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# Prenematic Behavior of the Electric-Field-Induced Increment of the Basic Thermodynamic Quantities of Isotropic Mesogenic Liquids of Different Polarity

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Temperature dependences of the static dielectric permittivity and its derivative, obtained for isotropic mesogenic liquids composed of the molecules of different polarity in relation to the basic thermodynamic quantities (internal energy, entropy, and Helmholtz free energy), are analyzed. A role of the molecular polarity in the dielectric behavior of the liquids in the vicinity of the isotropic to nematic phase transition is discussed.

## Introduction

Transition from the nematic (N) liquid crystalline phase to the isotropic (I) liquid is mostly classified as weakly first order or close to second order. That somewhat inexplicit attribution of the N–I transition results from the fact that, indeed, one detects the enthalpy change at the transition but of the order of 1 kJ/mol only and often even much less. At a typical first-order transition, namely, in the melting from the crystalline solid to the isotropic liquid, the enthalpy change is around 20–50 kJ/mol. Similarly, the other features of the first-order transition: the molar volume jump and the entropy change, when associated to the N–I transition, are only a few percent of those observed at a melting process.

Thermodynamic weakness of the N–I transition leads, in general, to large pretransitional effects. The prenematic phenomena are due to an existence of a short-range orientational order of the mesogenic molecules in the isotropic liquids, which leads to formation of the pseudonematic domains. The size of the domains increases as the temperature of the liquid approaches to the transition to the nematic phase. The phenomenon can be quantitatively described in terms of the intermolecular correlation length  $\xi$ . The Landau theory of the second-order phase transition, applied by de Gennes to the isotropic to nematic transition, leads to the following temperature dependence of the correlation length<sup>1</sup>

$$\xi(T) = \xi_0 \left[ \frac{T^*}{T - T^*} \right]^{1/2} \quad (1)$$

where the constant  $\xi_0$  is of the order of the molecular length and  $T^*$  denotes the temperature of virtual transition of the second order, i.e., the temperature limit of the thermodynamic stability of a supercooled isotropic phase. Usually, the value of  $T^*$  is about of 1 K below the N–I phase transition temperature ( $T_{NI}$ ), and as results from eq 1, at that temperature the correlation length reaches its infinitive value.

In the prenematic region of the isotropic liquids one observes an anomalously strong increase not only such thermodynamic quantities as the specific heat and the thermal expansion or the isothermal compressibility<sup>2,3</sup> but it also concerns other physical properties: the static magnetic<sup>4</sup> and electric<sup>5</sup> birefringence, the

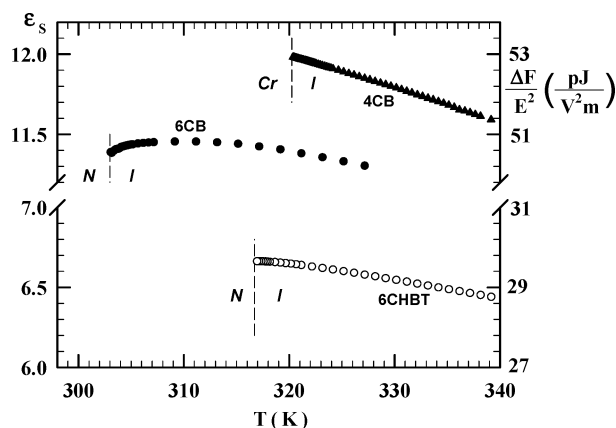
light scattering,<sup>6</sup> the nonlinear dielectric effect,<sup>7</sup> the molecular rotational diffusion<sup>8–10</sup> as well as the molecular spin–lattice relaxation,<sup>11,12</sup> the dynamic light scattering,<sup>13</sup> the transient grating optical Kerr effect,<sup>14,15</sup> and the nonlinear dielectric relaxation.<sup>16–18</sup>

In this paper we present the experimental results on the linear dielectric properties of mesogenic compounds of different polarity in the vicinity of the phase transition from the isotropic liquid to the nematic liquid crystal. Singularities, observed in the temperature behavior of the static permittivity and its derivative and followed from them the basic thermodynamic quantities (internal energy, entropy, and Helmholtz free energy), are analyzed.

