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Estimation of entropy and enthalpy of a nematic liquid crystal using time domain reflectometry studies

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Abstract Dielectric relaxation behavior of molecules in their pure form, a non-polar solvent, or mixtures of these substances at different microwave frequencies and over a range of temperatures and concentrations give an idea about inter- and intra-molecular forces. Such studies enable one to calculate thermodynamic parameters like change of activation energy for dipole orientation (ΔG^*), enthalpy (ΔH^*), and entropy (ΔS^*) of activation. Such studies in liquid crystals give additional information about the molecular behavior in different phases of liquid crystal under study. An experimental investigation on verity of systems is necessary to draw quantitative conclusions regarding the system of the molecules which are not studied so as to examine if the results obtained are in favor or against, to the general conclusions already arrived at, in other systems. With this in view, the complex dielectric permittivity spectra of *p*-pentyl phenyl-*p*-propylbenzoate (PPPB) a nematic liquid crystal are obtained using Time Domain Reflectometry (TDR) method over a frequency range 10 MHz–10 GHz at various temperatures covering both nematic and isotropic phases. The thermodynamic functions calculated using these measurements are presented and discussed in this article.

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Introduction

Studies involving the determination of thermodynamic functions as a function temperature have gained importance in view of the insight they provide about systems behavior at micro level at the temperature studied. Of the several methods [1–17], the methods involving measurement of dielectric relaxation [3, 5–7] behavior of polar molecules in a pure liquid phase and in dilute solutions at microwave frequencies and over a range of temperatures are being used extensively to measure thermodynamic functions like entropy and enthalpy. Especially, the studies on the temperature variation of dielectric dispersion and dielectric loss of liquid crystals at microwave frequency can yield valuable information regarding the structure of the molecule and the process of dipole orientation. These studies also give an idea about inter- and intra-molecular forces. Further, they enable one to calculate thermodynamic parameters, such as change in activation energy for dipole orientation ΔG^*, enthalpy ΔH^*, entropy of activation ΔS^*, and the other temperature-dependent parameters, such as relaxation time τ, the distribution parameter α, and the dielectric constant at an infinitely high frequency.

Liquid crystals [7] combine the material properties of solids with the flow properties of liquids. As such they have provided the foundation for a revolution in low-power flat panel display technology (LCDs). Most of the dielectric measurements of liquid crystals (LCs) have been performed on the aligned samples that have either a parallel or a normal orientation against the electric field. On the other hand, for molecules having a strong dipole moment directed along the long axis of the molecule, such studies concerning mainly the relaxation process connected with the molecular rotation around the short axis also make sense. Further, nematic liquid crystals are characterized by the presence of an orientation order of elongated rodlike molecules. Nematic phase is the least ordered of liquid crystalline phases, and hence the studies, even on unaligned samples give information which is very close to the aligned ones as far as those properties which are due to overall effects like dielectric behavior.

Among the various existing dielectric techniques to measure the dielectric properties, one uses the microwave cavity spectrometer in frequency domain and time-domain reflectometer (TDR) in time domain. The microwave cavity spectrometer and the time domain reflectometer are good techniques, as they need very small quantity of the sample; however, the microwave cavity spectrometer suffers from the disadvantage of its requiring the form factor to determine dielectric permittivity and dielectric loss. Using TDR, several dielectric studies have been reported on different organic molecules, with few of them being on liquid crystals and their mixtures [8–14], and especially on nematics. These studies are aimed at understanding dipole relaxation and short-range intermolecular correlation in nematic phase as well as in isotropic phase. However, studies using TDR technique are meager both in aligned and unaligned Nematic liquid crystals although TDR technique has got several advantages [15]. In light of this, the TDR spectra of *p*-pentyl phenyl-*p*-propylbenzoate (PPPB) using TDR technique are obtained at various temperatures in the range *K*—130 °C–*N*—170 °C–*I*. Using these data, thermodynamic functions were calculated. The results are reported and discussed.

