Experimental studies on the temperature behavior of the nonlinear dielectric effect in a critical binary solution

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Presented are results of experimental studies of the critical amplitude and exponent describing the behavior of the nonlinear dielectric effect on approaching the critical consolute point. Plots of the critical amplitude as a function of dielectric properties of components of binary solutions of limited miscibility show good agreement with the Goulon-Greffe-Oxtoby droplet model [J. Chem. Phys. 70, 4742 (1979)]. An analysis of temperature dependence of the critical exponent ψ suggests that an observed discrepancy between the experimental value of ψ and that predicted by the theoretical models is due to the relaxation of critical fluctuations.

I. INTRODUCTION

During recent years the application of nonlinear experimental methods such as the Kerr effect and the nonlinear dielectric effect (NDE) for studies on the critical properties of the limited-miscibility solutions has yielded valuable results, among other things "stretched exponential time" [1] in binary solutions of limited miscibility. NDE applied for o-nitrotoluene with n-alkanes solutions showed the occurrence of critical fluctuations accompanying phase separations taking place below the temperature of solution solidification [2]. NDE is one of the simplest methods for determining type of phase transition for multicomponent solutions [3,4].

Despite the undeniable achievements made with these methods up to now an essential discrepancy between experimental results and theoretical predictions still exists. In a critical, binary solution [4]

$$\frac{\Delta n}{E^2}, \frac{\Delta \epsilon}{E^2} \simeq \frac{1}{(T-T_C)^{-\psi}}, \quad T > T_C \tag{1}$$

where $\Delta n / E^2$ is the measure of the Kerr effect and $\Delta \epsilon / E^2$ is the measure of NDE ($\Delta \epsilon = \epsilon - \epsilon^E$, where ϵ and ϵ^E denote the electric permittivity of a critical solution in a weak and in a strong electric field E, respectively). T_C is the critical temperature. Theoretical models [5–7] predict $\psi \simeq 0.59$, for both effects. Experimental studies of the Kerr effect gave [8]

$$\psi = 0.71 - 0.88 .$$

The authors' studies on the NDE show that the "universal, experimental" value of the exponent is [9]

$$\psi = 0.370 \pm 0.005 .$$

Such a value of the exponent has been obtained in the immediate vicinity of the critical point ($0.003 < T - T_C < 0.1$) using a single power term [relation (1)] [9]. Further from T_C the additional power terms have to be taken into account [11]. An attempt is made here to explain this discrepancy for the nonlinear dielectric effect.

II. NONLINEAR DIELECTRIC EFFECT — MEASUREMENTS TECHNIQUE

In the range of strong electric fields used in practice (10^6 V/m) the changes of electric permittivity $\Delta \epsilon$ due to the application of a strong electric field E are almost always proportional to E^2, so the measure of NDE is the value $\Delta \epsilon / E^2$ [11]. This situation is also found in our studies [12]. For NDE's measurements we used the apparatus proposed by Małecki [13] in which, for a generator having a capacitor with the treated dielectric in the resonance circuit, measurements are made of frequency variations induced by the application of a rectangular impulse from a strong electric field. Working frequency of the measurement generator is usually of the order of a few MHz while time of duration of the impulse is about 1 ms. In our case the measurement frequency was about 5 MHz. Studies in liquids showed that NDE is very sensitive to a great number of varied molecular properties [10] of liquids. For this reason the noncritical background effect has to be very carefully taken into account [3]:

$$\left[\frac{\Delta \epsilon}{E^2}\right]_C = \left[\frac{\Delta \epsilon}{E^2}\right]_T - \left[\frac{\Delta \epsilon}{E^2}\right]_B \simeq A t^\psi , \tag{2}$$

where index T is for the total, measured NDE, and C and B are for the critical effect and the background effect, respectively.

For these studies two methods for determining NDE_B were used: the numerical fitting [3] and the isothermal extrapolation from three-component solution [14]. All calculations have been made using the linear and nonlinear least-squares method. All errors are given as three standard deviations.