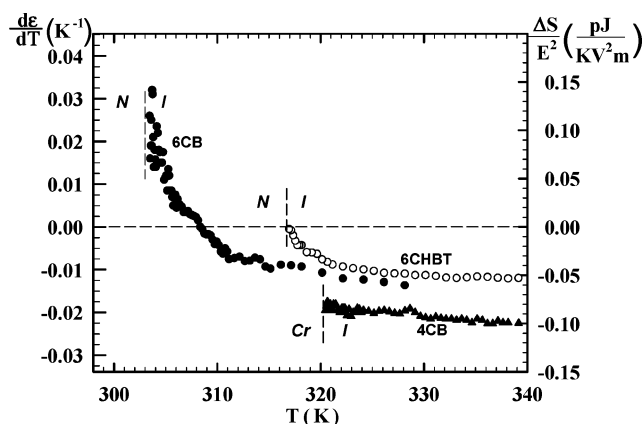
## Experimental Section

The subject of our studies are the compounds belonging to the two homologous series: *n*-alkylcyanobiphenyls,  $C_nH_{2n+1}$ -PhPhCN, *n*CB (studied  $n = 4$  and 6), composed of the strongly polar molecules (dipole moment  $\mu \approx 5D$ ), and 4-(*trans*-4'-*n*-alkylcyclohexyl)isothiocyanatobenzenes,  $C_nH_{2n+1}$ CyHxPhNCS, *n*CHBT (studied  $n = 6$ ), with the molecular dipole moment of about 2.5 D. The compound 4CB is a non-mesogenic one, and at the temperature of 320 K one observes the first-order phase transition from the isotropic liquid to the crystalline solid. The next two compounds, 6CB and 6CHBT, are mesogenic liquids exhibiting the transition from the isotropic to nematic phase at 303 and 316.8 K, respectively. The compounds were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compounds, checked by chromatography, was better than 99.5%. Dielectric characteristics were measured with an HP 4194A impedance/gain phase analyzer in the frequency region from 50 kHz to 100 MHz. The static values of the permittivity were taken as a low-frequency plateau of the real part of the complex dielectric permittivity. The measuring capacitor consisted of three plane electrodes: one central and two grounded on each side, with the distance between the electrodes of about 0.5 mm. The measuring voltage was 1 V rms. The electrical heating of high performance, with the use of the Scientific Instruments temperature controller, model 9700, assured a quite good stabilization of the temperature (at mK level) with the possibility of varying the temperature by steps of  $10^{-2}$  K. Such equipment allows us to determine the permittivity with a relative accuracy better than 0.5%.

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**Figure 1.** Temperature dependences of the static dielectric permittivity measured in the isotropic phase of the compounds of different polarity and the Helmholtz free energy increment calculated with eq 4.



**Figure 2.** Temperature dependences of the static dielectric permittivity derivative for the isotropic compounds of different polarity and the field-induced entropy increment calculated with eq 3.

## Results and Discussion

Figure 1 presents the temperature dependence of the static dielectric permittivity ( $\epsilon_s$ ) measured for 4CB, 6CB, and 6CHBT in the isotropic phase.

Some differences in the  $\epsilon_s(T)$  dependences in the vicinity of the first-order (Cr – I for 4CB) and the weakly first-order (I–N for 6CB and 6CHBT) phase transitions, manifest themselves very clearly if one analyses the temperature behavior of the permittivity derivative presented in Figure 2.

There are no dielectric pretransitional effects in the vicinity of the first-order phase transition: up to the I–Cr transition the derivative of the static permittivity of 4CB maintains its weakly temperature dependence. Similar behavior is observed for mesogenic 6CB and 6CHBT but far from the I–N transition only. In the vicinity of the transition, a noticeable increase in the  $d\epsilon_s/dT(T)$  dependences occurs and the effect is much more pronounced for strongly polar 6CB. It concerns both the temperature extension of the deviation (about 7° for 6CHBT and 15° for 6CB) and its strength. In case of a less polar 6CHBT, the permittivity derivative attains zero as its final value at the I–N transition, whereas for strongly polar 6CB, the  $d\epsilon_s/dT(T)$  dependence shows a critical-like behavior and at about 5° before the phase transition one observes a change of the permittivity derivative sign. The result seems to be important as the temperature behavior of the static dielectric permittivity and its derivative reflect a behavior of the basic thermodynamic quantities increment caused by an application of an external electric field to the system. As it was shown first by Fröhlich

