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Mesogenic Mixtures with Identical Moieties: Dielectric Properties and Dipole Moments

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Thermal variation of dielectric properties of two thermotropic liquid crystalline mixtures (code names: ZLI 1221 and ZLI 1291) containing identical moieties but possessing different mesogenic ranges have been investigated. Both mixtures contain the same constituents: phenyl cyclohexane, biphenyl cyclohexane, and cyclohexyl benzoate, but their distinct mesogenic ranges, due to different proportional constituents, make them interesting cases of study. In the present work, we have made a comparative study of the variation of dielectric permittivities ($\varepsilon_{\|}$ *and* $\varepsilon_{\perp}$*) as a function of temperature for both mixtures in an aligning magnetic field at different frequencies (1, 10, and 100 kHz). From the present study and optical studies (performed earlier) [1], a comparison of the temperature variation of the angle of inclination* β *of the molecular dipole moment with the director for both mixtures could be determined and compared. The variation of the dipole moment* μ_{sol} *of the mixtures in solutions of varying concentrations (in %wt) at a particular temperature have been investigated and the molecular dipole moment* μ_{iso} *of the isolated molecules have been determined. A method of estimating molecular weights using* μ_{sol} *values (when the proportional composition is unknown) has also been developed.*

Keywords Angle of inclination; dielectric; dipole moment; mesogenic mixture; thermotropic

Introduction

The tailoring of mesogenic properties by the synthesis of liquid crystalline mixtures is well known. The present case of study is an example of the tailoring of mesogenic behavior of liquid crystalline material not by changing the constituent moieties but by varying the proportionality of the constituents. The present study has been undertaken to investigate and compare the nature of changes caused in the dielectric behavior of the above mentioned mixtures. A comparative study of the optical properties has already been reported [1].

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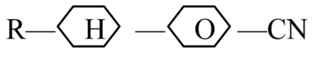
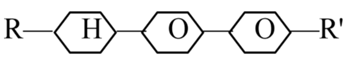
The mesogenic mixtures ZLI 1221 and ZLI 1291 (code names, manufactured by Merck Ltd.) contain the following moieties and exhibit the following phase transition temperatures:



(phenyl cyclohexane)



(biphenyl cyclohexane)

(cyclohexyl benzoate),

where $R = C_nH_{2n+1}$, $R' = C_mH_{2m+1}$.

Mixture 1: ZLI 1221

$$\text{Solid} \xrightarrow{-11^\circ\text{C}} \text{Nematic} \xrightarrow{90^\circ\text{C}} \text{Isotropic.}$$

Mixture 2: ZLI 1291

$$\text{Solid} \xrightarrow{-10^\circ\text{C}} \text{Nematic} \xrightarrow{107^\circ\text{C}} \text{Isotropic.}$$

These mixtures are nematics, exhibiting a nematic phase over a wide range of temperatures, and we note that the mesogenic range of mixture 2 (ZLI 1291) has an enhanced (by ~17°C) mesogenic range in comparison to that of mixture 1. The difference in the width of the nematic ranges and the enhancement of the nematic–isotropic phase transition temperature suggest that the moieties though identical are present in different proportions in the two mixtures and present a very good instance of the extent of tuning or tailoring of mesogenic behavior by varying proportional composition alone. We are, therefore, interested to explore the nature and degree of differences in mesogenic behavior of these two mixtures. The present work concentrates on the differences in dielectric behavior.

Experimental Methods

A. Optical Microscopy

Optical microscopy of both the samples, mixtures 1 and 2, was carried out to confirm the nature of the mesophase and the phase transition temperatures, prior to dielectric studies. Each sample taken on a clean glass surface and covered with a cover slip was introduced into a hot stage (Mettler FP 82 HT) whose temperature was raised at the rate of 1°C/min during heating. The texture was viewed through a polarising microscope (Leitz) having a magnification of 150X. Phase transition temperatures were noted during heating and cooling.

