# Shift of the Critical Mixing Temperature in Strong Electric Fields. Theory and Experiment

Kazimierz Orzechowski,*,† Mariusz Adamczyk,† Alicja Wolny,† and Yoav Tsori*,‡

†Faculty of Chemistry, University of Wroclaw, Wroclaw 50-383, Poland

‡Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 8410501 , Israel

ABSTRACT: We study the shift in the critical temperature T_c in binary mixtures in strong electric fields. In experiments we measure the nonlinear dielectric effect (NDE) in a mixture of nitrobenze and n-octane and calculate Piekara's factor. We find that the critical anomaly of Piekara's factor is a function of an electric field strength. We propose to explain this observation as a result of a downward shift of T_c, and this allows us to calculate $(\partial T_c/\partial E^2) = (-22 \pm 10) \times 10^{-16}$ (K m²)/V². In the theoretical part we amend Landau and Lifshitz's formula and show that the downward shift of T_c can be estimated from a simple mean-field theory taking into account the linear and quadratic terms in an expansion of the constitutive relation $\varepsilon(x)$ between the electric constant ε and mixture composition x.
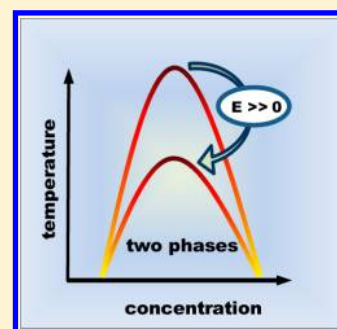
INTRODUCTION

The upper critical mixing point is the maximum of the coexistence curve in mixtures of liquids of limited mutual solubility. Phase transition at the critical point is classified as a continuous one and belongs to the universality class [3, 1], as for example a critical point of gases. The critical mixing temperature (T_c) is very sensitive to many factors, for example, to impurities,[1,2] to pressure,[3,4] and to shear flows.[5,6]

It would seem, therefore, that the critical temperature should be sensitive to the electric field too. The effect of an electric field on T_c was analyzed intensely experimentally[7–10] and theoretically,[7,9,11–17] but fundamental unresolved issues still remain.

Theoretical Expectations. Mean field approach to the shift of the critical temperature caused by electric field starts from the thermodynamic decription of the dielectric medium in the presence of the electric field. As explained by Landau and Lifsitz,[11] the electrostatic thermodynamic potential is different in the case of a constant charge and a constant potential. The selection of the case is crucial, because it leads to a reversal of the sign of the predicted shift to T_c. Debye and Kleboth were interested in the quantity $(\partial T_c/\partial E^2)_p$ that measures the shift of T_c.[7] They observed a negative shift to T_c and explained it by using the constant charge case; this choice was criticized later by authors who argued that the constant potential choice is the correct one.[8,12–16]

An important element of a mean field theory[7,14,16] for the sign and magnitude of $(\partial T_c/\partial E^2)_p$ is the constitutive relation between electric permittivity and order parameter, expressed by deviation of volume fraction from the critical value $(x - x_c)$:

$$\varepsilon \cong \varepsilon_c + \varepsilon_1(x - x_c) + \frac{1}{2}\varepsilon_2(x - x_c)^2 \tag{1}$$

where ε is the relative electric permittivity; x and x_c are the volume fraction and the critical volume fraction of the polar

component in the binary mixture. The original expression by Landau and Lifshitz was given to the critical point of liquid–vapor coexistence. When it is applied to binary mixtures, the predicted shift to T_c has the form

$$\left(\frac{\partial T_c}{\partial E^2}\right)_p = \pm \frac{\varepsilon_0 \varepsilon_2 v_0 x_c^2}{2k_B} \tag{2}$$

where ε_0 is the absolute permittivity of vacuum, v_0 is the volume of a molecule of polar component $(v_0 = V_{mol}/N_A$, where V_{mol} is the molar volume and N_A is Avogadro's number), and k_B is the Boltzmann constant. A positive sign concerns a constant potential case; a negative sign, a constant charge case. In the case of constant potential, eq 2 predicts that the sign of the derivative $(\partial T_c/\partial E^2)_p$ is the same as the second derivative of ε with respect to volume fraction (ε_2).

Experimental Status-Quo. In most cases ε_2 is positive[18] and an *increase* of the critical temperature in electric fields is predicted. However, most of experiments dealing with the direct influence of a strong uniform electric field lead to a small decrease of T_c. Debye and Kleboth[7] investigated light scattering in the presence of strong electric field in nitrobenzene + isooctane and found $(\partial T_c/\partial E^2)_p = -7.4 \times 10^{-16}$ (K m²)/V². The authors assumed this shift is consistent with the theoretical expectation. Orzechowski[10] measured a nonlinear dielectric effect (NDE) in the same system and found $(\partial T_c/\partial E^2) = -(8.7 \pm 0.5) \times 10^{-16}$ (K m²)/V². Beaglehole explored a discontinuity of the adsorption coefficient at the liquid–vapor interface at the critical temperature in aniline + cyclohexane.[8] Using this experiment he found $(\partial T_c/\partial E^2) = -8 \times 10^{-13}$ (K m²)/V². Wirtz et al. performed small angle light scattering measure-

ments of the structure factor in polymer solutions and in simple liquids.[9] In polystyrene + cyclohexane they found $(\partial T_c/\partial E^2) = -1.8 \times 10^{-10}$ (K m^2)/V^2 and in nitrobenzene + hexane $(\partial T_c/\partial E^2) \leq -2 \times 10^{-14}$ m^2/V^2. Direct measurements of the critical temperature shift under influence of a strong electric field are difficult and many additional effects could contribute the results.[14,19]

An alternative experimental way to obtain a shift of T_c is an analysis of the temperature dependence of electric permittivity in the critical region. According to theory[20−22] the effect of electric field on T_c could be deduced from the critical anomaly of permittivity measured at low electric field strength. The product $(\varepsilon \rho^{-1})$, could be approximated by a function

$$\varepsilon \hat{\rho}^{-1} = \varepsilon_c C_1 t + C_{1-\alpha} t^{1-\alpha} + C_{1-\alpha+\Delta} t^{1-\alpha+\Delta} + \dots \tag{3}$$

where ε is the relative electric permittivity, $\hat{\rho}$ is the reduced density ($\hat{\rho} = \rho/\rho_c$ where ρ and ρ_c are the density and the critical density, respectively), C_i are dimensionless system-dependent constants, $t = (T/T_c - 1)$ is the reduced temperature, α is the critical exponent of heat capacity, and Δ is the correction-to-scaling critical exponent. The critical amplitude $C_{1-\alpha}$ allows us to calculate the shift of T_c under the influence of the electric field.[18,23] Losada-Perez et al.[23] reviewed numerous experimental data and in most cases the negative derivative $(\partial T_c/\partial E^2)_p$ was obtained. Orzechowski and co-workers investigated recently an electric permittivity anomaly in the nitrobenzene + octane mixture[18] − the system under interrest in the current paper, and found that $(\partial T_c/\partial E^2)_p = (-3.9 \pm 0.3) \times 10^{-16}$ (K m^2)/V^2.

