Nonlinear Dielectric Effect in Liquids in the Vicinity of the Critical Point

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Results of systematic investigations carried out in our laboratory on the non-linear dielectric effect (NDE) in the critical mixtures of liquids and of liquid crystals are discussed and systematized. The objective of these studies was to determine experimentally the parameters of the critical NDE and to attempt to apply this research method to an examination of various aspects of critical phenomena. Also discussed are the most recent results.

1. INTRODUCTION

Nonlinear dielectric effect (NDE) investigations involve measuring the difference in electric permittivity ($\Delta\varepsilon$) in a strong (ε^E) and in a weak (ε^0) electric field E. For sufficiently strong electric fields the permittivity may be expressed as a series:

$$\varepsilon^E = \varepsilon^0 + \varepsilon^2 E^2 + \varepsilon^4 E^4 + \cdots \tag{1}$$

where ε^2 and ε^4 describe the nonlinear changes of the electric permittivity. In the case of a liquid this expansion may in practice be terminated after the second term [1]. For studing properties of solutions of limited mis-cibility the NDE method was first applied by Piekara and Piekara in 1936 [2]. Examining a solution of nitrobenzene–hexane they observed a marked positive rise in $\Delta\varepsilon/E^2$ (the value of the NDE) in the vicinity of the critical point. During the last 10 years this method has been applied to study, from the contemporary point of view of the physics of phase transitions, a

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number of solutions of ordinary liquids in the critical region [3–21] and liquid crystals in the vicinity of the phase transition from the isotropic phase [4, 22, 23].

The theoretical model of the phenomena taking place in a critical binary solution close to the critical temperature (T_c) was proposed by Goulon et al. [7] based on a droplet model. The value of the NDE, according to this model, may be expressed by the following relation:

$$\frac{\Delta\varepsilon}{E^2} = \left(\frac{\Delta\varepsilon}{E^2}\right)_B + \left(\frac{\Delta\varepsilon}{E^2}\right)_C \simeq \left(\frac{\Delta\varepsilon}{E^2}\right)_B + A_1 t^{-\Psi} + A_2 t^{-\xi} \qquad (2)$$

with the condition

$$A_1 \gg A_2 \qquad (3)$$

where the indexes C and B denote the critical effect and the noncritical background effect (associated with the molecular properties of the system), respectively, $t = (T - T_C)/T_C$ is the temperature distance from the critical point, $\Psi = \gamma - 2\beta \simeq 0.59$, $\xi = 1 - 2\beta \simeq 0.35$, and A_1 and A_2 are amplitudes. Since $A_1 \gg A_2$, according to the model, the critical NDE effect may be written as a single power law with the exponent $\Psi \simeq 0.59$. This effect is associated with the critical fluctuations, namely, droplets elongation in the direction of the electric field. A more explicit expression for the amplitude of the critical effect was given by Pyżuk [24]:

$$\left(\frac{\Delta\varepsilon}{E^2}\right)_C = A_1 t^{-\Psi} = \frac{D}{\varepsilon_c^2}\left(\frac{\partial\varepsilon}{\partial x}\right)^4 \frac{\Gamma^2}{\xi_0^3} t^{-\Psi} \qquad (4)$$

where D is a constant connected with the model, $\partial\varepsilon/\partial x$ is the static electric permittivity increment, x is a concentration of one of the solution components in mole fraction, ε_c is the permittivity of the solution, and ξ_0 and Γ are critical amplitudes defined for the correlation length and for the osmotic compressibility, respectively [25].

Hence, the critical amplitude depends in first approximation on the dielectric properties of the solution in the following manner:

$$A_1 \sim \frac{(\varepsilon_1 - \varepsilon_2)^4}{\varepsilon_c^2} \qquad (5)$$

where ε_i is the electric permittivity of the ith constituent of the solution $(i = 1, 2)$. A similar temperature dependence for the critical part of NDE was predicted by Høye and Stell [26].