B. 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 has been used to prepare the sample cells (or capacitor). The sample cells each have an effective size of 4.0 cm × 2.5 cm × 0.5 cm and with capacitance (air) ~21 pF. 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 mixture was introduced into the cell as an isotropic liquid through the open end which was subsequently sealed. The sample cell was encapsulated within a sample holder whose temperature was regulated by a temperature controller by (±1°C), was taken through a number of temperature cycles in the 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 permittivity $\varepsilon_{\parallel}$ 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 instabilities.

C. Measurement of Dipole Moment of Isolated Molecule

Solutions of different concentrations (by %wt) were prepared for each of the samples in a non-polar solvent (p-xylene). The solution was introduced into a fresh sample cell prepared and standardized as before and the dielectric permittivities ε_{12} of the solution were determined at 1 kHz for each of the concentrations of the solution at a fixed temperature (70°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 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 ~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 upto ±1°C with the help of a temperature controller, was placed in an aligning magnetic field of 8 kGauss. The laser beam was made incident on the solution through a hole in the sample holder and the emerging beam projected on a screen held several meters away (~5.0 m). From angular deflection on the screen, the refractive indices n_{12} of the solution could be determined at a particular temperature with knowledge of the prism angle. Details of the experimental arrangement and procedure are described in [2]. The refractive index of the solvent n_1 was likewise determined at the same temperature. The same procedure was repeated for each of the mixtures.

The dipole moments μ_{sol} of the molecules in a solution of concentration c (mole/cc) at a fixed temperature (°K) were obtained from the following relation [3]:

$$\mu_{\text{sol}}^2 = \frac{27KT\{(\varepsilon_{12} - n_{12}^2) - (\varepsilon_1 - n_1^2)\}}{4\pi N(\varepsilon_1 + 2)(n_1^2 + 2)c}$$

(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 moment μ_{sol} with the 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 for each mixture. The values in esu cm obtained above might be converted to a Coulomb meter using the factor of 3.3356×10^{-12}.

Results and Discussions

Optical Microscopy

From optical microscopy the phase transition temperatures observed are as follows:

Mixture 1 (ZLI 1221)

$$\text{Solid} \longrightarrow \text{Nematic} \underset{88.5^\circ\text{C}}{\overset{89.2^\circ\text{C}}{\rightleftarrows}} \text{Isotropic.}$$

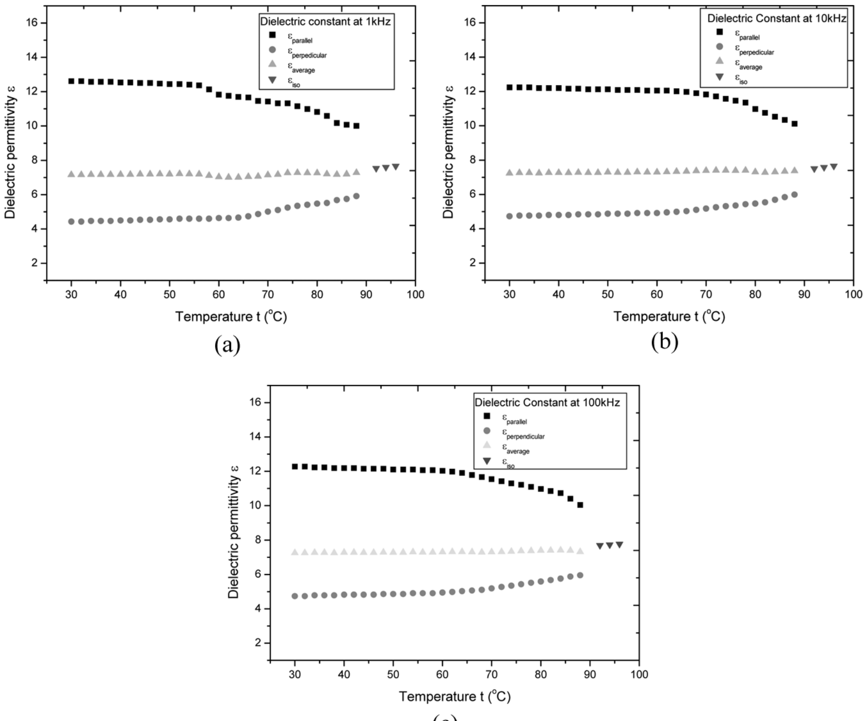
Mixture 2 (ZLI 1291)

$$\text{Solid} \longrightarrow \text{Nematic} \underset{106.1^\circ\text{C}}{\overset{106.5^\circ\text{C}}{\rightleftarrows}} \text{Isotropic.}$$