In this article, we return to the long-lasting controversy between the theory and the results of measurements of the effect of the electric field on T_c. In the first part of this paper we present an expression for the shift of T_c where the curvature of the constitutive relation and anisotropic composition fluctuations are treated on the same footing. In the second part we present direct measurements of the T_c shift by using the nonlinear dielectric effect (NDE). The NDE experiments were supplemented by measurements of permittivity as a fuction of temperature and concentration. This data is then used to compare the T_c shift obtained experimentally and that predicted by theoreticaly.

■ THEORY

The expression adopted from Landau and Lifshitz, eq 2, was derived by looking at how the electric field changes the quadratic term in a Landau expansion of the free energy of a binary mixture. When an electric field is present, the mixture composition is affected. Via Laplace's equation, local changes in the mixture's composition lead to long-range changes in the field. If the composition changes in a small amount, the field will change in a proportional way. This leads to a change in the energy that is quadratic in the small composition change. Crucially, if the small change is described by a plane wave such as exp(i**q**·**r**), where **q** is the wave-vector, then the change in the energy depends on the relative direction between **q** and the external field **E**$_0$.

We write the total free energy $F = F_m + F_{es}$ as the sum of the mixture (F_m) and electrostatic (F_{es}) energies. For the mixture energy we use the regular mixing energy

$$F_m = \frac{k_B T}{v_0} \int \{x \ln(x) + (1-x)\ln(1-x) + \chi x(1-x)\}\, d^3 r \tag{4}$$

Here x is the volume fraction of the more polar component, k_B is the Boltzmann constant, T is the absolute temperature, v_0 is the molecular volume (assumed the same for both liquids), and χ is the Flory−Huggins interaction parameter, $\chi = C/T$, where C is a constant. The critical temperature is given by $\chi_c = 2$, namely $T_c = C/2$. Close to the critical point one may use a Landau expansion of F_m to obtain an approximate expression

$$F_m \cong \frac{4k_B T}{v_0} \int \left(\frac{1}{2} t\varphi^2 + \frac{1}{3}\varphi^4\right) d^3 r$$

$$t = 1 - \chi/2 \cong \frac{T - T_c}{T} \tag{5}$$

Here the deviation from the average (critical) composition is assumed small: $\varphi = x - x_c \ll 1$ as is implied in eq 1. For dielectric liquids under fixed potentials the electrostatic energy is given by the integral

$$F_{es} = -\frac{1}{2} \int \varepsilon_0 \varepsilon(\varphi(\mathbf{r}))\, E^2(\mathbf{r})\, d^3 r$$

If φ is small, it follows that the electric field can be written as

$$\mathbf{E} \cong \mathbf{E}_0 + \mathbf{E}_1 + \mathbf{E}_2$$

where $\mathbf{E}_0$ is the field corresponding to a mixture at its average composition ($\varphi = 0$) and $\mathbf{E}_1$ and $\mathbf{E}_2$ correspond to linear and quadratic corrections in φ. The electrostatic energy density can now be written in orders of φ as[16]

$$-\frac{1}{2}\varepsilon_0 \varepsilon_c \mathbf{E}_0{}^2 - \frac{1}{2}\varepsilon_0\left(2\varepsilon_c \mathbf{E}_0 \cdot \mathbf{E}_1 + \frac{1}{2}\varepsilon_1 E_0{}^2 \varphi\right)$$

$$-\frac{1}{2}\varepsilon_0\left(\varepsilon_c(E_1{}^2 + 2\mathbf{E}_0 \cdot \mathbf{E}_2) + 2\varepsilon_1 \varphi \mathbf{E}_0 \cdot \mathbf{E}_1 + \frac{1}{2}\varepsilon_2 E_0{}^2 \varphi^2\right) + O(\varphi^3)$$

The first line contains the contribution of the uniform medium and the term linear in φ. Both do not contribute to the thermodynamics if the field $\mathbf{E}_0$ is spatially uniform. In the quadratic terms (second line), the term proportional to $\mathbf{E}_0 \cdot \mathbf{E}_2$ integrates to zero because $\mathbf{E}_2$ is a gradient that vanishes at the boundaries. The dependence of $\mathbf{E}_1$ and $\mathbf{E}_2$ on φ is given by the Laplace's equation $\nabla \cdot (\varepsilon \mathbf{E}) = 0$. When this equation is expanded in orders of φ, one finds to linear order that $\varepsilon_1 \nabla \varphi \cdot \mathbf{E}_0 + \varepsilon_c \nabla \cdot \mathbf{E}_1 = 0$ (the second-order perturbation to Laplace's equation yields the equation for $\mathbf{E}_2$). We may now write φ and $\mathbf{E}_1$ as a sum of plane waves with Fourier amplitudes $\varphi_\mathbf{q}$ and $\mathbf{E}_\mathbf{q}$, respectively, and find that

$$\mathbf{E}_\mathbf{q} = -\frac{\varepsilon_1}{\varepsilon_c}\varphi_\mathbf{q}\frac{(\mathbf{q}\cdot\mathbf{E}_0)^2}{q^2}\mathbf{q} \tag{6}$$