in 1958<sup>19</sup> and next by Becker,<sup>20</sup> Landau, Lifshitz, and Pitae-vskii<sup>21</sup> and Scaife,<sup>22</sup> the increments of the electric-field-induced internal energy  $U$ , the entropy  $S$ , and the Helmholtz free energy  $F$  are related to the static permittivity  $\epsilon_s$  and/or its derivative  $d\epsilon_s/dT$  and the applied field strength  $E$  as follows

$$\frac{\Delta U}{E^2} \equiv \frac{U(T,E) - U_0(T)}{E^2} = \frac{\epsilon_0}{2} \left( \epsilon_s + T \frac{\partial \epsilon_s}{\partial T} \right) \quad (2)$$

$$\frac{\Delta S}{E^2} \equiv \frac{S(T,E) - S_0(T)}{E^2} = \frac{\epsilon_0}{2} \frac{\partial \epsilon_s}{\partial T} \quad (3)$$

$$\frac{\Delta F}{E^2} \equiv \frac{F(T,E) - F_0(T)}{E^2} = \frac{\epsilon_0}{2} \epsilon_s \quad (4)$$

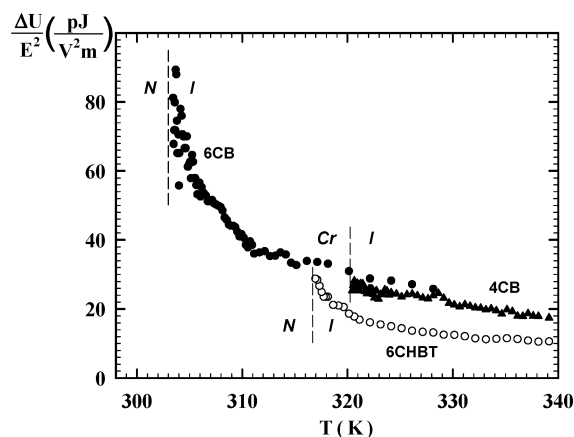
where  $U_0$ ,  $S_0$ , and  $F_0$  denote the values of the thermodynamic quantities in an absence of the electric field,  $T$  is the absolute temperature, and  $\epsilon_0 = 8.85 \text{ pF/m}$  is the permittivity of free space.

In eq 2, the term  $0.5\epsilon_0 T \partial \epsilon_s / \partial T$  represents a part of the dielectric internal energy, which is converted into heat during the isothermal charging of the capacitor filled with a dielectric material of the static permittivity  $\epsilon_s$ . The remaining term is the dielectric free energy (eq 4) stored in the capacitor, so the difference  $\Delta F = F(T,E) - F_0(T)$  represents a maximum of the energy which can be yielded during the isothermal discharge of the capacitor. Equation 4 shows that the temperature behavior of the electric part of the free energy is that of the static permittivity itself, what is illustrated in Figure 1. It can be seen that only in case of strongly polar 6CB the free energy clearly manifests, in its temperature dependence, an approaching of the I–N phase transition.

It seems to be interesting and important to analyze the pretransitional behavior of the field-induced entropy increment, which, according to eq 3, is determined by the permittivity derivative temperature dependence. In particular, the sign of the increment  $\Delta S = S(T,E) - S_0(T)$  depends straightly on the sign of the permittivity derivative. A negative value of  $d\epsilon_s/dT$ , i.e.,  $\Delta S < 0$ , means that due to an applying of an electric field to dielectric material, the entropy decreases (*the molecular order in the system increases*). It is a normal behavior of dipolar liquids.

However, in the case of 6CB the situation is a bit different. As shown in Figure 2, at the temperature of somewhat less than 10° before the I–N transition, the increment of the entropy changes its sign and becomes positive ( $\Delta S > 0$ ). So, an electric field applied to the isotropic dipolar liquid *decreases of the order* on the molecular level. A field-induced increase of the entropy can take place only when the dipolar molecules are partially self-organized in the isotropic liquid with a prevalence of the antiparallel arrangement. Then, the existing intermolecular entities (prenematic domains) are destroyed in some extent due to the imposition of an external electric field.