The transition temperatures (reported in [1]) from nematic to isotropic phase are in close agreement with the quoted values (Merck Ltd.). Since there is no arrangement to cool the sample below room temperature, the crystalline to nematic transition temperatures could not be verified, and no photographs were taken in this temperature region.

Dielectric Studies

The thermal variation of dielectric permittivities ($\varepsilon_{\|}$ and $\varepsilon_{\perp}$) for both mixtures at frequencies 1, 10, and 100 kHz are depicted in Figs. 1(a)–(c) and 2(a)–(c). The effect of electrode polarization or any other parasitic phenomenon is cancelled out during the process of standardization of the sample cell using standard liquids. Our observations show that the average dielectric permittivity ε_{ave} is higher for all the frequencies for mixture 2 than for mixture 1. However, a lowering of dielectric anisotropy is observed on comparing the $\Delta\varepsilon$ values of mixture 2 with that of mixture 1, the experimental $\Delta\varepsilon$ values at 1 kHz being 7.88 (50°C) for mixture 1, and 8.68 (50°C) for mixture 2. The quoted values (supplied by Merck Ltd): 8.0 and 8.6, respectively (temperatures not specified) compare very well with our experimental findings. It is also observed that the dielectric anisotropy $\Delta\varepsilon$ decreases with the increase in frequency for both the mixtures. The average values of dielectric permittivity ε_{ave} are 7.19, 7.29, and 7.28 at frequencies 1, 10, and 100 kHz, respectively, at a temperture of 50°C for mixture 1, and the corresponding values are 7.85, 7.60, and 7.57, respectively, at 50°C for mixture 2. The fall in ε_{ave} for mixture 2 may be attributed to the increase in dielectric loss with increasing operating frequency. No such comment may be made for mixture 1, except that $\varepsilon_{\|}$ decreases with increase in frequency, but $\varepsilon_{\perp}$ increases contributing to the increase in ε_{ave}. ε_{ave} is almost constant throughout the nematic range and continous with the respective ε_{iso} at T_{NI} for both the mesogenic mixtures. Similar behavior is exhibited by the refractive indices of



(a) (b)

(c)

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

the mixtures [1]. This is generally the case for liquids with small dipole moments [4], in contrast to liquids with strongly polar molecules of dipole moments (in the range of 4–5 D). The estimated error in determination of the dielectric permittvity is about 2%.

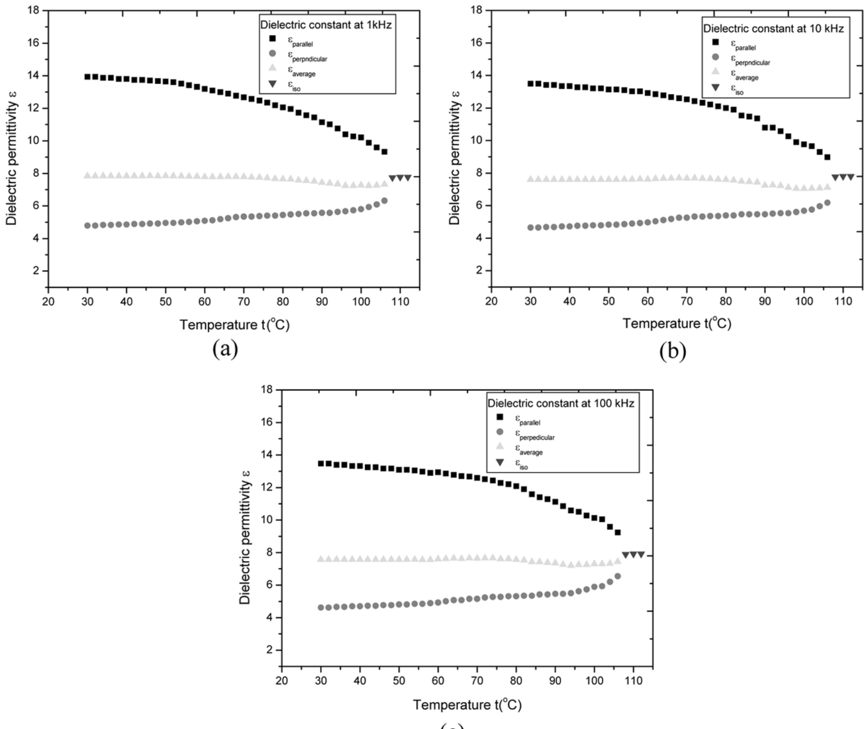
In the present study, since the proportional composition (in weight) of the constituents in the mesogenic mixtures are unknown, the molecular weight 'M' and hence the polarisability α cannot be determined. As a result the effective molecular dipole moment μ_{eff} could not be obtained. However, α/M values have been determined in our previous work [1], and in the present investigation μ_{eff} values have been determined in terms of molecular weight, i.e., $\mu_{\mathrm{eff}}^2/\mathrm{M}$ could be calculated using simple algebra as derived below and following the expression of Maier and Meier [5] viz.,

