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Static and dynamic dielectric properties of strongly polar liquids in the vicinity of first order and weakly first order phase transitions

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The paper presents the results of measurements of the linear dielectric properties of the compounds from the homologous series of alkylcyanobiphenyls (C_nH_{2n+1}PhPhCN, nCB) in the vicinity of the first order transition (from the isotropic liquid to the crystalline phase) of nonmesogenic nCB's ($n=2$–4) and the weakly first order transition (from the isotropic liquid to the nematic phase) of 5CB. The experimental method for the separation of the critical part of the static permittivity derivative and the activation energy for rotation of the mesogenic molecules, in the vicinity of weakly first order phase transition, is proposed. It is shown that the critical temperature dependence of the permittivity and the activation energy can be described with a function of $(T-T^*)^{-\alpha}$ type, with the same values of the temperature of virtual transition of the second order (T^*) and the critical exponent (α).

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I. INTRODUCTION

The properties of nematogenic liquids in the vicinity of the isotropic to nematic (I-N) phase transition are still a subject of numerous works, mainly experimental [1–9]. The basic reason for the constant interest is that the transition of the first order in nature is preceded by pretransitional phenomena that show a critical-like behavior, characteristic of the continuous, second order phase transitions. For a typical transition of the first order, as the crystallization, for example, the symptoms of the coming up transition are not observed. Therefore, the I-N transition is classified as weakly first order or close to second order.

The pretransitional phenomena are observed both for the decreasing temperature of pure nematogenic liquids and for the increasing concentration of nematogenic molecules in a nonpolar medium, at constant temperature. The phenomena appear nearly exclusively in the nonlinear studies, i.e., when an external stimulus is sufficiently strong. A peculiar temperature behavior of the linear static permittivity of strongly polar mesogens in the vicinity of I-N transition is rather an exceptional case of the pretransitional effect seen in a weak electric field [10–14]. However, the dynamics of the pretransitional effects can be studied with the nonlinear techniques, such as the Kerr effect or the nonlinear dielectric spectroscopy, only. The linear methods, the linear dielectric spectroscopy at the first place, are not able to detect the dynamic prenematic effects. Only when an additional, strong electric field is applied to the liquid, a new dielectric absorption band appears in the frequency region of about one order of magnitude lower than that recorded with the linear spectroscopy [15–17]. The relaxation time and the strength of the new band show a critical-like behavior as the temperature decreases towards the I-N transition [15] or as the number of mesogenic molecules in unit volume increases [16,17].

In the paper we present the experimental results obtained with the linear static and dynamic dielectric methods in the vicinity of first order (crystallization) and weakly first order (I-N) phase transitions. There are two aims of the paper. The first one concerns the empirical analysis of temperature behavior of the static permittivity of strongly polar compounds in the vicinity of phase transition. Our results give an experimental basis for the formulation of the permittivity background corresponding to noncritical (''normal'') behavior of the permittivity of strongly polar, nonmesogenic liquids. Up to now, the problem was open and only arbitrary assumptions concerning the background were made [11–14].

The second aim of the paper concerns the dielectric relaxation time. In some quite recently published papers, the linear dielectric relaxation method is listed among others as a method suitable for studies of the dynamics of prenematic effects. Therefore, we present the results of temperature dependence of the linear dielectric relaxation time determined with an exceptional care for mesogenic 5CB in the vicinity of I-N transition. The results are compared with those obtained for nonmesogenic 4CB [18].