A competition between the self-assembling of the mesogenic molecules in the prenematic region and the orienting action of the external electric field is, as a matter of fact, a competition between the spontaneous antiparallel dipolar arrangement in the pseudodomains and the parallel ordering of dipoles forced by the field. As the temperature approaches to the transition to the nematic phase, the effect is strongly enhanced, and its behavior takes a critical-like form. In the case of an essentially less polar 6CHBT, both the electric field–molecular dipoles interactions and the intermolecular dipole–dipole interactions are markedly reduced in comparison to those of 6CB molecules, and finally, at the temperature close to the I–N transition, the self-



**Figure 3.** Internal energy increment for studied compounds as a function of the temperature.

assembling process and the field-induced dipolar ordering are so compensated that  $\Delta S$  is close to 0.

Figure 3 presents the temperature dependence of the field-induced internal energy increment determined with the use of eq 2. One can clearly see that the internal energy of the isotropic polar liquids placed in the electric field increases according to the molecular dipole moment value: far of the I–N phase transition the energy increment has the same value and the same temperature dependence both for non-mesogenic 4CB and for mesogenic 6CB, the compounds of the same polarity. The  $\Delta U$  of less polar 6CHBT, far from the I–N transition, amounts of about half of the value corresponding to 6CB. An approaching of the nematic phase manifests itself by an essential increase of the energy increment. As in the case of the entropy, the critical-like temperature dependence of  $\Delta U$  is observed for strongly polar 6CB.

## Conclusions

The data presented in this paper show that the thermodynamic effects induced by an external electric field in the isotropic polar liquids are relatively small: the values of  $\Delta U$ ,  $\Delta S$ , and  $\Delta F$  are of the order of  $10^{-12}$  J per unit volume and unit field strength and the entropy per Kelvin. Critical-like increase of  $\Delta U(T)$  and  $\Delta S(T)$ , observed for strongly polar liquid in the vicinity of the liquid crystalline nematic phase, is a consequence of an appearance in that region of a second orientational effect. The first orientational effect, which concerns all the dipolar liquids placed in the electric field, is a simple perturbation of the randomly distributed molecular dipoles. The effect leads to the dipoles ordering in liquids, and the degree of the ordering depends on the ratio between the dipolar energy ( $\mu E$ ) and the thermal energy ( $kT$ ). In typical conditions ( $\mu = 1$  D,  $E = 1$  V/mm,  $T = 300$  K), the ratio  $\mu E/kT$  is of the order of  $10^{-5}$ . So, usually that ordering effect is rather small, but it is enough to observe, after switch off the field, the (dielectric) relaxation of the system without any special difficulties. An increase of the electric field strength leads here to the Langevin saturation of the dipoles orientation and consequently to a decrease of the dielectric permittivity value (a negative nonlinear dielectric effect).<sup>23</sup>

The second orientational effect appears in the prenematic regions where the intermolecular entities are formed in a spontaneous way as the precursors of the nematic state. As it was mentioned above this spontaneous process leads to the molecular assembles in which the antiparallel arrangement of dipoles predominates. An application of the electric field to the nematogenic liquid will cause, apart from the “first” orientational effect of the free molecules, a shift of an equilibrium within the prenematic domains toward to parallel arrangement of molecular dipoles, i.e., will cause an additional increase of the internal energy. The effect considerable increases with the growing of the domains, i.e., when the I–N transition approaches. However, the relaxation of this new orientational effect cannot be observed in normal experimental conditions because of the too-small amplitude of the dielectric response of the prenematic domains, which are still of the microscopic size (the liquids are totally transparent). Only by application of the electric field of a very high strength can one record in a prenematic region an increase of the permittivity (a positive nonlinear dielectric effect) and the dielectric absorption due to the relaxation of the discussed here orientational effect within the prenematic domains. For 6CB and 6CHBT studied here, the maximum of that dielectric absorption occurs in the frequency region of about 10 MHz, i.e., for the frequencies of about 1 order of magnitude lower than that were the linear (normal) dielectric relaxation occurs.<sup>16–18</sup>

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