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

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

$$\varepsilon_{\mathrm{ave}} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3, \quad \alpha_{\mathrm{ave}} = (\alpha_e + 2\alpha_{\mathrm{o}})/3, \quad F = 1/(1 - \alpha_{\mathrm{ave}}f);$$

N is the number of molecules per cc ($\mathrm{N} = \mathrm{N_A d/M}$, $\mathrm{N_A}$ is Avogadro number, d is the density measured at different temperatures, and M is the molecular weight).



(a) (b)

(c)

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

Expression for μ^2/M and β:

The average polarisability $\alpha_{\rm ave}$ using Vuk's formula[6] is given by,

$$\alpha_{ave} = \frac{1}{4\pi N}\left[\frac{2(n_o^2-1)+(n_e^2-1)}{n_{ave}^2+2}\right],$$

i.e.,

$$\alpha_{ave} = \frac{M}{4\pi N_A d}\left[\frac{2(n_o^2-1)+(n_e^2-1)}{n_{ave}^2+2}\right],$$

or

$$\alpha_{\rm ave} = {\rm Mx}, \qquad (2)$$

where

$$x = \frac{[2(n_o^2-1)+(n_e^2-1)]}{4\pi N_A d(n_{ave}^2+2)}.$$

Using Eq. (2) in Eq. (1),

$$Mx + \frac{F\mu^2}{3KT} = \frac{(\varepsilon_{ave} - 1)}{4\pi N_A dhF} M$$

or

$$\frac{\mu^2}{M} = \frac{3KT}{F}\left[\frac{(\varepsilon_{ave} - 1)}{4\pi N_A dhF} - x\right]. \tag{3}$$

The density ‘d’ at different temperatures have been determined in our previous work [1] and used for calculating μ^2/M. F may be calculated since the unknown ‘M’ values get cancelled off in the ‘α_{ave}f’ part in the expression for F mentioned in Eq. (1). From measured values of ε and experimental values of refractive indices [1] (obtained earlier), the right-hand side of Eq. (3) and, therefore, μ^2/M may be determined.

μ^2/M values thus obtained have been tabulated (Table 1) for both the mixtures at different temperatures at a frequency of 1 kHz.

For calculation of β we start with the following expression of Maier and Meier [5]:

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

Table 1. Variation of μ^2/M with temperature for mixtures 1 and 2

	μ^2/M (Debye^2/gm)	
Temperature °C	Mixture 1	Mixture 2
50	0.0091	0.0075
52	0.0095	0.0077
54	0.0099	0.0080
56	0.0102	0.0083
58	0.0104	0.0085
60	0.0106	0.0088
62	0.0109	0.0091
64	0.0113	0.0094
66	0.0117	0.0097
68	0.0121	0.0099
70	0.0127	0.0102
72	0.0132	0.0104
74	0.0138	0.0107
76	0.0142	0.0109
78	0.0145	0.0111
80	0.0149	0.0114
82	0.0151	0.0117
84	0.0154	0.0119

