Critical behavior of the isotropic–smectic-A transition in p-decyloxy-benzylidene-p-amino-2-methyl-butyl-cinnamate studied by the nonlinear dielectric effect method

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Results are presented of measurements of $\Delta\varepsilon/E^2$ versus temperature for the isotropic–smectic-A transition in p-decyloxy-benzylidene-p-amino-2-methyl-butyl-cinnamate (DOBAMBC). For the first time a negative value of the pretransitional effect was observed. In all previous research on the nonlinear dielectric effect in liquids, critical fluctuations gave a large, positive increment. Experimental data satisfy the power relation $\Delta\varepsilon/E^2 \simeq -19.3/(T-T^*)$ (10^{-18} $\mathrm{m^2\,V^{-2}}$) for $T>T_c$ and $\Delta T = T_c - T^* \simeq 3.4\,^\circ\mathrm{C}$.

The nonlinear dielectric effect (NDE), similar to the Kerr effect or light scattering, is extremely sensitive to nonhomogeneities in the medium's dielectric properties caused by critical fluctuations. This method was first used by Piekara in 1936 in order to investigate a critical solution of nitrobenzene-hexane.[1,2]

NDE studies depend on measurements of the difference in the electric permittivity ($\Delta\varepsilon$) in a strong (ε_E) and a weak (ε_0) electric field ($\Delta\varepsilon=\varepsilon_E-\varepsilon_0$). For sufficiently strong electric fields (E) the permittivity may be written in the form of a series:[2]

$$\varepsilon_E=\varepsilon_0+aE^2+bE^4+\cdots \ . \tag{1}$$

In the case of a liquid, in practice, this series may be broken off after the second term. In accordance with the Debye theory and based on the Langevin expansion,[3]

$$\frac{\Delta\varepsilon}{E^2}=-C\frac{\mu^4}{T^3}f(\varepsilon)\ , \tag{2}$$

where C is a coefficient depending on the system of units, μ is the dipole moment of a molecule, T is temperature, and $f(\varepsilon)$ is a parameter depending on the type of local field assumed.

As may be seen from the preceding formula, in the case where the origin of the nonlinearity is an effect associated with orientation of the dipole moments, NDE has a negative sign. This is, in principle, the sole mechanism causing a negative value of $\Delta\varepsilon$. All the remaining known molecular mechanisms give a positive contribution to the NDE value.[2] This refers also to the critical, pretransitional effect in solutions of liquids of limited miscibility[4,5] and in liquid crystals (isotropic-nematic[4] and isotropic–blue-phase transition[6]).

A theoretical model of the effects causing a critical NDE effect in such systems was proposed by Goulon, Greffe, and Oxtoby.[7] According to this model the following relation is satisfied:

$$\frac{\Delta\varepsilon}{E^2}\sim(T-T^*)^{-\psi}\ . \tag{3}$$

For critical solutions T^* is the temperature of phase separation and $\psi\simeq 0.59$. The experimentally obtained values of the exponent are somewhat lower, about 0.4.[5,8] For the isotropic-liquid–liquid-crystal phase transition $T^*=T_c-\Delta T$ (T_c is the clearing temperature) and $\psi=1$. Such a value was ascertained in the case of an isotropic-nematic transition in MBBA (Ref. 4) and for the isotropic–blue-phase transition in cholesteryl oleate (CO) and cholesteryl oleyl carbonate (COC).[6]

Up to now, there were no studies of the NDE for the isotropic-smectic transition. In this paper such measurements have been conducted in the isotropic phase of DOBAMBC (p-decyloxy-benzylidene-p-amino-2-methyl-butyl-cinnamate) in the vicinity of the phase transition to smectic A. The temperature of the isotropic–smectic-A transition was 119.25 °C and smectic A–smectic C^* about 96 °C. They are in agreement with values earlier observed.[9]

Measurements of $\Delta\varepsilon/E^2$ were performed on an apparatus constructed according to the concept of Małecki.[10] This method depends on a comparison of working frequencies of two generators. In the circuit of one of them is a measurement capacitor containing the tested liquid. The frequency of the measurement field was of the order of 1 MHz. The intensity of the strong electric field did not exceed 3.5 $\mathrm{kV\,mm^{-1}}$. It was applied in the form rectangular impulses of duration time 1 ms. They were repeated with a frequency of about 30 Hz. A flat-parallel capacitor was used with a gap of 0.385 mm between electrodes. The capacitor with the tested liquid was placed in a thermostat filled with oil. Temperature stability was 0.01 °C.