In Section 3, a description is given of studies conducted in our laboratory in order to determine experimentally the basic characteristics of

the critical NDE effect and its utilization for studing various aspects of critical phenomena in liquids. In these investigations, a type of apparatus as proposed by Małecki [27] was used. The method relied on the principle of comparing the operating frequencies of two generators, one of which has in the resonance circuit a capacitor with the tested liquid. The operating frequency of the generators was about 1 MHz. High voltage was applied to the capacitor in the form of rectangular impulses with a time duration of about 1 ms and repetition frequencies in the range 30–300 Hz. The tested liquid was placed in a parallel plate capacitor [20], to which a voltage of up to 1400 V was applied. Depending on the liquid, the capacitor gap had a value of 0.2–1 mm.

2. THE NONLINEAR DIELECTRIC EFFECT IN CRITICAL BINARY SOLUTIONS

Investigations of the nonlinear dielectric effect in solutions of partial miscibility reported by various researchers give values for the exponent Ψ in the range 0.3–0.6 [12, 19] and even up to 0.8 [8]. The main reason for this scatter of experimental exponent values is most probably due to the noncritical background effect. The magnitude of the NDE is very sensitive not only to critical fluctuations in the vicinity of the critical point, but also to many other mechanisms taking place both macroscopically and microscopically [1]. Hence the essential problem is how to separate from the total measured value that part which may be taken as the critical effect, treating the remainder as the background. In publications dealing with this problem the following solutions can be found:

(1) extrapolating data far away from the temperature of transition to the critical region, based on the assumptions implied in specific models for the behavior of the molecules of the solution components [4, 8];

(2) taking as background the effect measured in a reference solution, i.e., a solution in which one of the components (the solvent) is replaced by another which mixes well with the second component of the tested solution [8, 12–15, 20] (in the case where it may be assumed that the background originates from one of the solution constituents);

(3) assuming as background the effect originating from isothermal (at the critical temperature of the tested, binary solution) measurements as a function of the third component in a ternary solution—the third component is a substance which mixes well with the two principal components;

    (4)   applying a fit of the experimental data to a relation describing simultaneously the critical and the background parts of the effect [12, 19].

As an example, in Ref. 12 the results of an analysis of the NDE behavior for the critical benzonitrile–isooctane solution are given for various types of background effects, various temperature distances from the critical point, and various definitions of this distance.

    The method of numerical fitting was applied for the interpretation of NDE data for more than a dozen solutions differing in the mechanisms which can affect the value of the background. In all cases the value of the exponent Ψ was found to be approximately 0.4. Hence, this value may be considered, in the limits of the error (equal to ± 0.03), as the universal experimental value of this exponent [12, 19, 21]. This value is different from the theoretically predicted $\Psi \simeq 0.59$.

    The best approximation for the critical parameters can be obtained in systems where the background effect is determined by means of experimental methods. This is connected with the fact that a greater number of free parameters means poorer quality of the fitting. This condition is particularly fulfilled for the nitrobenzene–eicosane critical solution, where it may be even assumed that $(\Delta\varepsilon/E^2)_B \simeq 0$ in the vicinity of T_C [19]. It gave $\Psi = 0.39 \pm 0.01$ over a large temperature interval (18 K). It was also verified that the disagreement between the experimental and the theoretical value of this exponent could be associated with neglecting the second term in Eq. (2). The above-mentioned solution seems to be particularly suitable for this aim.

    The NDE data in this system may be described by the double power relation

$$\frac{\Delta\varepsilon}{E^2} \simeq 0.19 t^{-0.55} + 0.5 t^{-0.37}, \qquad (10^{-16}\ \mathrm{m}^2 \cdot \mathrm{V}^{-2}) \tag{6}$$

The relative error (given as three standard deviations) is about 10 % for each value in the above equation. Values obtained for the exponents are approximately the same as those predicted from the droplet model [7]. However, the amplitudes do not satisfy Eq. (3).