II. EXPERIMENT

The compounds studied belong to the homologous series of the strongly polar (dipole moment $\approx 5D$) alkylcyanobiphenyls (C_nH_{2n+1}PhPhCN, nCB). For $n=2$, 3, and 4, the compounds are nonmesogenic with the melting points at 348.2 K, 339 K, and 320.1 K, respectively. Some data point out towards the existence of a monotropic, very unstable nematic phase of 4CB at a temperature of about 20 K below the melting point, but we did not avoid the crystallization of 4CB at 320.1 K in each of our experiments. For $n=5$, a stable nematic phase occurs with the I-N transition temperature equal to 308.4 K. The compounds were synthesized and

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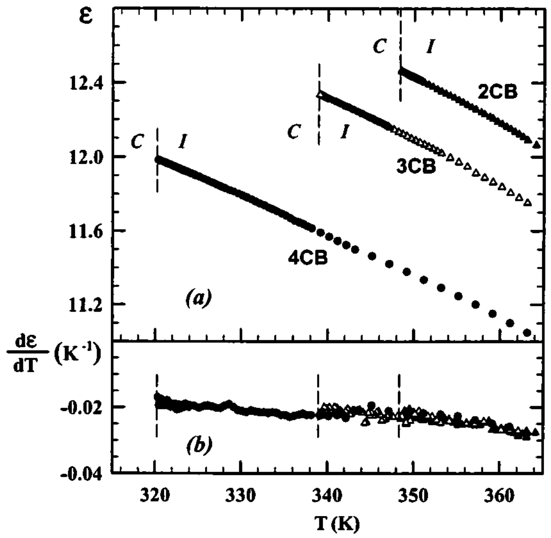

FIG. 1. Temperature dependence of the static permittivity (a) and its derivative (b) for nonmesogenic nCB's, $n=2$–4, in the vicinity of isotropic (I) to crystal (C) first order phase transition.

purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compounds, checked by chromatography, was better than 99.5%.

The measurements of the dielectric properties of liquid nCB's were performed with a HP 4194A impedance/gain-phase analyzer in the frequency range of 50 kHz–100 MHz. The static values of the permittivity were taken as a low-frequency plateau of the real part of the permittivity. The accuracy of the permittivity determination was better than 0.5%. The measuring capacitor consisted of three plane electrodes: one central (''hot'') electrode and two grounded electrodes on each side. The electrical heating of high performance, with the use of UNIPAN 650H controller, assured a temperature stabilization better than 10^{-3} K and a possibility of the temperature change of 10^{-2} K.

III. RESULTS AND DISCUSSION

Figure 1(a) presents temperature dependence of the static permittivity measured for the nonmesogenic cyanobiphenyls. The electric permittivity shows no pretransitional effects in the vicinity of first order transition from the isotropic liquids to the crystalline (I-C) phase. In the studied temperature range, the $\varepsilon(T)$ dependence for nonmesogenic compounds is only slightly nonlinear, as shown in Fig. 1(b). Temperature dependence of the permittivity derivative can be reproduced here with the linear relation

$$\frac{d\varepsilon}{dT}(T)=\left(\frac{d\varepsilon}{dT}\right)_{I\text{-}C}-\xi(T-T_{I\text{-}C}), \tag{1}$$

where the first term on the right side of the equation corresponds to the derivative value at $T=T_{I\text{-}C}$ of given nCB ($n=2$–4), and the slope ξ, within the experimental errors, is the same for 2CB, 3CB, and 4CB; and equals 1.88×10^{-4} K^{-2}.

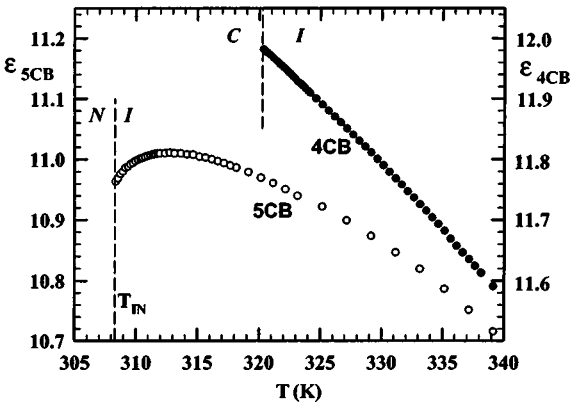

FIG. 2. Static permittivity in the vicinity of first order (4CB) and weakly first order (5CB) phase transitions as a function of temperature.