Once we know $\mathbf{E}_1$ we can substitute it back in F_{es} and calculate the terms quadratic in φ. The total free energy to quadratic order can then be written as a Fourier sum

$$F_m + F_{es} = \frac{1}{2}\int\left[\frac{4k_B T}{v_0}t - \frac{1}{2}\varepsilon_0\varepsilon_2 E_0{}^2 + \varepsilon_0\frac{\varepsilon_1{}^2}{\varepsilon_c}(\hat{\mathbf{q}}\cdot\mathbf{E}_0)^2\right]\varphi_\mathbf{q}\varphi_{-\mathbf{q}}\, d^3 q \tag{7}$$

This expression shows that the effect of the electric field is to renormalize the critical temperature by adding an E-dependent term to t. To the best of our knowledge the anisotropy in the structure factor has not been detected directly in near-critical liquids but it could be deduced from birefringence of polarized light (Kerr effect).[14] If fluctuations all have the same magnitude

and are isotropic in direction, one may write that t is renormalized according to

$$t \rightarrow t - \frac{v_0}{4k_\mathrm{B}T}\varepsilon_0\left(\frac{1}{2}\varepsilon_2 - \frac{1}{3}\frac{\varepsilon_1^2}{\varepsilon_c}\right)$$

namely T_c is shifted by

$$T_c \rightarrow T_c + \Delta T_c$$

$$\Delta T_c = \frac{v_0}{4k_\mathrm{B}}\varepsilon_0\left(\frac{1}{2}\varepsilon_2 - \frac{1}{3}\frac{\varepsilon_1^2}{\varepsilon_c}\right)E_0^2 \qquad (8)$$

The result of this derivation is enlightening: it shows that the curvature of the constitutive relation, ε_2 in eq 1, can lead to mixing or demixing; as noted before, usually $\varepsilon_2 > 0$ and hence it leads to demixing. But the systems "pays" an electrostatic energy penalty for having composition variations leading to dielectric interfaces perpendicular to the direction of the field. This penalty is proportional to ε_1^2 and always favors *mixing*, and it was absent from previous works on the shift of T_c in binary mixtures.

Equation 8 assumes that composition fluctuations are spatially symmetric. However, depending on the exact setup, experiments can be more sensitive to composition fluctuations whose **q**-vector is parallel to the field.[14,24,25] In this case one finds that

$$T_c \rightarrow T_c + \Delta T_c$$

$$\Delta T_c = \frac{v_0}{4k_\mathrm{B}}\varepsilon_0\left(\frac{1}{2}\varepsilon_2 - \frac{\varepsilon_1^2}{\varepsilon_c}\right)E_0^2 \qquad (9)$$

Concluding the present theory, the derivative $(\mathrm{d}T_c/\mathrm{d}E^2)$ depends not only on the curvature of the constitutive relation $\varepsilon(x)$ but also on the "dielectric contrast" between the components expressed by ε_1. For weaker electric fields and spatially isotropic composition fluctuations the shift in T_c is expressed by eq 8. For stronger electric fields, dielectric interfaces perpendicular to the field's direction can become dominant and the shift to T_c should be expressed by eq 9.

■ EXPERIMENTAL METHODS

Nonlinear Dielectric Effect (NDE). The nonlinear dielectric effect compares electric permittivities in high- and low-intensity electric fields.[26] In our experiments, the investigated liquid was located between circular electrodes of diameter 20 mm separated by a distance of 0.36 ± 0.02 mm. A scheme of the sample holder is presented in Figure 1.

The capacitor was a part of high-quality parallel LC circuit of Colpitt's oscillator. Any change of the capacity results in a change of the oscillation frequency detected by a fast frequency counter (HP-5503 Modulation Domain Analyzer). The investigated sample was subjected to a superposition of two fields: a low-voltage, high-frequency measuring field ($f \approx 4$ MHz) and high-voltage rectangular pulses of a polarizing field (HV). The voltage of the HV pulses was operated between 1300 and 4700 V, duration time 1.3 ms, rise time of the pulse 0.3 ms, repetition frequency 10 Hz, and output current of HV supply up to 100 mA. The scheme of the experimental setup is presented in Figure 2.

The resonance frequency of the LC circuit allows to calculate the capacity of the condenser containing the liquid sample by $c_x = A/f^2 + B$, where A and B are constants obtainable in
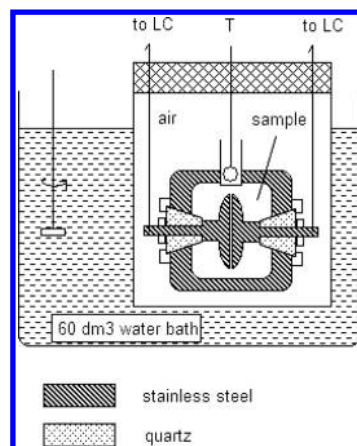

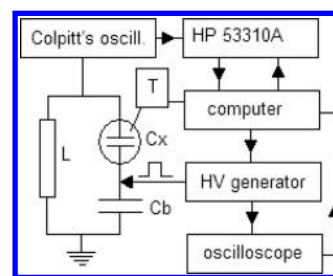**Figure 1.** Scheme of the capacitor used in NDE measurements.

Figure 2. Experimental setup used in NDE measurements: c_x, capacitor with the investigated liquid; c_b, blocking capacitor of capacity of 1 n; L, inductance 10 μH.

calibration using standard capacitors. Application of strong electric field changes the electric permittivity and, as a consequence, the frequency of oscillation of the LC circuit. The NDE increment $\Delta\varepsilon$ was calculated as follows:

$$\Delta\varepsilon = \varepsilon_\mathrm{E} - \varepsilon = \frac{Ad}{\varepsilon_0 S}\left(\frac{1}{f_\mathrm{E}^2} - \frac{1}{f_0^2}\right)$$

where ε_E and ε are the relative permittivities measured in strong and in low electric field strengths, respectively, A is a constant obtained in calibration, d is a distance between electrodes, ε_0 is the absolute permittivity of vacuum, S is the surface of the electrodes, f_E and f_0 are the resonance frequency in the presence and in the absence of electric field. The absolute error of $\Delta\varepsilon$ and resolution were 10% and 2%, respectively. The amplitude of high-voltage pulses were measured by a resistive divider 1:1000 using a TDS1000 Digital Oscilloscope with the absolute precision of ±15 V.