    NDE measurements carried out in the two-phase region would be interesting, although presenting considerable experimental difficulties. Such measurements were carried out in the upper phase of the nitrobenzene–heptane solution (Fig. 1) [13]. It was found, after allowing for the background effect, that the measurements may be described by a power law with an exponent value similar to that describing the effect in the single-phase region. The ratio of critical amplitudes in the two- and one-phase region was 0.68 ± 0.15.
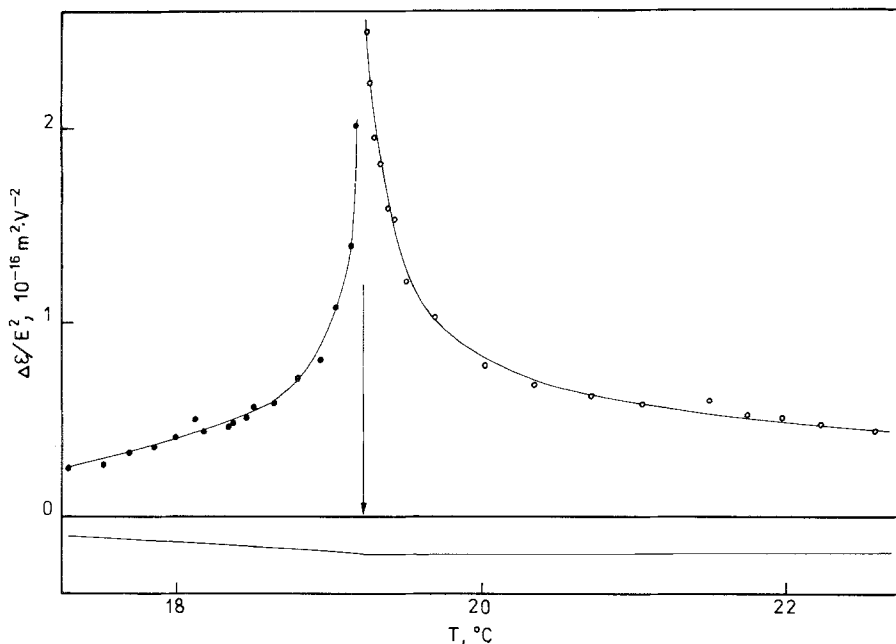
Fig. 1. Relation $\Delta\varepsilon/E^2$ versus temperature for a nitrobenzene–heptane solution of critical concentration. ●, Results of measurements for $T < T_c$, in the upper phase of the two-phase region. ○, Results for the homogeneous solution, above T_c.

3. OTHER INVESTIGATIONS ON LIQUID MIXTURES

From temperature studies in a critical solution it is possible to determine the basic properties of the critical effect of the given critical quantity. Further data may be obtained when investigating more complex systems.

The first, and simplest, modification is changing the concentration of the solution to noncritical. Tests of this kind were carried out in nitrobenzene–hexane (nb–hx) solutions and in benzonitrile–hexane (bn–hx) solutions [15]. These results are illustrated in Fig. 2. Substituting

$$t = \frac{T - T_C}{T_C} \rightarrow t' = \frac{T - T_{Sp}(x)}{T_{Sp}(x)} \tag{7}$$