Theory

There are some theories available, which give insight into the different processes of dielectric relaxation involved in the case of molecules the resultant dipole moment of which lies parallel to the long molecular axis or inclined to it both in the aligned and unaligned samples. For example, dielectric measurements performed on some unaligned samples show the presence of two dispersion regions, one in the range of MHz while another in GHz frequency range [11]. Using TDR technique, one can obtain TDR spectra at various temperatures in the temperature range required, and the dielectric parameters, ε_s, ε_∞, τ, and β can be evaluated [11]. The Cole–Cole and Cole–Davidson models have been considered for interpretation. Using the dielectric spectrum in liquid crystalline state, an attempt has been made to fit the data. The Debye theory has been applied to the dielectric spectrum in isotropic phase.

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_{S1} - \varepsilon_{S2}}{(1 + j\omega\tau_1)^\beta}$$

The phenomenon of dielectric relaxation can be viewed as the rotation of dipoles between two positions of equilibrium, separated by a potential barrier. The dielectric relaxation time τ depends on this height of the potential barrier, a temperature-dependent constant, and the average time required by an excited molecule to rotate from one equilibrium position to the other. Eyring postulating on the analogy between the processes of the dipole rotation and unimolecular chemical reactions identified a relation with molar-free activation energy ΔG^*.

Experimental

The PPPB was supplied by Eastman Kodak Co. Rochestar and is used without further purification. The complex permittivity spectrum was studied using time domain reflectometry (TDR) method as described elsewhere in the literature [12, 16]. The processing of the data was carried out as described by Cole et al. [17] to get the complex permittivity at 110 frequencies ranging from 10 MHz to 10 GHz, and the dielectric parameters ε_s, ε_∞, τ, and β are obtained by nonlinear least squares fit method [18]. The temperature of the sample was controlled within ±0.20 °C. The reliability of this experimental setup was tested by determining dielectric parameters of some standard liquids like Chlorobenzene, Acetone, and 1,2-Dichloroethane.

Results and discussion

The Cole–Cole plots for two typical temperatures are presented in Figs. 1 and 2. The Fig. 1 corresponds to the temperature of 15 °C (nematic phase), while Fig. 2, represents for 40 °C (isotropic phase). The various values calculated including β values at various temperatures are presented in Table 1 assuming single relaxation (The calculation of relaxation studies of this nature have already been published earlier [19]). These data have been reproduced here along with the values of entropy and enthalpy calculated in Table 1 as per the theory presented below. The values of ΔH^* and ΔS^* are derived from the slope and the intercept of the linear plot of ln $(T\tau)$ vs. $1/T$.

According to Eyring theory the expression for τ is

$$\tau = (h/KT)\exp(\Delta G^*/RT) \tag{1}$$

That is,

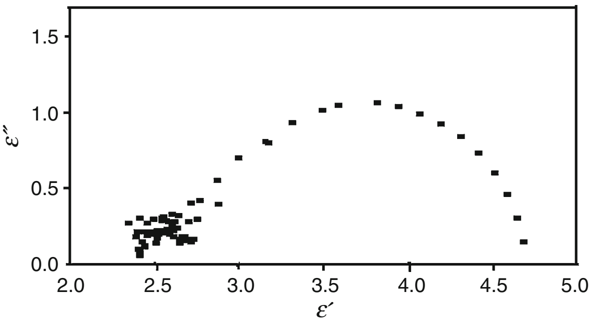

Fig. 1 Cole–Cole arc at 15 °C of PPPB phase

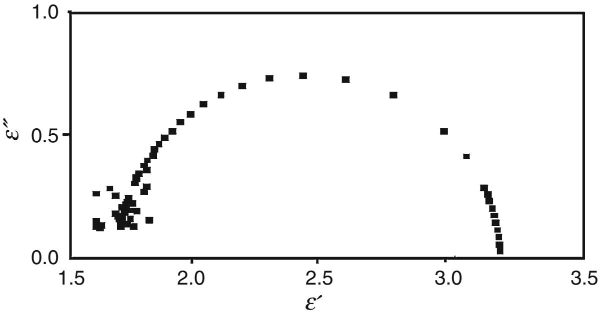

Fig. 2 Cole–Cole arc at 40 °C of PPPB in I Phase

Table 1 Variation of dielectric constants and relaxation times with temperature in N and I phases of PPPB assuming single relaxation process