III. THEORETICAL MODELS DESCRIBING THE INFLUENCE OF CRITICAL FLUCTUATIONS ON NDE

Several theoretical models describing the properties of NDE and the Kerr effect in the critical region for binary solutions of limited miscibility [5–7] are available. All

these models predict the same value of the critical exponent:

$$\psi = \gamma - 2\beta = 0.59 \ ,$$

where γ and β are critical exponents for the susceptibility and the order parameter, respectively. For the (3,1) universality class $\gamma \simeq 1.18$ and $\beta \simeq 0.325$ [14].

Hoye and Stell [6] obtained this value considering the anisotropy of a particle-particle correlation function due to the action of a strong electric field.

Goulon, Greffe, and Oxtoby (GGO) [5] basing on a droplet model obtained both the exponent ψ and the critical amplitude A. Their model connects the critical amplitude with the dielectric properties of the tested critical solution:

$$A \sim \frac{(\epsilon_1 - \epsilon_2)^4}{\epsilon_S^2} \ , \tag{3}$$

where ϵ_1, ϵ_2 are the permittivities of solution components and ϵ is the permittivity of the solution.

Recently this result has been confirmed by Onuki and Doi [7]. The authors based this model on the formulas, later used for macromolecules, connecting anisotropy of the structure factor caused by the strong electric field with the tensor of electric permittivity.

It should be stressed that the GGO droplet model is also one of the basic theoretical approaches which make it possible to describe the weak critical anomaly of the electric permittivity in critical solutions.

IV. RESULTS AND DISCUSSION

Experimental studies have shown that the critical increase of NDE depends markedly on the difference in electric permittivity of the solution components [3,4,10,12,14,15]. This is illustrated in Fig. 1, where results of measurements in three different solutions are presented on a semilogarithmic scale: (1) propylene carbonate–n-butylbenzene; this exhibits the greatest observed and analyzed critical effect; (2) nitroethane-isooctane; the value of $\epsilon_1 - \epsilon_2$ here is smaller (about 27). It is noteworthy that for this solution $n_1 - n_2 \simeq 0$ (n is the index of refraction) [3]; and (3) MBBA-isooctane; this exhibits the smallest analyzed critical effect. Both components have very close values of electric permittivity. It is of interest that N-(4'-methoxybenzylidene)-4-(n-butyl)aniline (MBBA) is a liquid-crystal material [16]. The dependence of the critical amplitude on the dielectric properties of a solution is analyzed quantitatively in Fig. 2. The analysis has been prepared based on data from the authors' studies on a series of critical, binary solutions. The straight line obtained confirms the validity of relation (3). As mentioned in the Introduction, the experimental, universal value of ψ has been obtained in the vicinity of T_C, where the critical effect is large. Remote from T_C studies of the influence of the critical fluctuations require a very exact determination of the background effects. This is a very serious problem for NDE which is sensitive to many molecular properties.

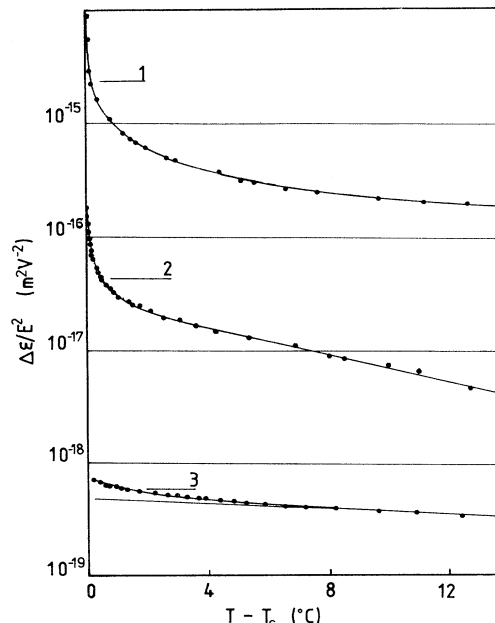Results of an attempt at analysis of NDE in a broad

FIG. 1. The semilogarithmic plot of the NDE vs the temperature distance form the critical point for solutions of critical concentrations of (1) propylene carbonate–n-butylbenzene, (2) nitroethane-isooctane, and (3) MBBA-isooctane.