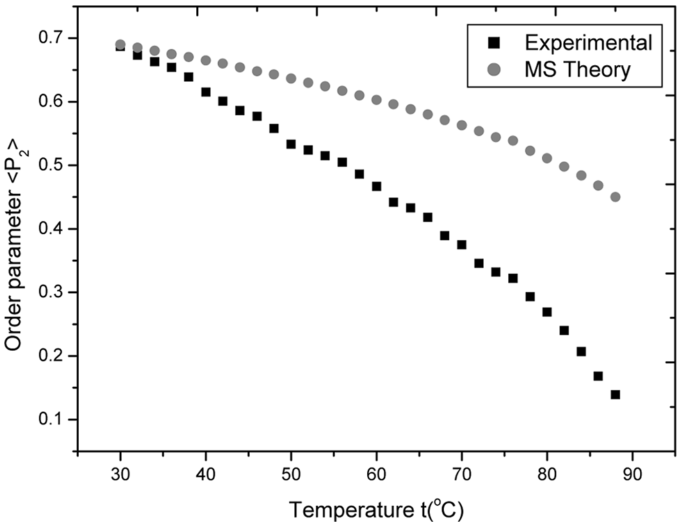


Figure 3. Thermal variation of order parameter of mixture 1.

i.e.,

$$\Delta\varepsilon = \frac{4\pi N_A dhF}{M}\left[\Delta\alpha - \frac{F\mu^2(1-3\cos^2\beta)}{2KT}\right]\langle P_2\rangle, \tag{4}$$

where

$$\Delta\alpha = \alpha_e - \alpha_o = \mathrm{M}x' \tag{5}$$

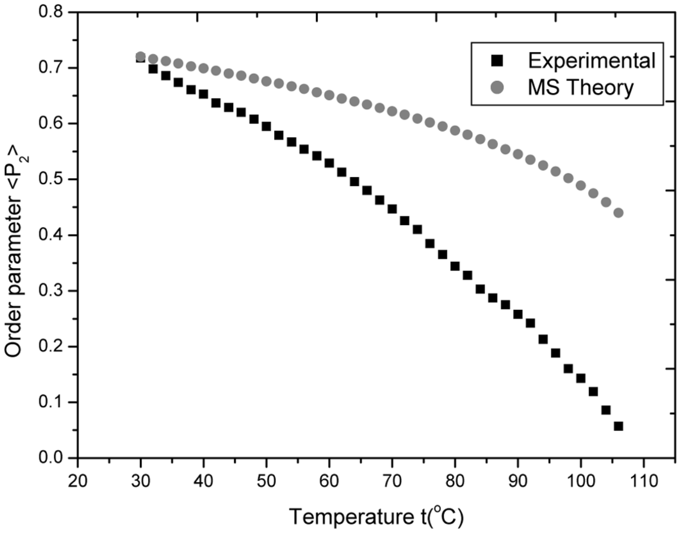


Figure 4. Thermal variation of order parameter of mixture 2.

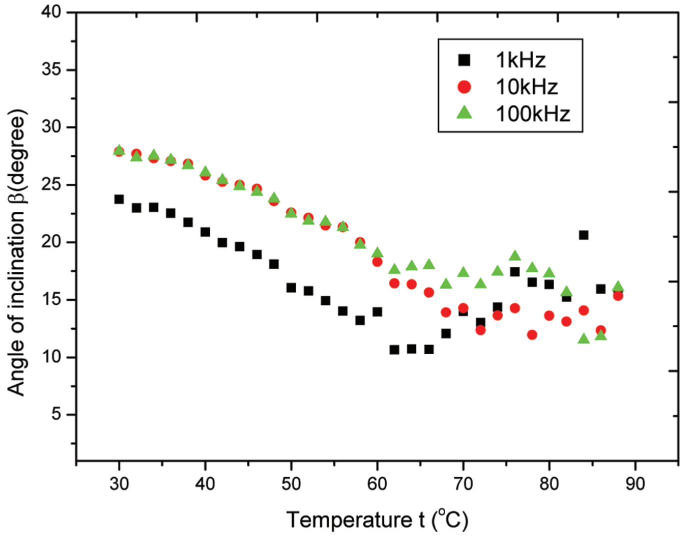


Figure 5. Thermal variation of angle of inclination β of mixture 1.

