Z. (1990). *Mol. Cryst. Liq. Cryst.*, *191*, 171.

[5] Sawada, T., Satonaka, H., & Arai, I. (1985). *11th Jpn. Symp. Liq. Cryst.*, Kanazawa 2S05.

[6] de Jeu, W. H. (1980). *Physical Properties of Liquid Crystalline Materials*, Gordon & Breach: London, p. 35.

[7] Bhowmick, K., Mukhopadhyay, A., & Mukherjee, C. D. (2003). *Phase Trans.*, *76*(7), 671.

[8] Guggenheim, E. A. (1949). *Trans. Faraday Soc.*, *45*, 714.

[9] Raja, V. N., Krishna Prasad, S., Shankar Rao, D. S., and Chandrasekhar, S. (1992). *Liq. Cryst.*, *12*(2), 239.

[10] de Jeu, W. H., & Lathouwers, T. W. (1974). *Z. Naturforsch*, *29a*, 905.

[11] Gauza, S., Wu, S. T., Spadlo, A., & Dabrowski, R. (2006). *J. Disp. Tech.*, *2*(3), 247.

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

[13] Maier, W., & Meier, G. (1961). *Z. Naturforsch*, *16a*, 1200.

[14] Kirkwood, J. G. (1939). *J. Chem. Phys.*, *7*, 911.

[15] Frohlich, H. (1949). *Theory of Dielectrics*, Oxford University Press: London.

[16] Bottcher, C. J. F. (1973). *Theory of Electric Polarisation*, 2nd ed., Vol. 1, Sec. 39, Elsevier: Amsterdam.

[17] Onsager, L. (1936). *J. Am. Soc.*, *58*, 1486.

[18] Smyth, C. P. (1980). *Molecular Interactions*, Vol. II. New York: John Wiley & Sons Ltd.