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Pretransitional behavior of dielectric permittivity on approaching a clearing point in a mixture of nematogens with antagonistic configurations of dipoles

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The results of studies of static dielectric permittivity $\varepsilon(T)$ in the isotropic phase of 4-cyano-4-pentylalkylbiphenyl and n-p-methoxybenzylidene-p'-butylaniline (5CB-MBBA) mixtures are presented. 5CB and MBBA are nematogens with antagonistic permanent dipole moments configurations. An increase in MBBA concentration strongly decreases the pretransitional effect. However, a derivative analysis detected the existence of a pretransitional anomaly even if its weakness made a straightforward $\varepsilon(T)$ fit impossible. The obtained anomalies can be well portrayed by *fluidlike* equations, isomorphic to that applied in critical binary mixtures. Every time the same value of the specific heat critical exponent $\alpha\approx 0.5$ was obtained. A preliminary discussion of the influence of the permanent dipole configuration on the pretransitional behavior of dielectric permittivity was also possible.

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INTRODUCTION

Properties of the isotropic phase on approaching the nematic clearing point have been a subject of intensive research for the last three decades [1–13]. One of the reasons for such a long-standing interest is probably the lack of congruence between the dominated mean-field description and the experimental results [14,15]. Only recently an essential breakthrough has been possible due to the appearance of *complex liquid* [16–20] and *fluidlike* descriptions [14,15,19,20]. For the latter, the nematic clearing point is placed on a branch of a hypothetical coexistence curve [14 and refs therein] and the behavior in the isotropic phase can be associated with the vicinity of the *pseudospinodal critical or tricritical* point [20–22]. The latter seems to be strongly supported by recent experimental results in the nematic phase giving $\beta\approx 0.25$ for the order parameter exponent [23–25]. One of the basic experimental facts supporting the *fluidlike* hypothesis is the pretransitional behavior of dielectric permittivity [15,20]:

$$\varepsilon(T)=\varepsilon^{*}+a(T-T^{*})+A(T-T^{*})^{\phi}, \tag{1}$$

$$\frac{d\varepsilon}{dT}\propto a+A(1-\alpha)(T-T^{*})^{-\alpha}, \quad \text{and} \quad T>T^{C}, \tag{2}$$

where the exponent $\phi=1-\alpha$. The experimentally obtained value of the specific heat critical exponent α is 0.5 ± 0.02. The validity of Eqs. (1) and (2) was shown up to $T^{C}+100\,\mathrm{K}>T>T^{C}=T^{*}+\Delta T$. T^{C} denotes the isotropio-nematic (*I-N*) clearing temperature, T^{*} is the temperature of a hypothetical continuous phase transition, and ΔT is the measure of the discontinuity of the transition.

Equation (2) may at first sight seem a simple consequence of Eq. (1). However, a differential analysis of the experimental data reduces the number of fitted parameters and may reveal possible discrepancies from Eq. (2) hardly visible in a straightforward analysis of $\varepsilon(T)$ data [20]. Earlier investigations of the heat capacity C_p and density ρ also pointed to the nonzero value of the exponent α in the isotropic phase [4,6,26–29]. However, the weakness of these anomalies and their limited range of appearance (less than 10 K) strongly limited the validity of the quantitative results. It is noteworthy that Eqs. (1) and (2) were originally derived for a homogeneous phase of critical mixtures [30–32], where $\phi=1-\alpha\approx 0.88$ and $d\varepsilon/dT\propto C_v$ [33] and instead of T^{*} the critical consolute temperature or the pseudospinodal temperature should be substituted [32].

The relatively prominent anomaly of dielectric permittivity can be associated with its molecular origins [3,6,20]. It reflects the cancellation of permanent dipole moments that are ordered in an antiparallel way in prenematic fluctuations. This does not occur when the permanent dipole moment is perpendicular to the long axis of the molecule. In such a case $\varepsilon(T)$ remains as a linear function of temperature up to T^{C} [3,34]. To the best of the authors knowledge, for dielectric permittivity, there are no results discussing further the influence of the configuration of the permanent dipole on the pretransitional behavior. Regarding properties for which this molecular factor is important, quantitative discussion is probably available only for the electrooptic Kerr effect (EKE) where [5,35]

$$\mathcal{E}_{\mathrm{EKE}}=\frac{A_{\mathrm{EKE}}}{T-T^{*}}=\frac{1}{3\lambda a}\varepsilon_{0}\frac{\Delta n\Delta\varepsilon}{T-T^{*}}, \tag{3}$$

$$\text{for} \quad \Delta\varepsilon=C\left[\Delta\alpha^{P}+\frac{\mu^{2}F}{2k_{B}T}(3\cos^{2}\beta_{D}-1)\right],$$

where λ is the applied light wavelength, Δn, $\Delta\varepsilon^{0}$, and $\Delta\alpha$ are anisotropies of refractive index, polarizablity, and static dielectric permittivity for the perfectly ordered sample, μ is the apparent dipole moment, F is the local field, C is the factor associated with the applied local field model, and β_D is the angle between the permanent dipole moment and the long axis of the rodlike molecule.