The data of $\Delta\varepsilon/E^2$ measurements in DOBAMBC are shown in Fig. 1 (lower part) and collected in Table I. For comparison, in the upper part of the figure is shown the plot for the transition to the nematic phase in MBBA based on Ref. 4, and for the transition to the blue phase in CO based on Ref. 6. The most remarkable result is the reversed sign of the effect in DOBAMBC. In all previous research on NDE in liquids, the critical fluctuations

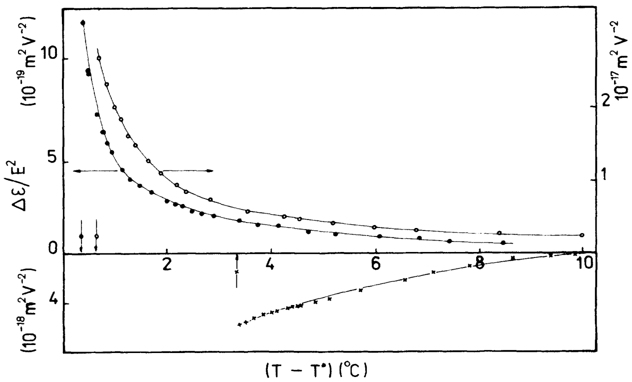

FIG. 1. The temperature dependence of $\Delta\varepsilon/E^2$ for MBBA (○) (Ref. 4), cholesteryl oleate (●) (Ref. 6), and DOBAMBC (×). The units of NDE are 10^{-17} m^2V^{-2}, 10^{-19} m^2V^{-2}, and 10^{-18} m^2V^{-2}, respectively. The data are presented vs $(T-T^*)$, which makes differences in values of ΔT clearly visible. The vertical arrows indicate the values of ΔT.

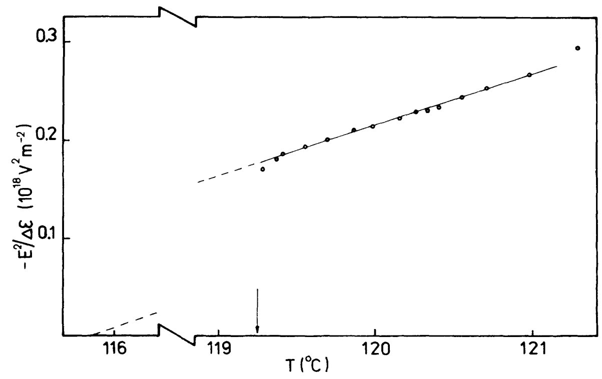

FIG. 2. The plot of $(\Delta\varepsilon/E^2)^{-1}$ vs temperature for DOBAMBC.

caused strong, positive changes in the electric permittivity $(\Delta\varepsilon>0)$ while approaching the phase-transition temperature. For DOBAMBC the sign of these changes is negative $(\Delta\varepsilon<0)$. Their temperature dependence may be described by a power relation (see Fig. 2)

$$\frac{\Delta\varepsilon}{E^2}\simeq\frac{-(19.3\pm0.5)}{(T-T^*)^{1\pm0.04}}\,10^{-18}\ \mathrm{m^2V^{-2}}\quad \text{for } T_c<T<T_c+1.5 \qquad (4)$$

TABLE I. Measurement of $\Delta\varepsilon/E^2$ vs temperature.

T (°C)	$\frac{\Delta\varepsilon}{E^2}$ $(10^{-18}\ \mathrm{m^2V^{-2}})$
119.28	−5.85
119.38	−5.51
119.50	−5.30
119.56	−5.215
119.69	−5.00
119.87	−4.75
119.98	−4.70
120.17	−4.49
120.27	−4.41
120.34	−4.35
120.40	−4.28
120.55	−4.08
120.71	−3.95
120.98	−3.74
121.29	−3.40
121.57	−3.04
122.40	−2.20
122.92	−1.655
123.68	−1.05
124.16	−0.67
124.47	−0.41
125.17	−0.10
130.10	0

where $T^*=T_c-\Delta T$, $\Delta T=3.38\pm0.1$ °C is the measure of the discontinuity of the phase transition. On receding from T_c the effect tended to zero, making it possible to neglect the noncritical background effect. The fit was done by means of the least-square method.[11] The goodness of the fit was $\chi_\nu^2=1.59$.

For temperatures lying in the immediate vicinity of T_c (e.g., for $T<T_c+0.25$) the experimental values of the NDE are a bit different than those arising from the above relation. Similar discrepancies took place in the previously mentioned NDE studies and also for the Kerr effect and light-scattering investigations in the vicinity of the nematic phase.[12] The value of $\Delta T\simeq3.4$ °C for DOBAMBC is relatively large in comparison to those obtained in our earlier studies of liquid crystals, e.g., $\Delta T\simeq0.7$ °C for MBBA (Ref. 4) and $\Delta T\simeq0.4$ °C for CO and COC,[6] as it is shown in Fig. 1.

The most interesting result of this paper is the negative sign of the critical effect. It can be caused by the fact that the dominating mechanism responsible for the critical NDE effect may be of orientational nature. In the isotropic phase fluctuations of smectic structure appear and their magnitude increases while approaching the clearing temperature. If ordering of the molecules' dipole moments occurs in these fluctuations, then there is a negative growth in the value of $\Delta\varepsilon$. A similar pretransitional, qualitative effect has only been observed in investigations on nonlinear effects (i.e., nonlinear changes in electric permittivity or magnetic susceptibility) in the solid state.[13–15]

On the other hand, the frequency of the measurement field ($f\simeq1$ MHz) may have a substantial influence on the sign and value of the effect. Its value may be too high for some mechanisms contributing to the total value of the NDE. The strong dispersion of $\Delta\varepsilon$ in smectic phases of DOBAMBC seems to point to such a possibility.[16–18] In DOBAMBC not only smectic-A but also ferroelectric smectic-C^* fluctuations may appear in the isotropic phase.

All these lead to the question: is the obtained result characteristic for the isotropic–smectic-*A* transition? It can be answered by further studies of systems without the ferroelectric phase.

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