Peculiarity in the permittivity dependence on temperature observed for isotropic 5CB (Fig. 2) is certainly related to the approaching transition to the nematic phase. The effect is much more pronounced in the permittivity derivative, which shows a critical-like behavior as temperature approaches the I-N phase transition (Fig. 3). Of course, the experimental data presented in Fig. 3 for 5CB concern two phenomena: the first one refers to the ''normal,'' noncritical permittivity behavior of the polar liquids, and the second one is related to the pretransitional effects. If one assumes that for mesogenic 5CB the noncritical $d\varepsilon/dT$ dependence on temperature corresponds to that obtained for nonmesogenic 4CB (solid line in Fig. 3), a critical part of the permittivity derivative of 5CB can be represented as a difference

$$\left(\frac{d\varepsilon}{dT}\right)_{crit}=\left(\frac{d\varepsilon}{dT}\right)_{meso}-\left(\frac{d\varepsilon}{dT}\right)_{nonmeso}. \tag{2}$$

The results obtained according to Eq. (2) are depicted in Fig. 4. The data are perfectly reproduced in the whole studied temperature range with the following equation:

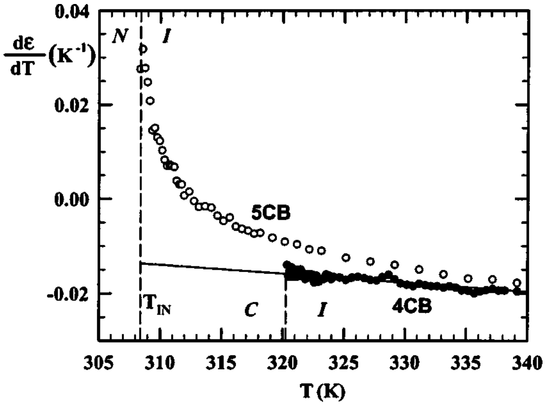

FIG. 3. Temperature dependence of the derivative of the static permittivity of nonmesogenic 4CB and mesogenic 5CB. The solid line corresponds to the noncritical temperature dependence of the derivative according to Eq. (1).

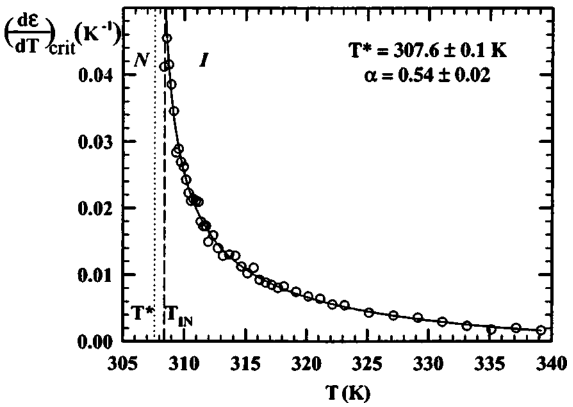

FIG. 4. The critical part of the derivative of the static permittivity of 5CB as a function of temperature. The solid line corresponds to the best fit of Eq. (3) to the experimental data (points).

$$\left(\frac{d\varepsilon}{dT}\right)_{crit} = A(T - T^*)^{-\alpha}, \tag{3}$$

where T^* denotes the temperature of virtual transition of the second order, α is the critical exponent, and A is a parameter. T^* is, in general, slightly below the *I-N* transition temperature. The best fit of Eq. (3) to the data (shown in Fig. 4 as the solid line) gives the following values of the parameters: $T^* = 307.6$ K and $\alpha = 0.54$. The difference, $T_{IN} - T^* = 0.8$ K, obtained is typical for *I-N* phase transition. The value of the critical exponent is close to that obtained in studies of the specific heat [10] and dielectric studies by Rzoska *et al.* [11–14], so our results seem to support the fluidlike hypothesis of prenematic behavior of 5CB [11–14,17].