range of temperatures are presented in Fig. 3. As may be seen, the behavior of $(\Delta\epsilon/E^2)_C$ may be described by different values of the critical exponent in the vicinity of T_C and remote from the critical point. For the first range $(T - T_C < 10$ K
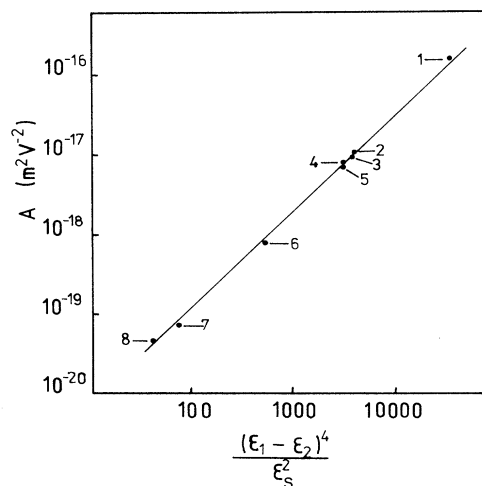
$$\psi \simeq 0.4 \ .$$

FIG. 2. Dependence of the critical amplitude vs $(\epsilon_1 - \epsilon_2)^4/\epsilon_S^2$ for solutions of (1) propylene carbonate–n-butylbenzene, (2) nitrobenzene-heptance, (3) nitrobenzene-eicosane, (4) nitroethane-isooctane, (5) benzonitrille-isooctane, (6) phenylethanole-octane, (7) veratrole-heptane, and (8) MBBA-isooctane.
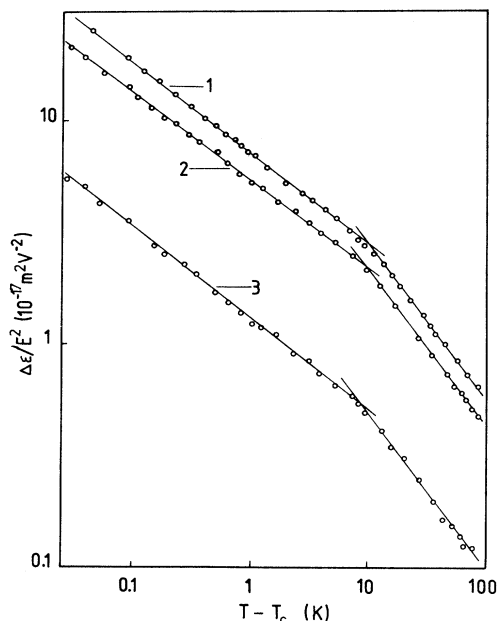
FIG. 3. The log-log dependence of NDE vs the temperature distance from the critical point for solutions: (1) nitrobenzene-heptane, (2) nitrobenzene-eicosane, and (3) benzonitrille-isooctane.

This is a typical value of the exponent when additional correction power terms are not taken into account. Further from the critical point $(T - T_C > 17 \text{ K})$ a quite different value has been obtained, that is,

$$\psi = 0.62 \pm 0.05 \ .$$

Within the limits of experimental error this agrees with the theoretical value $\psi = 0.59$.

Interpretation of this fact may be associated with the relaxation of critical fluctuations. On approaching the temperature of phase separation the magnitude of critical fluctuations and also of relaxation time increases. For instance, for the nitrobenzene-heptane solution at a distance of 0.004 K relaxation time is of the order of 1 ms while at a distance 0.1 K is only one-tenth of this (0.1 ms [1]. In all considered theoretical models stability of the measurement electric field is assumed. This condition may be fulfilled only far from the critical point. Results presented would appear to indicate that the discrepancies hitherto observed between theoretical predictions and experimental results could be a consequence of the fact that up to now the conditions for conducting NDE studies (the value of the measurement frequency) and the theoretical assumptions have not been fully taken into account.

On approaching the critical miscibility point the values of critical exponents change while the relation between critical amplitude and dielectric properties remains unchanged. It is noteworthy that for another type of system—liquid-crystal materials—the agreement between experiment and theory (Landau–de Gennes model) is very good. In both cases the classical value $\psi = 1$ has been obtained. Discrepancies, also due to the relaxation processes, appear from nematogens with a large, positive anisotropy of electric permittivity.

ACKNOWLEDGMENT

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