Temperature Control. The capacitor was located in a brass cylinder mounted in a water thermostat of 60 dm^3 volume (Figure 1). The temperature of the water was controlled up to 0.1K accuracy. Because of the large heat capacity of the stainless steel capacitor and slow exchange of heat between the water thermostat and the capacitor, the temperature of the investigated sample was controlled to better than 0.005K. Temperature was measured using a calibrated thermistor with the absolute precision of ±0.1K and resolution of ±0.005K.

Electric Permittivity Measurements. Electric permittivity was measured using the capacitor presented in Figure 1, but the distance between electrodes was expanded to 2 mm. Measurements were performed by HP Precision LCR Meter 4284A. Geometrical capacity and uncompensated lead capacity,

necessary for calculation of the electric permittivity, were found by calibration. Electric permittivity was measured with the resolution of ±0.01.

Chemicals. Nitrobenzene (Sigma-Aldrich, purity ≥99.0%) was recrystallized three times and stored over molecular sieves A3. *n*-octane (Sigma-Aldrich, purity 99%) was used without additional purification. The density of liquids, necessary for calculation of volume fraction, were taken from the literature.[27] All operations were done in dry nitrogen atmosphere.

■ RESULTS

Nonlinear Dielectric Effect (NDE). According to Debye–Langevin theory the NDE increment in simple dipolar liquids should be negative and proportional to E^2.[26] Contrary to Debye–Langevin theory, in many cases the NDE increment is positive. A positive NDE increment is observed, for example, in the vicinity of a critical mixing point both in binary[24,25,28−32] and in ternary mixtures.[33] When the temperature and concentration are approaching the critical value, the NDE increment exhibits a divergence according to the equation

$$\frac{\Delta \varepsilon}{E^2} = D_{\mathrm{bg}} + D_z t^{-z} \qquad (10)$$

where D_{bg} is the background contribution, D_z is the positive critical amplitude, and $z = \gamma + 2\beta \approx 0.59$.[12,34] The negative sign of the exponent in eq 10 proves the large sensitivity of NDE method to critical phenomena.

NDE experiments were done at the critical concentration (equal to 0.509 mole fraction of nitrobenzene) as a function of temperature. The correctness of the critical concentration was checked by the equal volume criterion. After filling the capacitor with the investigated mixture, the capacitor was mounted in the thermostat and heated to the one phase region at 25 °C. After 1 h of equilibration a programmed decrease of temperature at a rate of 1 K/h was carried out. NDE measurements were done automatically every 0.05 K in the course of cooling from 23 °C to the phase separation temperature. At each temperature, the NDE increment was measured at six voltages ranging from 1400 to 4850 V (field intensity 3.7−12.7 MV/m). An example of the dependence of ε on time is presented in Figure 3.

The rise time of HV pulse was relatively long, 0.3 ms, to avoid parasitic effects when the HV field was turned on/off. The dependence of ε on time during the HV pulse has a negative slope that is related to Joule heating.[26] The effect was corrected by extrapolation of the permittivity to the middle of the rise-period of a HV pulse. This slope of ε(time) allows us to estimate the heating caused by the application of HV pulses. For the strongest HV pulse the increase of temperature did not exceeds 0.006 K.

The shape of the NDE response in most cases was similar to that presented in Figure 3. However, very close to T_c the response was different. At the beginning of DC pulse a rapid increase of $\Delta \varepsilon$ was observed followed by a relatively slow saturation. Figure 4 presents the NDE response in the vicinity of T_c.

The shape of the near-critical response seems to prove an existence of additional effects incorporating the NDE response. We suspect that the saturation-like response could be related to the relaxation of critical fluctuations predicted by dynamic droplet model[35] and/or anisotropy of a dielectric tensor in the presence of an external electric.[12] To obtain a corrected value of
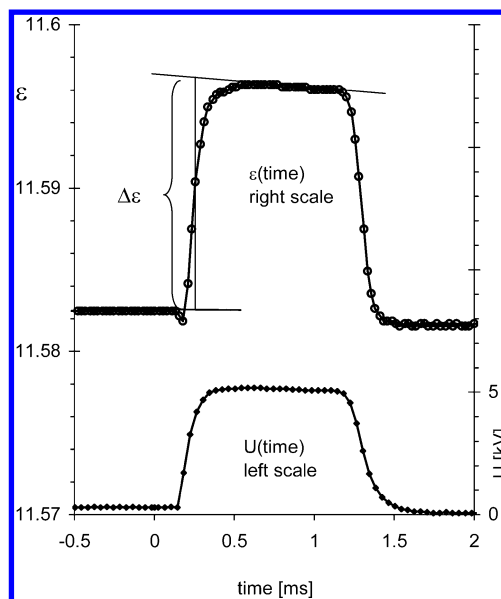
Figure 3. Upper curve presents the ε(time) dependence observed at $T \geq T_c + 0.1$. Lower curve presents the shape of HV pulse.
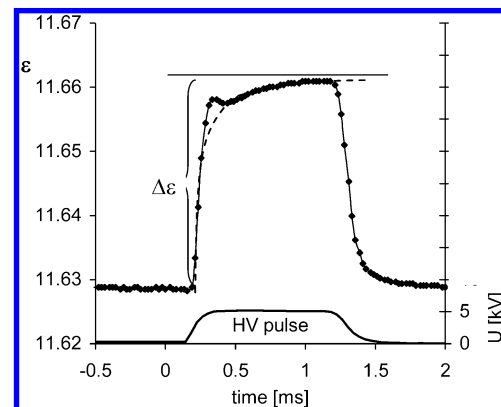


Figure 4. ε(time) dependence obtained at $T_c < T < (T_c + 0.1\ \mathrm{K})$.

$\Delta \varepsilon$ in the immediate vicinity of T_c, an extrapolation according to an exponential is performed (dashed line in Figure 4).

NDE experiments were made at the critical concentration of nitrobenzene + *n*-octane mixture as a function of temperature and strength of HV pulses, ranging from 1.2 to 13.6 MV/m. As pointed out before, according to Debye–Langevin theory the $\Delta \varepsilon$ increment was proportional to E^2 and this was precisely fulfilled in most simple liquids and liquid mixtures.[26] In our experiments we found that far from the critical temperature the $\Delta \varepsilon$ increment was a linear function of E^2; however, close to T_c a negative curvature was growing. An example of the obtained $\Delta \varepsilon(E^2)$ dependence at different distances from T_c is presented in Figure 5.