In agreement with this relation EKE boosts towards positive values for $T\rightarrow T^{C}$ in nematogens with the permanent dipole moment parallel to the long axis of the molecule, for instance, in nematogenic nCB ($n=5-8$ $\beta\approx 0°$) [1–13]. The

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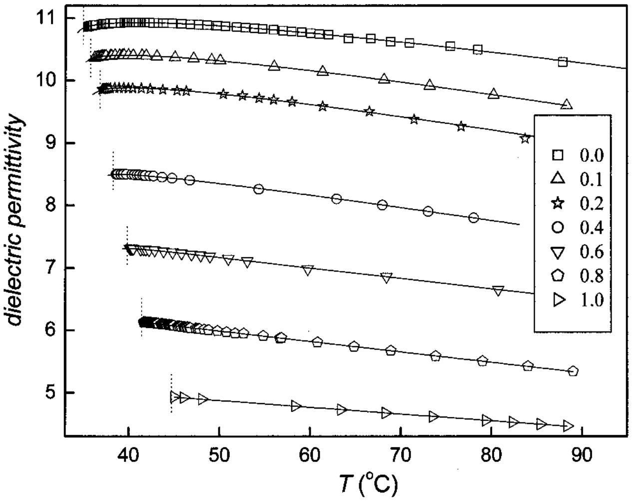

FIG. 1. Results of measurements of static dielectric permittivity ($f=10\,\mathrm{kHz}$) in the isotropic phase of MBBA-5CB mixtures. Concentrations in mass fraction of MBBA are given in the figure. Solid lines are parametrized by relation (1) with parameters collected in Table I. For MBBA ($x=1$): $\varepsilon(T)=5.415-0.01082T$. Dashed lines denote clearing temperatures.

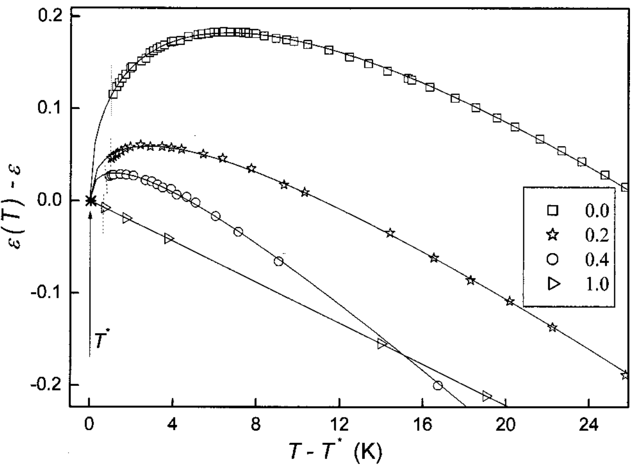

FIG. 2. Selected data from Fig. 1 near clearing in a normalized scale. Solid lines are parametrized as in Fig. 1. The arrow shows the position of the extrapolated virtual critical temperature T^*. Dashed lines denote clearing temperatures.

opposite sign of EKE occurs for nematogens with an almost perpendicular permanent dipole moment, for instance, MBBA ($\beta\approx 86°$) [36]. In *p*-azoxyanisole ($\beta\approx 62°$) [5,35] the initially positive value of EKE becomes negative for $T-T_{1-N}<7\,\mathrm{K}$. It was shown in Ref. [12] that relation (3) may also describe the behavior in mixtures of nematogens with antagonistic dipole configurations. In such a case, the *effective* molecule can be introduced where the position of the permanent dipole moment is defined by [12]

$$\beta_D=\beta_{\mathrm{Magic}}=\tan^{-1}\left[\frac{\Phi\mu_{\perp,A}+(1-\Phi)\mu_{\perp,B}}{\Phi\mu_{\parallel,A}+(1-\Phi)\mu_{\parallel,B}}\right], \qquad (4)$$

where Φ is the volume fraction of one of compounds (A, B) and $\mu_{\parallel}$ and $\mu_{\perp}$ are components of the permanent dipole moments perpendicular and parallel to the long axis of the molecule.

The interesting feature of such tests is that the angle $\beta_D=\beta_{\mathrm{Magic}}$ can take an arbitrary value in the well-defined *homologous series*.