T/°C	τ/ns	β	ΔH^*/kJ mol^{-1} K^{-1}	ΔS^*/kJ mol^{-1} K^{-1}
13	1.356	0.892	93.258 (N)	+0.251(N)
15	1.150	0.852		
17	0.778	0.762		
20	0.536	1.0	10.883 (I)	−0.030 (I)
25	0.482	1.0		
30	0.440	1.0		
40	0.355	1.0		
50	0.326	1.0		
60	0.272	1.0		

$$\Delta G^* = 2.303RT\log(\tau KT/h) \tag{2}$$

with, $\Delta G^* = \Delta H^* - T\,\Delta S^*$, one can write from Eq. 1,

$$\begin{aligned}\ln(\tau T) &= \ln(h/K) + (\Delta H^* - T\Delta S^*)/RT\\ &= [\ln(h/K) - (\Delta S^*/R)] + [(\Delta H^*)/RT]\end{aligned}$$

Thus, the slope of the linear plot between ln (τT) and ($1/T$) gives (ΔH^*)/2.303R. With obtained value of ΔH^*, ΔS^* can be calculated and ΔG^* with relation

$$\Delta G^* = \Delta H^* - T\Delta S^*.$$

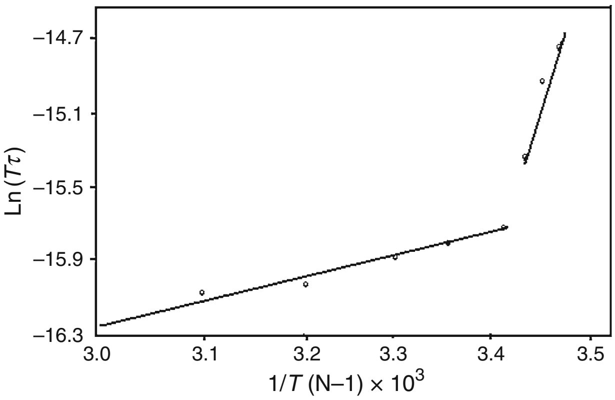

Fig. 3 Plot of ln ($T\tau$) vs. 1/T (N–I) × 10^3 in N- and I-phases

The values of ΔH^* and ΔS^* from the slope and the intercept of the linear of plot ln ($T\tau$) vs. 1/T (Fig. 3) are given in the Table 1. It can be seen from the table that ΔH^* in N phase is larger compared with that in I phase. This is in line with the nematic potential involved in the relaxation process. The molar entropy of activation ΔS^* in N and I phase are, respectively, +0.251 and −0.030 kJ mol^{-1} K^{-1}. This is in consistent with the earlier observations [20, 21]. The negative value of ΔS^* is indicative of a relatively high-ordered arrangement in this activated state. Although the sign is indicative of this inference, the actual value cannot be of much importance in view of the inaccuracy in the measurement of these values. The ΔH^* value being more in nematic phase than in isotropic phase can be explained by assuming that relaxation process is essentially an "end-over-end" tumbling motion of the molecules, which has to surmount the nematic potential barrier. The absence of value 1 for β in nematic phase is in line with this argument.

Conclusions

Nematic phase is the least ordered of liquid crystalline phases and hence the studies even on the unaligned samples give information which is very close to the aligned ones as far as those properties which are due to overall effects like dielectric behavior. The entropy and enthalpy values obtained are in line with the above observation. The value of β being not equal to zero over a range of temperature is a clear indication of nematic phase. The value of β, as it tends to isotropic phase, tending to 1 is as per the expected lines for a nematic