A nonlinear dependence of $\Delta \varepsilon$ on E^2 in critical mixtures was rarely reported. In our opinion the reason for this situation has an experimental nature. The NDE equipment is constructed for measurements of very small changes of ε ($\Delta \varepsilon$ as small as 10^{-7}). In the vicinity of T_c, the $\Delta \varepsilon$ increment could attain a value of 0.01, and this forces to decrease the HV pulses to help the experiments and to prevent spark discharge. In the current experiments we tried to use as strong as possible HV pulses to detect a nonlinearity as presented in Figure 5. A similar nonlinearity in the vicinity of T_c was observed in previous
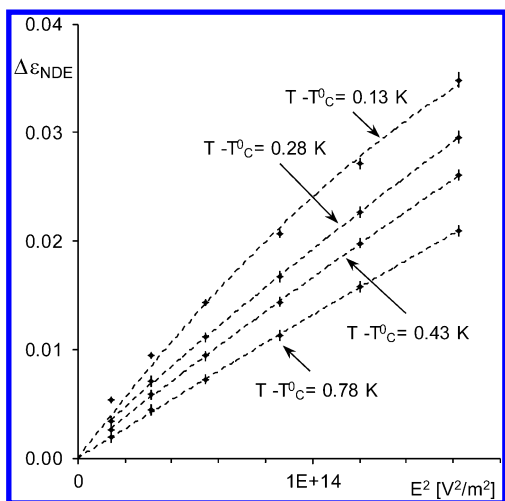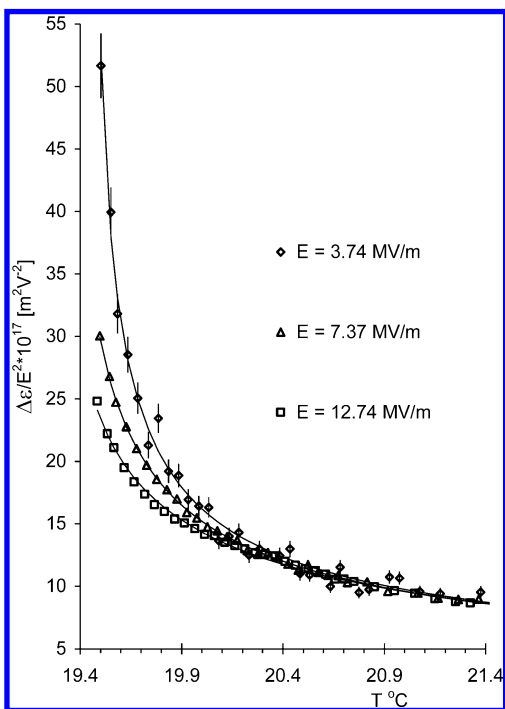
Figure 5. $\Delta\varepsilon(E^2)$ dependence obtained at the critical concentration of nitrobenzene + n-octane mixture for different distances from T_c.

experiment performed in nitrobenzene + 2,2,3-trimetypentane mixture.[10]

A usual way of presenting the NDE experiments is a ratio of NDE increment and a square of the electric field, $\Delta\varepsilon/E^2$, called Piekara's factor, the quantity independent of E.

Figure 6 presents $\Delta\varepsilon/E^2$ obtained in three characteristic strengths of HV pulses. Piekara's factor increases markedly as T

Figure 6. Temperature dependence of Piekara's factor ($\Delta\varepsilon/E^2$) in the critical mixture on nitrobenzene + n-octane obtained at three strengths of HV pulses.

approaches T_c. This is a characteristic feature in critical mixtures. However, when we compare the critical anomaly $\Delta\varepsilon/E^2$ for different strengths of HV pulses, it is clear that the $\Delta\varepsilon/E^2$ anomaly in stronger HV pulses is smaller and less divergent at T_c than in weaker pulses, contrary to the theoretical predictions (eq 10).

Electric Permittivity. According to theoretical expectations $(\partial T_c/\partial E^2)$ could be estimated from the analysis of the dependence $\varepsilon(x)$ in the vicinity of critical point. For this it is necessary to determine the correct frequency for the measurement of $\varepsilon(x)$. In NDE measurements a superposition of two fields is used: a low-intensity measuring field of frequency of 4 MHz and high-intensity pulses of polarizing field. It is reasonable to suppose that the frequency for measurements of $\varepsilon(x)$ should be correlated with HV pulses. In our experiments, the duration time of the HV pulse is on the order of 0.8 ms and this forces to suppose that the frequency for measuring of $\varepsilon(x)$ should be smaller than 0.3 kHz (length of the pulse is a half of the wave period). In the case of simple noncritical mixtures of low conductivity, such as nitrobenzene + n-octane, the electric permittivity has dielectric relaxation at much larger frequencies (of order of gigahertz[36]) and the electric permittivity measured in the range of 100 Hz to 100 MHz should be constant. Following that, the selection of frequency of the permittivity measurements is subject to the requirements of the most precise data. But this is not the case in critical mixtures. It was proved that in the critical region of binary mixtures a low-frequency dispersion occurs, explained by a precritical Maxwell–Wagner (MW) polarization caused by large and long-lived concentration fluctuations.[37−43] The MW dispersion changes the $\varepsilon(t)$ anomaly. At low frequencies ($f < f_{MW}$, where f_{MW} is the relaxation frequency of Maxwell–Wagner polarization) an increase $|d\varepsilon/dT|$ was observed when T_c was approached (positive deviation of ε from the value extrapolated from the noncritical region), whereas at high frequency ($f > f_{MW}$) a decrease of $|d\varepsilon/dT|$ was observed (negative deviation from the value extrapolated from the noncritical region).

The character of the critical anomaly of ε was a reason for a controversy discussed widely in the literature before discovering the low-frequency dispersion. A presence of the Maxwell–Wagner dispersion makes the question of an optimal frequency for $\varepsilon(x)$ measurements important. If the frequency of MW is located at frequencies higher than 0.3 kHz, the $\varepsilon(x)$ dependence should be measured in low-frequency region, preferably at $f \ll 0.3$ kHz. Contrary to that, if the frequency of MW relaxation is smaller than 0.3 kHz the $\varepsilon(x)$ dependence could be measured even at the MHz region.