The next part of the paper concerns the dynamics of the linear dielectric properties of nonmesogenic 4CB and mesogenic 5CB. The dielectric relaxation spectra, recorded for the compounds in the isotropic phase, were resolved into two components (corresponding to the molecular rotation around their principal axes) of the Cole-Cole type:

$$\varepsilon^* = \varepsilon_\infty + \frac{A}{1 + (i\omega\tau)^\sigma}. \tag{4}$$

In Eq. (4) ε_∞ denotes the permittivity measured at a frequency sufficiently high to prevent the dipolar reorientation, A is the dielectric strength, ω the angular frequency, and τ the relaxation time. Equation (4) reduces to the Debye equation for the exponent value $\sigma = 1$. As for the rodlike molecules with the dipole moment directed along the long axis (the case of nCB's), the most informative is the dielectric relaxation time corresponding to the rotation around the short axis (strongly dominated band), we will discuss temperature behavior of that relaxation time (τ) in the vicinity of *I-C* and *I-N* transitions.

As follows from Fig. 5, the dielectric absorption band, corresponding to the rotation of 4CB and 5CB molecules around the short axis, shows a deviation from the Debye's form ($\sigma = 1$). The deviation is very subtle for nonmesogenic 4CB and is quite distinct for mesogenic 5CB. The observation seems to be important, as nowadays the theory of anomalous dielectric relaxation (for $\sigma < 1$) develops successfully [19–22] and reliable experimental data are needed. One expects that the extension of the classical theory of Brownian motion to the fractional dynamics in a system exhibiting anomalous diffusion, i.e., diffusion in disordered fractal structures, can explain peculiar temperature behavior of the Cole-Cole exponent σ in the vicinity of *I-N* phase transition [23].

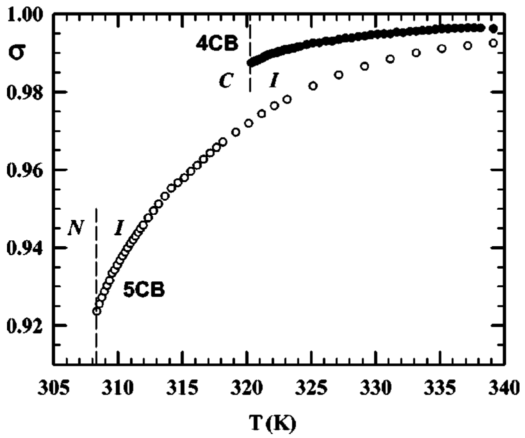

FIG. 5. Temperature dependence of the Cole-Cole exponent σ resulting from the best fit of the expression (4) to the experimental absorption band corresponding to the rotation of 4CB and 5CB molecules around the short axis.

The results presented in Fig. 6 show that at first sight there is no obvious difference in the $\tau(T)$ dependence obtained for 4CB and 5CB. In particular, in the vicinity of *I-N* transition the dielectric relaxation time of 5CB exhibits no critical behavior. Figure 7 shows that the relaxation time of both compounds does not fulfill the Arrhenius dependence:

$$\ln\tau = C + \frac{E_A}{RT}, \tag{5}$$

where E_A is the activation energy, R the gas constant, T the absolute temperature, and C is the constant. The deviation from the linear dependence $\ln\tau$ versus T^{-1} is much more

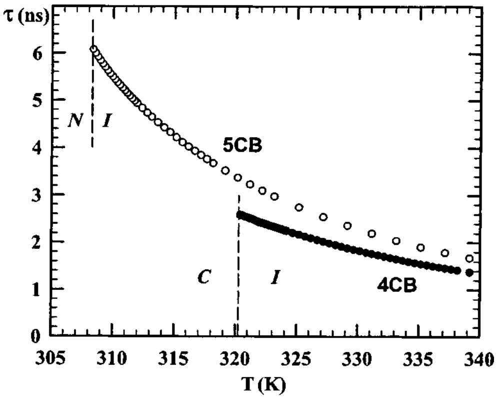

FIG. 6. Temperature dependence of the dielectric relaxation time corresponding to the rotation around the short axis of 4CB and 5CB molecules in the vicinity of *I-N* and *I-C* phase transitions.