and

$$x' = \frac{3(n_e^2 - n_o^2)}{4\pi N_A d(n_{ave}^2 + 2)}.$$

Using Eqs. (4) and (5),

$$\cos^2\beta = \frac{\langle P_2\rangle[\frac{3}{2}(\varepsilon_{ave} - 1) - 6\pi N_A dhFx - 4\pi N_A dhFx'] + \Delta\varepsilon}{\frac{9}{2}\langle P_2\rangle[\varepsilon_{ave} - 1 - 4\pi N_A dhFx]}. \tag{6}$$

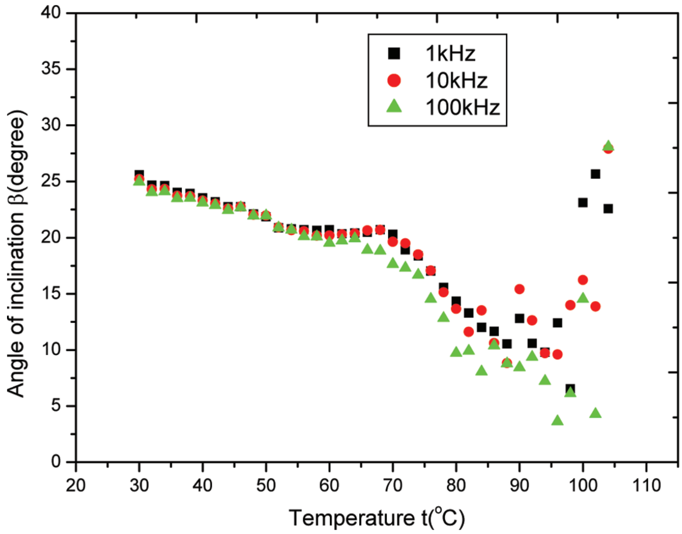


Figure 6. Thermal variation of angle of inclination β of mixture 2.

The orientational order parameter $\langle P_2 \rangle$ values have been obtained from our optical studies [1] (reproduced here in Figs. 3 and 4 for easy reference) and used with the present data from our dielectric measurements to compute β values from Eq. (6).

The variation of the angle of inclination β with temperature at frequencies of 1, 10, and 100 kHz for both mixtures are depicted in Figs. 5 and 6. β values are found to increase significantly with increase in frequency from 1 to 10 kHz and marginally for increase in frequency from 10 to 100 kHz for mixture 1, whereas in general the trend is opposite in case of mixture 2. With increase in temperature β values are observed to decrease upto a point for both the mixtures though the nature of decrease is different. However, as the isotropic temperature is approached, this trend is disturbed; β values show significant fluctuation and an overall tendency to increase. This behavior may be ascribed to vigorous vibration of the molecules as the nematic–isotropic phase transition is approached. The effect is more prominent in case of mixture 2. The estimated error in determination of the angle of inclination is about 4%.

Dipole Moment in Solution and Estimation of Molecular Weight

Variations of the dipole moment in solution μ_{sol} with concentration c (%wt) are shown in Figs. 7 and 8 for both the mixtures at a temperature of 70°C and operating frequency of 1 kHz. By extrapolating the curves to an infinite dilution, the isolated or free molecular dipole moments μ_{iso} of mixtures 1 and 2 are found to be 2.05 D and 2.3 D, respectively. On comparing these μ_{iso} values with μ_{eff}^2/M values (0.0127 and 0.0102 D^2/gm for mixtures 1 and 2, respectively (Table 1)) at 70°C and 1 kHz, estimates of M (molecular weight) have been obtained for both mixtures. The estimated values are ~330 and 500; i.e., the molecular weight of mixture 2 is significantly greater than that of mixture 1. We are aware that in this procedure of estimation where μ_{eff}^2 has been replaced by μ_{iso}^2, we have indirectly considered the absence of correlation between molecules which is not a realistic situation and a correlation factor $g = \mu_{eff}^2/\mu_{iso}^2$ (following the Kirkwood–Frohlich theory [7,8]) may be defined