The relaxation frequency and the amplitude of the MW dispersion in critical binary mixtures depend on the difference of permittivity of components and on the conductivity of the mixture.[39] To know the frequency of the Maxwell–Wagner relaxation, measurements of $\varepsilon(f)$ in a mixture of critical concentration are performed. Figure 7 presents the results of these experiments. The two curves presented at the bottom were obtained in a one-phase mixture ($T > T_c$) and the upper curve in the two-phase system. In the one-phase region, in the investigated frequency range the Maxwell–Wagner effect is not visible. An increase of ε at $f < 1$ kHz is not related to the critical phenomena; probably it is a consequence of the electrode polarization.

The $\varepsilon(x)$ dependence was measured at the temperature 19.94 °C in volume fractions of nitrobenzene ranging from 0.345 to 0.455 at a frequency of 80 kHz. The experimental data was fitted by eq 1. The critical volume fraction of nitrobenzene was checked by equal volume criterion and was equal to $x_c = 0.396$. The parameters of eq 1 obtained by fitting to a polynomial were as follows: $\varepsilon_c = 11.782 \pm 0.004$; $\varepsilon_1 = 31.46 \pm 0.08$; $\varepsilon_2 = 40 \pm 5$.
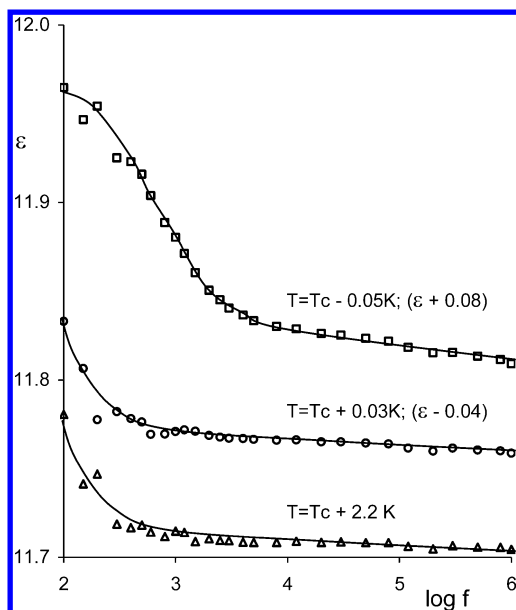
Figure 7. Electric permittivity vs frequency measured in a critical mixture of nitrobenzene + n-octane. Two sets of experiments presented at the bottom were obtained in the one phase region ($T > T_c$) whereas the upper curve was obtained in two phase region, just after phase separation.

■ **DISCUSSION**

The application of the NDE method to estimate the T_c shift assumes that the nonlinearity of $\Delta\varepsilon(E^2)$ as well as peculiarities of the Piekara's factor in the vicinity of the critical point arise from a change of the critical temperature in a strong electric field. The negative curvature of $\Delta\varepsilon(E^2)$ and the reduction of the precritical increase of $\Delta\varepsilon/E^2$ in a strong electric field indicate a decrease of T_c. Onuki argues[14] that in the vicinity of T_c a crossover is expected where in weak fields $\Delta\varepsilon \sim t^{-0.59}E^2$, and in strong fields $\Delta\varepsilon$ should saturate to a constant value. To test this possibility, we plot $\Delta\varepsilon_c = \Delta\varepsilon - D_{bg}$ (D_{bg} is collected in Table 1) as a function of E in a double logarithmic scale (Figure 8).

Table 1. Results of the Fit of Eq 10 to the NDE Data Obtained in Different Electric Field Strengths[a]

E [MV/m]	T_c [°C]	D_{bg}	D_z	z	χ^2
3.7	19.46[b]	0.98	0.58	0.52[b]	0.500
3.7	19.44 ± 0.05	2.03	0.35	(0.59)	0.505
5.6	19.32 ± 0.05	0.91	0.43	(0.59)	0.524
7.4	19.28 ± 0.05	1.25	0.40	(0.59)	0.386
9.3	19.22 ± 0.05	0.87	0.42	(0.59)	0.717
11.0	19.14 ± 0.07	0.52	0.46	(0.59)	2.022
12.7	19.09 ± 0.10	0.46	0.46	(0.59)	2.937

[a]Parameters in parentheses were kept constant. [b]Critical temperature and critical exponent are very strongly correlated, leading to an unreliable estimation of errors.

The linearity of the obtained relations indicate that the experiments are still in a low-field regime.

As stated above, the nonlinearity of $\Delta\varepsilon(E^2)$ and depression of the $\Delta\varepsilon/E^2$ anomaly close to T_c are related to the decrease of T_c in electric fields. In our previous work devoted to the same problem,[10] we analyzed the dependence $\Delta\varepsilon(E^2)$ and the shift to T_c was estimated from the curvature of that dependence. In this
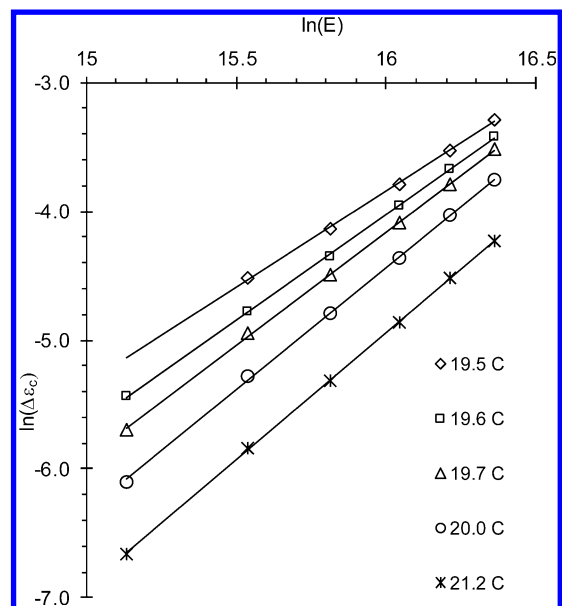
Figure 8. Critical part of $\Delta\varepsilon$ defined as $\Delta\varepsilon_c = \Delta\varepsilon - D_{bg}$ as a function of electric field strength E in a double logarithmic scale.

paper we propose to use a more direct method, where eq 10 is fitted to experimental points and T_c is treated as an adjustable parameter. Equation 10 contains a background term (D_{bg}) responsible for correct description of experimental data in noncritical region. For larger temperature intervals the temperature dependence of the background term is very important.[31,44] Here a relatively narrow temperature interval is analyzed (3.5 K), and this allows us to approximate the background term by a constant value. According to theoretical expectation, the critical exponent z has a value of 0.59. Some experiments confirmed this value,[10,31,32] but in many cases a somewhat smaller exponent was obtained.[24,25,44] Rzoska and co-workers[24,45,46] pointed out that the critical exponent $z = 0.59$ is validated in an asymptotic region (far from T_c and not very strong electric fields), whereas in the mean-field region (close to T_c and strong E field) the exponent 0.37 seems to be supported.