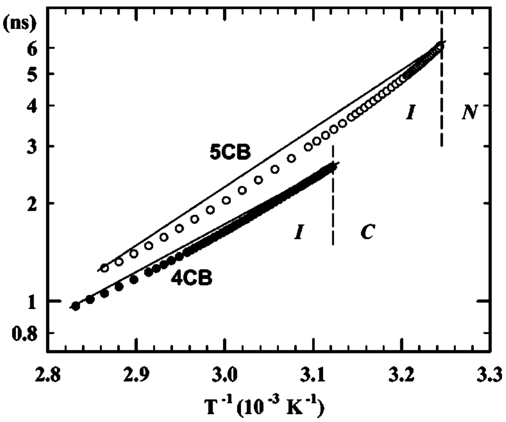

FIG. 7. Arrhenius plot for the dielectric relaxation time of 4CB and 5CB molecules in the isotropic phase.

pronounced for mesogenic 5CB. It is obvious that in such a situation a reliable value of the activation energy for the molecular rotation cannot be determined as the slope of dependence (5). Two issues of the situation are in common practice in literature. Often one ignores the experimental nonlinearity in $\ln\tau$ versus T^{-1} dependence and the activation energy is calculated as a mean slope of the dependence. That way is used when the nonlinearity is not too pronounced, what happens in the experiments performed in a not too large temperature range. The second way leads through an introduction of some modifications of the Arrhenius equation [24,25]. In the above mentioned ways one assumes that the activation energy E_A should be temperature independent. As a matter of fact, there are no physical reasons for that assumption. As the basic properties of liquids, the number of molecules in unit volume and the viscosity, at the first place, depend essentially on temperature; one may expect an increase of the activation energy for the molecular rotation with decreasing temperature. The prenematic region is of special interest on that score.

The procedure we propose here for the determination of the activation energy E_A consists in the differentiation of the experimental $\ln\tau$ versus T^{-1} dependence. As results from Eq. (5), the derivative $\partial \ln\tau/\partial(T^{-1})$ gives directly the activation energy at a given temperature, so that allows one to analyze temperature dependence of E_A. Of course, the procedure requires very accurate values of the relaxation time determined for an appropriate step of the temperature change, especially in the vicinity of the phase transition studied. The experimental results presented in Fig. 7 fulfill these requirements. In the vicinity of both *I*-*C* and *I*-*N* transitions the step of the temperature change was equal to 10^{-2} K.

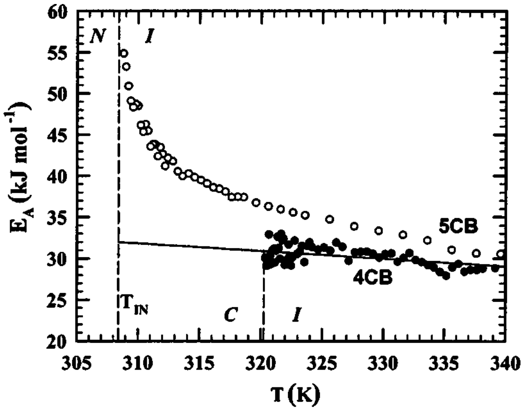

FIG. 8. Temperature dependence of the activation energy for the molecular rotation around the short axis in the vicinity of first order (4CB) and weakly first order (5CB) phase transitions. The solid line corresponds to the noncritical temperature dependence of the activation energy according to Eq. (6).