for

$$T_{Sp}(x) < T_B(x), \qquad T_{Sp}(x_C) = T_C, \qquad T > T_B(x)$$

where $T_{Sp}(x)$ is the temperature of the pseudospinodal in a solution of concentration x, and $T_B(x)$ is the temperature of the binodal for the given
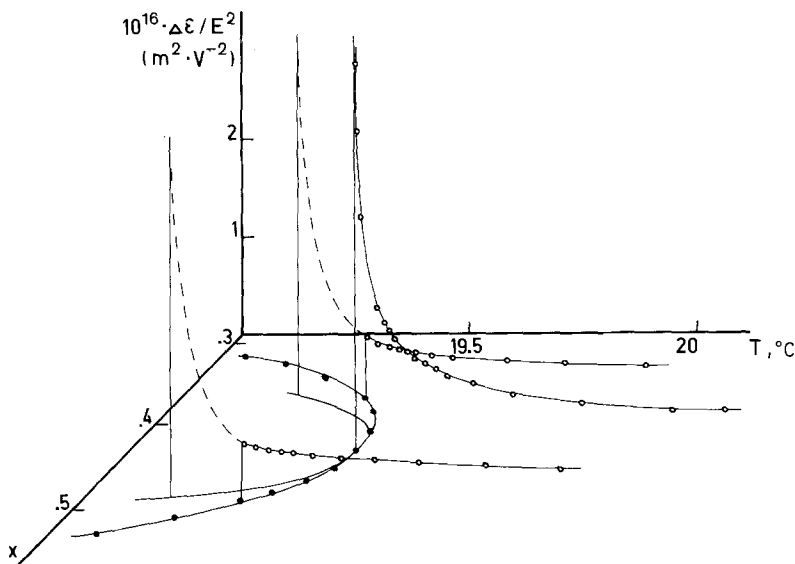
Fig. 2. The binodal and the pseudospinodal curves for the nitrobenzene–hexane solution, determined by means of the nonlinear dielectric effect method. ●, The coexistence curve. ○, The NDE measurements for the critical ($x_c = 0.43$ mole fraction of nb) and noncritical ($x = 0.37$ and 0.49 mole fractions, respectively) solutions.

concentration x, the experimental data on critical and noncritical isopleths may be described by the same single power law. For the NDE the critical exponent becomes slightly smaller on receding from the critical concentration ($\Psi \simeq 0.4$ for $x = x_C$ and $\Psi \simeq 0.3$ for $x = x_C \pm 0.06$). A similar behavior was observed earlier for light scattering ($\gamma \simeq 1.24$ for $x = x_C$ and $\gamma \simeq 1$ for $x = x_C \pm 0.1$) [28]. This change in value may be caused by an increase in $\Delta T = T_B - T_{Sp}$ on moving away from x_C, because the data were analyzed at ever-increasing distance from T_{Sp}, which is the equivalent of T_C for $x = x_C$. In a critical solution on moving away from T_C the influence of additional higher-order terms affects the apparent critical behavior and there may also be a crossover to the classical region [29]. For the tested solutions the characteristic universal parameters of the coexistence curves and pseudospinodals are given in Table I. The values obtained for the universal quantities are in agreement with those deduced from Refs. 30–32. It is noteworthy that in Ref. 33, for a chosen system, a good agreement has been obtained for the spinodal and pseudospinodals obtained by various physical methods.

Usually, experiments on solutions of limited miscibility are conducted under atmospheric pressure. When changing the pressure p a line of critical

Table I.   The Universal Parameters of Pseudospinodals Determined
by the NDE Method and of Binodals for Nitrobenzene–Hexane
and Benzonitrile–Hexane Solutions

	Critical exponent		Ratio of amplitudes X_{Sp}/X_B
Solution	Binodal (B)	Pseudospinodal (Sp)	
Nitrobenzene–hexane	0.345 ± 0.015	0.391 ± 0.02	0.704 ± 0.1
Benzonitrile–hexane	0.346 ± 0.015	0.377 ± 0.02	0.732 ± 0.1

points $T_C(p)$ is found. For the NDE such investigations were carried out
with the solution nb–hx (Fig. 3) [11]. The plot of $T_C(p)$ obtained may be
presented approximately by a cubic polynomial. On approaching a given
point on the $T_C(p)$ curve, isothermally versus p or isobarically versus T,
the NDE critical effect may be described by the same exponent within the
limits of error. This behavior is in agreement with the consequences of
smoothness postulate [34, 35]. It is difficult to find a definitive interpreta-
tion of the decrease of Ψ with increasing p. This could be due, for instance,
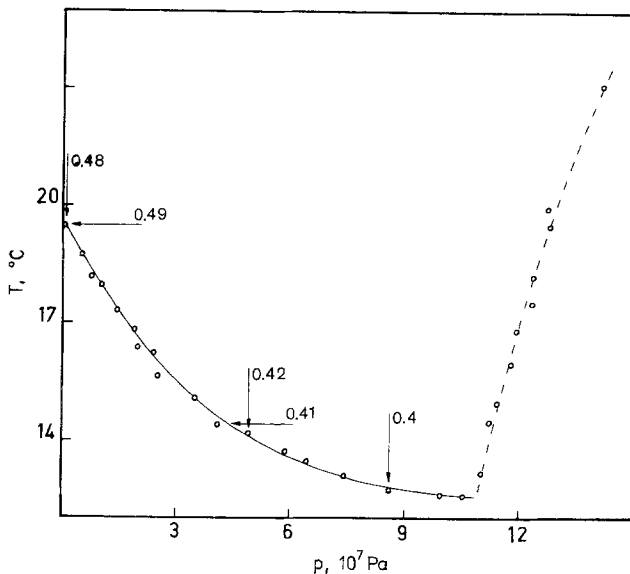