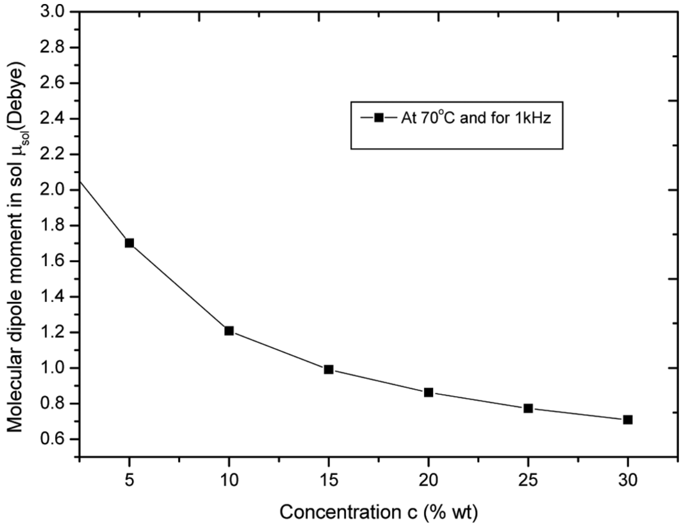


Figure 7. Variation of molecular dipole moment of mixture 1 in solution with concentration.

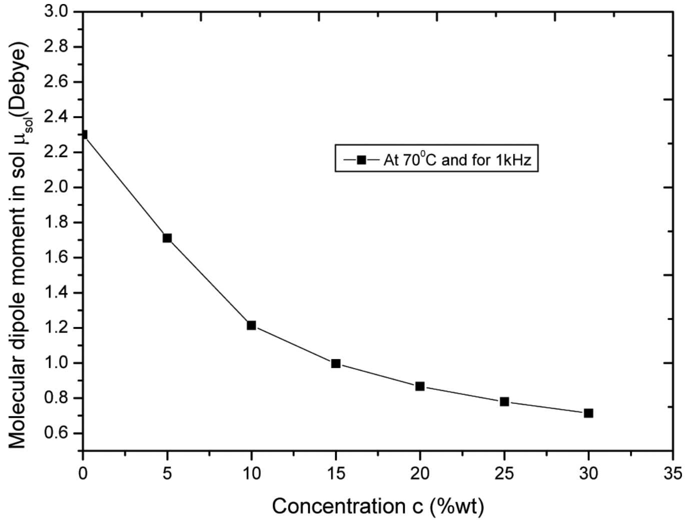


Figure 8. Variation of molecular dipole moment of mixture 2 in solution with concentration.

whose deviation from unity indicates association between molecules. Nevertheless, it would not be reckless to say that this approach gives a means of estimating approximately the molecular weight from which a comparison of the molecular weights of the two mixtures may be conclusively made. Thus it may be said with certainty that the molecular weight of mixture 2 is significantly greater than that of mixture 1.

Conclusion

The present study is a continuation of our work on the above samples which provide a good example of property tuning and tailoring of mesomorphic range by varying the proportionality of constituents alone. Though there is no significant difference in the dielectric behavior of the two mixtures, the dielectric anisotropy of mixture 2 is found to be greater than mixture 1 and so is the isolated molecular dipole moment μ_{iso} (though only slightly). A method of estimating approximately the effective molecular weights of the samples (when the composition is unknown) has been developed and it is found that mixture 2 with an enhanced mesogenic range has a significantly larger molecular weight. Whether this is due to longer chain length of mixture 2 or the relatively higher proportion of the moiety with heavier core group may be ascertained by determining the apparent molecular length.The higher fluctuation of β in mixture 2 compared to mixture 1 may be indicative of the former possibility (i.e., longer chain length). X-ray investigation on this aspect is in progress.

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