To the best of the authors knowledge, studies of the pretransitional behavior of dielectric permittivity were conducted only in one-component mesogens with the permanent dipole moment parallel to the long axis of the rodlike molecule [[20,24,32,34], and references therein]. This paper aims to study the possible universality of the value of the exponent α in a mixture of nematogens with permanent dipole moments parallel and perpendicular to the long axis of the molecule. Two classical materials were used for studies: 4-cyano-4-pentylalkylbiphenyl (5CB, $\beta\approx 0°$ $\mu\approx 5.0\,\mathrm{D}$ [6], $T^C(I\text{-}N)=35.4\,°\mathrm{C}$) and *n*-*p*-methoxybezylidene-*p*′-

TABLE I. Results of fitting experimental data $\varepsilon(T)$ by means of Eq. (1) and (2). Values of the latter (Fig. 3) are marked (*). For $x=0.6$ and 0.8 parameters T^*, A, a, and α were taken from the derivative analysis (Fig. 3) and substituted in Eq. (1). Cleaning temperatures were determined experimentally as a jump in dielectric permittivity when moving from the isotropic phase to the mesophase. The lack of the error means that it is equal to the last significant digit.

X (mass. f. MBBA)	T^C (°C)	T^* (°C)	ε^*	A (K^1)	A ($\mathrm{K}^{0.5}$)	α
0	35.38	34.3		$-0.029_{\pm 0.003}$	0.127	$0.49_{\pm 0.02}$
			$10.773_{\pm 0.003}$	(*)-0.033	(*)0.154	(*)0.5
0.1	36.15	35.2	$10.264_{\pm 0.005}$	$-0.030_{\pm 0.003}$	$0.110_{\pm 0.002}$	$0.52_{\pm 0.03}$
				(*)-0.031	(*)0.132	(*)0.5
0.2	37.02	36.0	$9.828_{\pm 0.005}$	$-0.023_{\pm 0.005}$	$0.075_{\pm 0.003}$	$0.49_{\pm 0.03}$
				(*)-0.0284	(*)0.107	(*)0.5
0.4	38.50	37.5	$8.48_{\pm 0.02}$	$-0.025_{\pm 0.007}$	$0.060_{\pm 0.005}$	$0.48_{\pm 0.05}$
				(*)-0.026	(*)0.060	(*)0.5
0.6(*)	(*)40.60	39.7	7.30	(*)-0.022	(*)0.033	(*)0.5
0.8(*)	(*)41.64	40.8	6.13	(*)-0.018	(*)0.015	(*)0.5

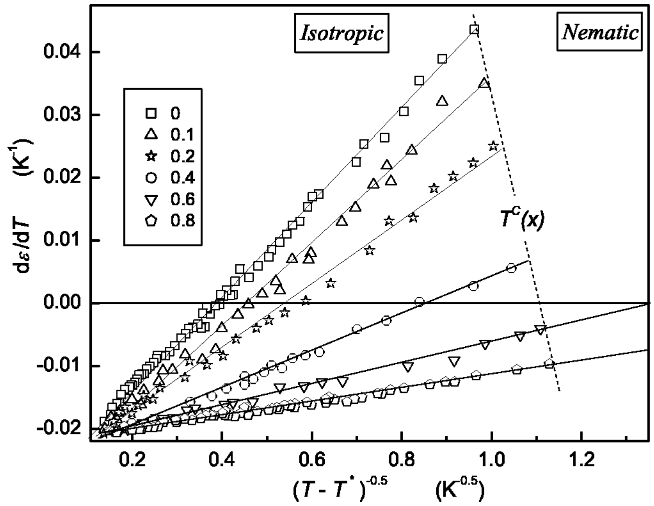

FIG. 3. Results of derivative analysis of experimental data from Fig. 1 presented in the scale showing the validity of Eq. (2). The dashed line indicates clearing temperatures. The intersections of the horizontal line $d\varepsilon/dT=0$ with lines parametrizing experimental data determine positions of $T_{\max}$ at which $\varepsilon(T)$ dependencies start bending down on approaching T^*. Parameters of lines portraying experimental data are given in Table I.

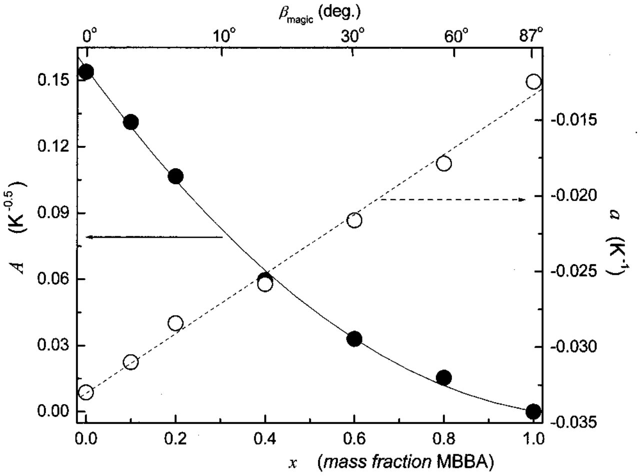

FIG. 4. Values of the critical amplitude and the amplitude of the linear term in Eq. (1) that resulted from the derivative analysis [Fig. 3, Eq. (2)]. The solid curve and the dashed line are parametrized by: $A(x)=0.155-0.27x+0.12x^2$ and $a(x)=-0.0331+0.0197x$. The upper scale shows values of the magic angles calculated by means of Eq. (4).

butylaniline (MBBA, $\beta\approx 87°$, $\mu\approx 1.983$ D [36], $T^C(I\text{-}N)=44.9\,°\mathrm{C}$). The mentioned results made also a preliminary discussion of the position of the dipole moment on the pretransitional behavior of dielectric permittivity possible.