The selection of the exponent z is crucial and influences strongly the fitting results. A fitting procedure with both T_c and z as adjustable parameters is not possible because the strong correlation between parameters precludes any definite conclusion. We decided to use the value predicted theoretically, $z = 0.59$. To check the correctness of this value, the experimental data obtained for the weakest HV pulses (3.7 MV/m) are fitted twice, either the z exponent is treated as an adjustable parameter or it is fixed at $z = 0.59$. Results of these procedures are presented in the first two lines of Table 1.

The quality of the fits was controlled by χ^2 defined as

$$\chi^2 = \frac{1}{N - p - 1} \times$$

$$\sum_{i=1}^{N} \frac{(y_i - y_{i,\text{cal}})^2}{\left[\left(\frac{\partial y}{\partial \Delta\varepsilon}\right)_i \delta\Delta\varepsilon\right]^2 + \left[\left(\frac{\partial y}{\partial U}\right)_i \delta U\right]^2 + \left[\left(\frac{\partial y}{\partial T}\right)_i \delta T\right]^2}$$

where $y = \Delta\varepsilon/E^2$, N is the number of experimental points, and p is the number of adjustable parameters. In calculations of χ^2 we used $\delta\Delta\varepsilon = 0.0001$, $\delta U = 15$ V, and $\delta T = 0.0025$ K. The uncertainty of the fitted critical temperature, declared in Table

1, was obtained as the possible deviation of T_c that does not produce a fit error (χ^2) greater than unity. For the data obtained at HV intensity of 11.0 MV/m and 12.7 MV/m the criterion used for error estimation was a doubling of χ^2.

The fits of eq 10 when the z exponent is an adjustable parameter or when it is fixed lead to similar results. In addition, in both cases χ^2 is much smaller than unity, which makes it impossible to discriminate between both fits. This supports an assumption to use the theoretical value $z = 0.59$. Figure 9 presents the resulting fitted critical temperatures as a function of the square of electric field strength.
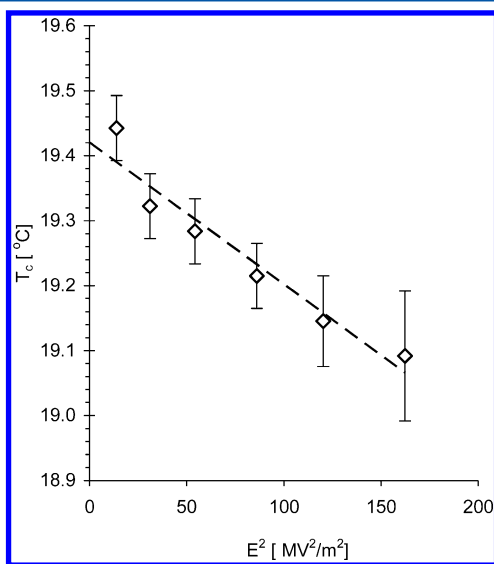
Figure 9. Dependence of the critical temperature on the electric field squared.

The critical temperature decreases proportionally to E^2. The slope of the line is $(\partial T_c/\partial E^2) = (-22 \pm 10) \times 10^{-16}$ (K m^2)/V^2. The decrease of T_c is consistent with our previous calculations performed by an analysis of critical anomaly of $\varepsilon(t)$,[18] but the absolute value obtained here is much larger than that obtained from $\varepsilon(t)$ experiments.

CONCLUSIONS

The theory of the influence of electric fields on the critical temperature uses the constitutive relation $\varepsilon(x)$. A fit of a polynomial defined in eq 1 to the experimental data gave the parameters: $\varepsilon_c = 11.782 \pm 0.004$; $\varepsilon_1 = 31.46 \pm 0.08$; $\varepsilon_2 = 40 \pm 5$. The theory described in this paper offers two solutions of the question of electric field effect on T_c. When concentration fluctuations are spatially symmetric, eq 8 applies and the derivative $(\partial T_c/\partial E^2)$ is calculated to be $(\partial T_c/\partial E^2) = (-2.8 \pm 0.4) \times 10^{-16}$ (K m^2)/V^2. This is very close to the experimental value obtained previously $(\partial T_c/\partial E^2) = (-3.9 \pm 0.3) \times 10^{-16}$ (K m^2)/V^2 from the analysis of the $\varepsilon(T)$ dependence measured at low-intensity electric field.[18] The proposed expression eq 9 is controlled by composition fluctuations in the direction parallel to the field. For high fields it yields the value $(\partial T_c/\partial E^2) = (-22 \pm 4) \times 10^{-16}$ (K m^2)/V^2, which is very close to $(\partial T_c/\partial E^2) = (-22 \pm 10) \times 10^{-16}$ (K m^2)/V^2 obtained from the direct measurement using the NDE method. These equations give the correct value of $(\partial T_c/\partial E^2)$ to a surprisingly high accuracy.

AUTHOR INFORMATION

Corresponding Authors
*K. Orzechowski (experiment): phone, +48-375-7114; e-mail, kazimierz.orzechowski@chem.uni.wroc.pl.
*Y. Tsori (theory): phone, +972-8-6477794; e-mail: tsori@bgu.ac.il.