Fig. 3.   Temperature of phase transition as a function of pressure for a
nitrobenzene–hexane solution of concentration $x = 0.43$ mole fraction of
nitrobenzene. Arrows indicate values of the exponent Ψ for the isother-
mic and the isobaric cases. Broken line denotes a first-order transition to
the solid state.

to problems in allowing for the background effect (the construction of the pressure chamber caused certain limitations in sensitivity of the NDE apparatus) or also undetectable [35] (lying within the limits of error) but significant changes in x_C with increases in pressure [36].

In general, a third additional variable characterizing the properties of the solution could be also a density variable. In the experiment it could be achieved by adding a third component to the binary solution. For small concentrations of this component, the properties of ternary system are modified by means of Fisher's renormalization [37]:

$$\Delta T = |T - T_C| \rightarrow \Delta T^* = f_t \, |\Delta T|^{1/(1-\alpha)} + f_x \, |\Delta x^t|^{1/(1-\alpha)} + \cdots \quad (8)$$

where ΔT^* describes the distance from the critical point in the doped mixture, Δx^t is the concentration distance from the critical point relative to the dopant's critical concentration x^t, f_t, and f_x are the normalizing amplitudes, and α is the critical exponent for the specific heat ($\alpha \simeq 0.11$) [25, 34].

Very probably the experimental difficulties are the reason that such investigations are usually conducted as a function of temperature in the doped binary solution [i.e., $\Delta x^t = 0$ in Eq. (8)]. The renormalized region then appears in the immediate vicinity of T_C and increases with the concentration of the dopant [25, 37, 38]. In a critical nitrobenzene–heptane (nb–hp) solution doped with carbon tetrachloride (CCl_4) (for x^t less than 0.03 m.f. of CCl_4), no change was observed in the amplitude and critical exponent of NDE [12]. As anticipated, only T_C decreased [38]. Similar studies performed in a veratrole–heptane (ve–hp) solution doped with 2-nitropropane (2-np) (for x^t less than 0.04 m.f. of 2-np) showed a reduction of Ψ with increase in x^t [12]. The critical temperature rose. We note that 2-np dissolves very nonuniformly in the solution constituents. It may be altogether ruled out, however, that reduction in Ψ was caused by an influence of the dopant on the concentration (critical) in the binary system [35].

It would appear that a more unequivocal answer to the question of how the exponent Ψ behaves as a result of Fisher's renormalization could be obtained from isothermal studies [$\Delta T = 0$ in Eq. (8)]. In this way the problems involved in the occurrence of two regions—renormalized and unrenormalized—and also in the possible discontinuity of the phase transition may be avoided. Also, there are no problems with the noncritical background as it is simple to go to an infinite distance from the critical point.

NDE tests of this kind were carried out in a nitrobenzene–hexane solution of critical concentration and temperature as a function of concen-

tration of added benzene [17], ideally mixing with nitrobenzene and hexane. Since the temperature studies in a critical nb–hx solution gave a value $\Psi = 0.43 \pm 0.01$ [12], it was anticipated that the renormalized value of the exponent would be $\Psi' = \Psi/(1 - \alpha) \simeq 0.48$. The value obtained was 0.47 ± 0.015.