EXPERIMENT

Measurements of the static dielectric permittivity were conducted using Solartron 1260 A impedance analyzer giving a five-digit resolution. The sample was placed in a capacitor made of Invar, with 0.5-mm gap [20]. The temperature was stabilized by means of Julabo HD 45D circulating thermostat with precision ±0.01 K and was measured using a miniature platinum resistor (DIN 43 260) placed in a cover of the capacitor and Keithley 195 A multimeter with ±0.01 K resolution. MBBA was purchased from Aldrich and 5CB was obtained from the Technical Military University, Warsaw, Poland due to the courtesy of Roman Dabrowski and Krzysztof Czupryński. The samples were carefully degassed immediately prior to the measurements. The analysis was conducted using ORIGIN 6.1 software

RESULTS AND DISCUSSION

Figure 1 shows the experimental behavior of the static dielectric permittivity in the isotropic phase of 5CB-MBBA mixtures. An increase in the amount of MBBA in the mixture decreases the pretransitional bending down of $\varepsilon(T)$ for $T\to T^C$ from an almost linear behavior remote from T^C. This is clearly visible in Fig. 2 where data are presented in the normalized scale to remove the large shift of values visible in Fig. 1. All pretransitional effects are well portrayed by relation (1) (solid lines in Figs. 1 and 2). For each case the same value of the critical exponent $\alpha\approx 0.5$, within the limit of experimental error, was obtained. The discontinuity of the transition gradually decreases from $\Delta T\approx 1.1\,\mathrm{K}$ in 5CB to $\Delta T\approx 0.7\,\mathrm{K}$ in MBBA [14,37]. These values agree well with those obtained earlier in nonlinear dielectric effect studies. Figure 3 shows a derivative analysis of experimental data from Fig. 1. The clear validity of Eq. (2) shows that Mistura's proposal [33] for the homogeneous phase of critical mixtures is well fulfilled also for the tested case. Despite the remarkable sensitivity to distortions of the derivative analysis they show that relations (1) and (2) remain valid in the whole tested range of temperatures with the same value of the exponent $\alpha=0.5$ for all tested mixtures. Moreover, the derivative analysis easily detects the existence of the pretransitional anomaly even if the fit by means of Eq. (1) is not possible: the pretransitional bending down of $\varepsilon(T)$ on approaching the clearing point does not occur ($x=0.6$ and 0.8 in Figs. 1 and 2). For $x=0.8$ experimental $\varepsilon(T)$ dependence may even seem to be a linear function. Intersections of the horizontal line $d\varepsilon/dT=0$ with lines parametrizing experimental data determine positions of $T_{\max}$ at which the bending down starts. For $x=0.6$ and 0.8, temperatures $T_{\max}$ shift below the clearing point. The application of the derivative analysis made it possible to determine amplitude A and a in Eqs. (1) and (2) for all tested concentrations or alternatively for all tested values of the magic angle (Fig. 4).

Concluding, it was shown in Ref. [38] that *fluidlike* Eqs. (1) and (2) will remain valid if the influence of ionic impurities on decreasing the measurement frequency occurs. This paper shows that the same takes place in a mixture of nematogens with antagonistic positions of permanent dipole moments or alternatively on increasing $\beta_D=\beta_{\text{Magic}}$ angle. The same value of the specific heat critical exponent $\alpha\approx 0.5$ was obtained, every time. An increase in MBBA concentration (increase of β_{Magic}) causes a systematic decreases of the *critical* amplitude A and the shift of the temperature $T_{\max}$ towards the virtual critical temperature T^*. The lack of a pretransitional behavior in MBBA shows that dielectric permittivity registers pretransitional fluctuations not as density fluctuations, but exclusively as orientational ordering fluctuations. The detection of pretransitional behavior is possible only if the cancellation of the component of the dipole moment parallel to the main axis of the rodlike molecule is notable. The sensitivity of dielectric permittivity exclusively to the antiparallel ordering may be responsible for the fact that Eqs. (1) and (2) also portray the behavior of the dielectric permittivity on approaching the I-SmA and I-SmE phases [39,40].

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