Figure 8 presents the temperature dependence of the activation energy for the rotation of 4CB and 5CB molecules in the vicinity of *I*-*C* and *I*-*N* phase transitions, respectively, obtained from the differentiation of the dependences shown in Fig.7. When the temperature approaches the phase transition, the activation energy behaves quite differently depending on the type of the transition. In case of the first order *I*-*C* transition (4CB), E_A shows a small (but beyond the experimental errors) increase with decreasing temperature. The dependence can be approximated with the linear function analogous to Eq. (1):

$$E(T)=(E_A)_{I\text{-}C}-\eta(T-T_{I\text{-}C}), \tag{6}$$

where $(E_A)_{I\text{-}C}$ denotes the activation energy at $T=T_{I\text{-}C}$. The slope η of the dependence shown in Fig. 8 for 4CB is equal to 9.2×10^{-3} kJ/(mol K). In the temperature range studied, the value of E_A for nonmesogenic 4CB changes from 28 kJ/mol to about 33 kJ/mol.

The $E_A(T)$ dependence obtained for 5CB exhibits a peculiar behavior: as the temperature approaches the *I*-*N* transition, the activation energy for the rotation of mesogenic molecules shows a critical-like increase. If one assumes that the $E_A(T)$ dependence of nonmesogenic 4CB represents a "normal" behavior of the compound of the same polarity and structure as 5CB, the difference of the dependences from Fig. 8 represents a critical part of the activation energy of mesogenic 5CB:

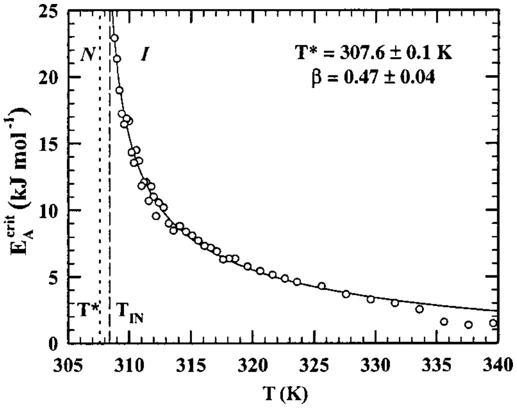

FIG. 9. The critical part of the activation energy of 5CB as a function of temperature in the vicinity of weakly first order *I*-*N* phase transition. The solid line is the best fit of Eq. (8) to the experimental data (points).

$$E_A^{crit}(T) = E_A^{meso}(T) - E_A^{nonmeso}(T). \qquad (7)$$

The difference is shown in Fig. 9. The solid line presents the best fit of equation:

$$E_A^{crit}(T) = B(T - T^*)^{-\beta}, \qquad (8)$$

to the experimental data. The values of both T^* and β resulting from the fit of Eq. (8) to $E_A^{crit}(T)$ experimental data coincide with T^* and α obtained in the static dielectric studies.

IV. CONCLUSIONS

On the basis of present results of precisely performed measurements of the linear dielectric properties of the mesogenic and nonmesogenic compounds composed of strongly polar molecules, the following conclusions can be drawn.

(i) The dielectric behavior of the nonmesogenic compounds in the vicinity of first order phase transition can adequately be taken as a reference for a critical-like behavior of the mesogenic compounds, of the same polarity and structure, in the vicinity of weakly first order phase transition.

(ii) The activation energy for the rotation of mesogenic molecules around the short axis, in the vicinity of the isotropic to nematic transition, shows a critical-like behavior in contrast to the nonmesogenic ones, for which the activation energy only weakly depends on temperature (close to the Arrhenius behavior) also in the vicinity of the first order transition to the solid state. Simultaneously, the corresponding dielectric absorption band of mesogenic compound shows a deviation from the Debye's form and an approaching of the transition to the nematic phase manifests itself in a considerable increase of the deviation.

(iii) For the mesogenic compound studied, the temperature dependence of the critical part of both the permittivity derivative and the activation energy fulfills the equation of $(T - T^*)^{-\alpha}$ type with practically the same values of the fitting parameters T^* and α.

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