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References

1. Cabral TA, Monteiro RAR, Rocha MAA, Luís MN, Acree SWE, Maria Ribeiro da Silva DMC Jr. Molecular energetics of alkyl substituted pyridine *N*-oxides: an experimental study. J Therm Anal Calorim. 2010;100:431–9.
2. Kilit E, Yurtseven H. Analysis of the specific heat of *p*-azoxyanisole (PAA) near the phase transitions. Phys Chem Liq. 2010;48:450–60.
3. Madhurambal G, Mariappan M, Mojumdar SC, Thermal. UV and FTIR spectral studies of urea-thiourea zinc chloride single crystal. J Therm Anal Calorim. 2010;100:763–8.
4. Rajasekaran M, Anbusrinivasan P, Mojumdar SC. Growth, spectral and thermal characterization of 8–hydroxyquinoline. J Therm Anal Calorim. 2010;100:827–30.
5. Vasan ST, Ayachit NH. On the effect of temperature on the dielectric relaxation time of some benzene derivatives and certain of their binary mixtures. Phys Chem Liq. 2006;44:513–8.
6. de Cominges BE, Piñeiro MM, Mascato E, Mosteiro L, Iglesias TP, Legido JL. Relative permittivities of binary mixtures of 1-butanol + *n*-alkane at 298.15 k. J Therm Anal Calorim. 2003; 72:129–33.
7. Collings PJ, Hird M. Introduction to liquid crystals, chemistry and physics. London: Taylor and Frances; 1997.
8. Williams G, Sinton SE, Anthony G. Dielectric relaxation spectroscopy and alignment behavior of a polymer-dispersed liquid crystal and its component materials. J Polym Sci B. 2001;39: 1173–8.
9. Ermolina V, Zuev YF, Polygalov EA, Romanychev GD, Fel'dman YD. Application of nonuniform sampling in time-domain dielectric spectroscopy. Measure Tech A. 2005;46:7763–72.
10. Zeller HR. Dielectric relaxation in nematic mixtures. Phys. Rev A. 1981;23:1434–6.
11. Singh Avneesh Kumar, Manohar Rajiv, Shuklaa JP, Biradar AM. Dielectric relaxation and anisotropy of nematic mixture E-24. J Phys Chem Solids. 2005;66:1183–8.
12. Shere IG, Pawar VP, Mehrotra SC. Temperature dependent dielectric relaxation study of acetonitrile with chlorobenzene at microwave frequency using time domain reflectometry, J Mol Liq. 2007;133:116–9.
13. Schonhals A, Zubowa HL, Fricke R, Frunza L, Moldovan R. On the dielectric behavior of unaligned samples of 4-*n*-Octyl-4′-cyanobiphenyl (8CB). Cryst Res Technol. 1999;34:1309.
14. Bose TK, Champbell B, Yagihara S. Dielectric-relaxation study of alkylcyanobiphenyl liquid crystals using time-domain spectroscopy. Phys Rev A. 1987;36:5767.
15. Helambe SN, Chaudhari A, Mehrotra SC. Temperature dependent dielectric study of n-nitriles in methanol using time domain reflectometry. J Mol Liq. 2000;84:2235–44.
16. Jad yna J, Legrandb C, dzioraa PK, Baumanc D. Study of molecular dynamics in nematic and isotropic phases of 4-isothiocyanatophenyl 4-hexyl-bicyclo [2,2,2]octane-1carboxylate by dielectric spectroscopy. J Mol Struct. 1997;412:213–9.
17. Cole RH, Berberian JG, Mashimo S, Chryssikos G, Burns A, Tombari E. Time domain reflection methods for dielectric measurements to 10 GHz. J Appl Phys. 1989;66:793.
18. Bevington PR. Data reduction and error analysis for Physical Science. New York: McGraw Hill Book Co.; 1969.
19. Fattepur RH, Ayachit NH, Mehrotra SC. Time domain reflectometry studies on a nematic liquid crystal. Mol Cryst Liq Cryst. 2009;501:20–7.
20. de Gennes PG, Prost J. The physics of liquid crystals. 2nd ed. Oxford: Clarendon Press; 1993.
21. Thoen J, Bose TK. Dielectric behavior in liquids: critical mixtures and liquid crystals. In: Nalwa HS, editor. Handbook of low and high dielectric constant materials and their application, vol. 1. San Diego: Academic Press; 1999. p. 501.