   In all the cases discussed the sign of the nonlinear dielectric effect was positive. But this could be changed by doping a critical solution having small, positive, critical and noncritical effects with a third component giving a large, negative contribution. This scheme was implemented for a perfluoromethylcyclohexane–CCl_4 (pfmchx–CCl_4) system doped with nb (Fig. 4) [20]. The dopant influenced the sign of the total effect, changed the nature of the background, and caused a rise in the critical effect. The electric permittivities of pfmchx and CCl_4 are very small and almost equal. For nb the electric permittivity is about 29. Moreover, nb dissolves ideally in CCl_4 and very weakly in pfmchx. Hence, in first approximation, one can speak of a quasibinary system nb + CCl_4–pfmchx. The difference in permittivities of the constituents and also, according to Eq. (3), the critical amplitude of the NDE increase with nb concentration. It is clear that the increment in the critical effect above the background effect is positive in this case, as in all the previous cases discussed, i.e., $\varepsilon_E > \varepsilon_0$.
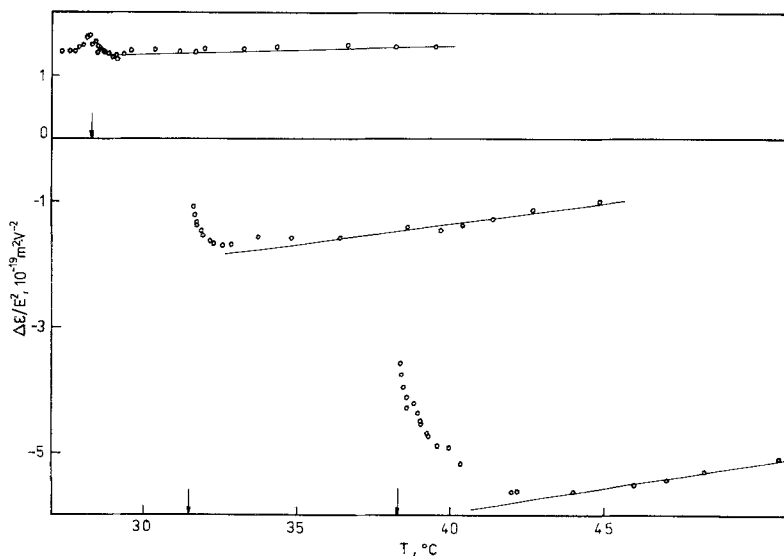

Fig. 4. The NDE versus temperature for three binary perfluoromethyl–cyclohexane–carbon tetrachloride solutions doped with nitrobenzene. Their parameters are the following: (1) 28.35, 0.285, 0; (2) 32.0, 0.290, 0.01; (3) 38.5, 0.300, 0.027. The first number gives the critical temperature (°C). The second the pfmchx concentration of the binary solution, and the third the dopant's concentration (mole fractions). Arrows indicate the points of phase transition.

4. NDE IN THE VICINITY OF THE PHASE
TRANSITION ISOTROPIC–LIQUID CRYSTAL

As mentioned in Section 1, NDE behavior was also studied in liquid crystals, in the isotropic phase in the vicinity of the phase transition temperature to a liquid crystal phase. The first measurements of this type were carried out for the isotropic–nematic transition in MBBA [4]. Similar studies were conducted also for the isotropic–blue phase transition in cholesteryl oleate (CO) and cholesteryl oleyl carbonate (COC) [22, 23]. In both cases the experimental data could be expressed by a relation derived from mean-field theory [39]:

$$\left(\frac{\Delta\varepsilon}{E^2}\right)_C \sim \frac{1}{T-T^*} \qquad \text{for} \quad T_C > T^* \quad \text{and} \quad T > T_C \qquad (9)$$

Here T_C is the clearing temperature of the discontinuous phase transition to the liquid crystal phase, while T^* is the hypothetical extrapolated temperature of the continuous phase transition. The measure of the discontinuity is the magnitude $\Delta T = T_C - T^*$. As an example ΔT has a value 0.7 K for MBBA [4] and 0.4 K for CO [23] (Fig. 5). It is noteworthy that for the isotropic–blue phase transition a numerical analysis did not exclude the possibility that the optimum critical exponent describing NDE behavior has a value in the range 0.8–0.9.
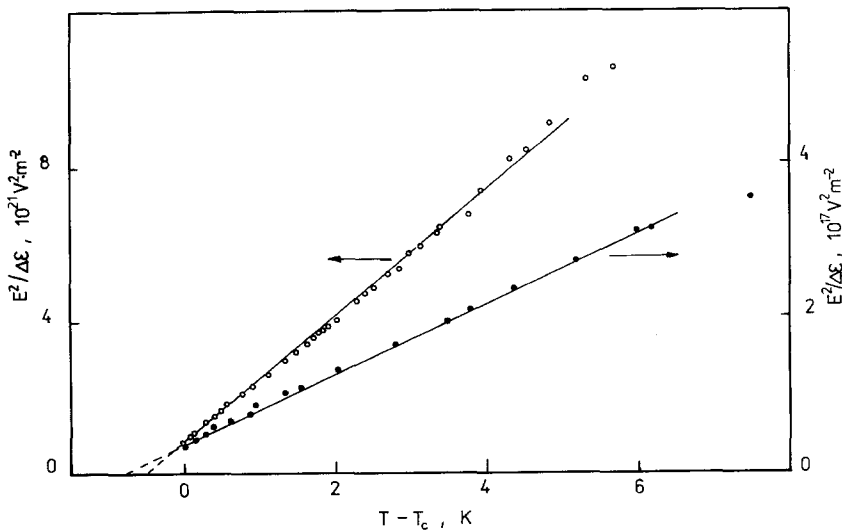

Fig. 5. Inverse of the NDE versus temperature for MBBA and CO. MBBA: ●, 10^{17} V$^2\cdot$m^{-2} units. CO: ○, 10^{21} V$^2\cdot$m^{-2} units.

Very recently the NDE has been investigated near the transition to the smectic phase. In 6-DBT and 7-DBT (5-*trans-n*-alkyl-2(4′-isothiocyanianophenylo)-1,3-dioxane, $n = 6, 7$) the classic behavior was observed only for $T > T_C + 4°$ [40]. In DOBAMBC (*p*-decyloxy-benzylidene-*p*-amino-2-methyl-butyl-cinnamate) the effect behaved according to Eq. (9) also in the vicinity of T_C, but its sign was negative [41]. In all previously studied cases the sign of the NDE critical effect was positive.

5. SUMMARY

The objective of the investigations reported here was to determine experimentally the basic NDE properties of liquids in the vicinity of the phase transition point. Results obtained made it possible to verify certain predictions of the modern theory of phase transitions. Certain of these results could obviously have been achieved with other methods, but every research method has its individual specific features.

Similarly to the Kerr and Cotton–Mouton effects, the NDE is very sensitive to the appearance of critical fluctuations, making it feasible, for instance, to determine the type of phase transition from measurements in a homogeneous phase. It is noteworthy that the source of all the effects mentioned above is the anisotropy of critical fluctuations induced by a strong field (electric or magnetic), which causes them to be, to a large extent, complementary.

Every research method has its limitations. The sensitivity of the NDE method is proportional only to the anisotropy of the electric permittivity of the medium (e.g., see Figs. 2 and 3). The optical method has, in our opinion, many more limitations, because the possibility of approaching the critical point is limited by the appearance of critical opalescence, which is not of significance for the NDE. On the other hand, the sensitivity of the Kerr and Cotton–Mouton effects is proportional to the anisotropy of the refractive index (and electric or magnetic permittivity anisotropy, respectively).

In our opinion an additional advantage of the NDE approach is that, of the experimental methods mentioned here, it is technically the least complicated and also the least expensive, although it has failed up to now to gain popularity.

ACKNOWLEDGMENT

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