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Bounaz, M.; Beysens, D. Effect of Ion Impurities on a Binary Mixture of Isobutyric Acid and Water. *Chem. Phys. Lett.* **1994**, *231*, 105−10.
(2) Toumi, A.; Bouanz, M.; Gharbi, A. Coexistence Curves of the Binary Mixture Isobutyric Acid-Water with Added Ions (K+, Cl-). *Chem. Phys. Lett.* **2002**, *362*, 567−73.
(3) Urbanowicz, P.; Rzoska, S.; Paluch, M.; Sawicki, B.; Szulc, A.; Ziolo, J. Influence of Intermolecular Interactions on the Sign of dT(c)/dp in Critical Solutions. *J. Chem. Phys.* **1995**, *201*, 575−82.
(4) Losada-Perez, P.; Blesic, M.; Perez-Sanchez, G.; Cerdeirina, C. A.; Troncoso, J.; Romani, L.; et al. Solution Thermodynamics Near the Liquid-Liquid Critical Point I. First-Order Excess Derivatives. *Fluid Phase Equilib.* **2007**, *258*, 7−15.
(5) Nakatani, A. I.; Morrison, F. A.; Douglas, J. F.; Mays, J. W.; Jackson, C. L.; Muthukumar, M.; et al. The Influence of Shear on the Ordering Temperature of a Triblock Copolymer Melt. *J. Chem. Phys.* **1996**, *104*, 1589−99.
(6) Beysens, D.; Perrot, F.; Baumberger, T. Phase Separation in Liquids Due to Quench by Cessation of Shear. *Physica A* **1994**, *204*, 76−86.
(7) Debye, P.; Kleboth, K. Electrical Field Effect on the Critical Opalescence. *J. Chem. Phys.* **1965**, *42*, 3155.
(8) Beaglehole, D. A Critical Binary Liquid in an Electric Field. *J. Chem. Phys.* **1981**, *74*, 5251−55.
(9) Wirtz, D.; Fuller, G. G. Phase Transitions Induced by Electric Fields in Near-Critical Polymer Solutions. *Phys. Rev. Lett.* **1993**, *71*, 2236−39.
(10) Orzechowski, K. Electric Field Effect on the Upper Critical Solution Temperature. *Chem. Phys.* **1999**, *240*, 275−81.
(11) Landau, L. D.; Lifshitz, E. M. *Elektrodynamika Sploshnykh Sred*; Nauka: Moscow, 1957.
(12) Onuki, A.; Doi, M. Electric Birefringence and Dichroism in Critical Binary Mixtures. *Europhys. Lett.* **1992**, *17*, 63−68.
(13) Onuki, A. Electric-Field Effects in Fluids Near the Critical Point. *Europhys. Lett.* **1995**, *29*, 611−16.
(14) Onuki, A. Electric Field Effects Near Critical Points. In *Nonlinear Dielectric Phenomena in Complex Liquids*; Rzoska, S., Zhelezny, V., Eds.; NATO Sciences Series, vol. 157; Kluwer Adademic Publishers: Dordrecht, The Netherlands, 2005; pp 113−41.
(15) Samin, S.; Tsori, Y. Stability of Binary Mixtures in Electric Field Gradients. *J. Chem. Phys.* **2009**, *131*, 194102.
(16) Tsori, Y. Colloquium: Phase Transitions in Polymers and Liquids in Electric Fields. *Rev. Mod. Phys.* **2009**, *81*, 1471−94.
(17) Tsori, Y.; Andelman, D.; Lin, C.-Y.; Schick, M. Block Copolymers in Electric Fields: A Comparison of Single-Mode and Self-Consistent-Field Approximations. *Macromolecules* **2006**, *39*, 289−93.
(18) Orzechowski, K.; Kosmowska, M.; Adamczyk, M. Electric Permittivity Anomaly Close to the Critical Consolute Point of a

Nitrobenzene + Octane Liquid Mixture. *J. Phys. Chem. B* **2012**, *116*, 2492−97.

(19) Orzechowski, K. Change of Critical Mixing Temperature in a Uniform Electric Field. In *Polymers, Liquids and Colloids in Electric Fields. Interfacial Instabilities, Orientation and Phase transitions*; Tsori, Y., Steiner, U., Eds.; Series in Soft Condensed Matter, Vol. 2; Word Scientific: Singapore, 2009; pp 87−112.

(20) Sengers, J. V.; Bedeaux, D.; Mazur, P.; Greer, S. C. Behavior of the Dielectric Constant of Fluids near a Critical Point. *Physica A* **1980**, *104*, 573−94.

(21) Pérez-Sánchez, G.; Losada-Pérez, P.; Cerdeiriña, C. A.; Sengers, J. V.; Anisimov, M. A. Asymmetric Criticality in Weakly Compressible Liquid Mixtures. *J. Chem. Phys.* **2010**, *32*, 154502.

(22) Bertrand, C. E.; Sengers, J. V.; Anisimov, M. A. Critical Behavior of the Dielectric Constant in Asymmetric Fluids. *J. Phys. Chem. B* **2011**, *115*, 14000−7.

(23) Losada-Pérez, P.; Pérez-Sánchez, G.; Cerdeiriña, C. A.; Thoen, J. Dielectric Constant of Fluids and Fluid Mixtures at Criticality. *Phys. Rev. E* **2010**, *81*, 041121.

(24) Ziolo, J.; Rzoska, S. J. Classical-Nonclassical Crossover Behavior of Critical and Noncritical Liquid Binary Solutions in a Strong Electric Field. *Phys. Rev. E* **1999**, *60*, 4983−85.

(25) Rzoska, S. J. Kerr Effect and the Nonlinear Dielectric Effect on Approaching the Critical Consolute Point. *Phys. Rev. E* **1993**, *48*, 1136−41.

(26) Chelkowski, A. *Dielectric Physics*; Elsevier Scientific Pub. Co.: Amsterdam, 1980.

(27) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 84th ed.; CRC Press: Boca Raton, FL, 2003.

(28) Pyzuk, W. Induced Birefringence and Electric Permittivity Changes in Critical Binary Liquids. *J. Phys. Chem.* **1986**, *90*, 699−702.

(29) Rzoska, S. J.; Chrapec, J.; Ziolo, J. Nonlinear Dielectric Effect in the Vicinity of the Critical Point of Binary and Doped Critical Solutions. *Physica A* **1986**, *139*, 569−584.

(30) Rzoska, S. J.; Ziolo, J.; Drozd-Rzoska, A. Stretched Relaxation After Switching Off the Strong Electric Field in a Near-Critical Solution Under High Pressure. *Phys. Rev. E* **1997**, *56*, 2578−81.

(31) Orzechowski, K. Nonlinear Dielectric Effect in Ethanol-Dodecane Critical Mixture. *Physica B* **1991**, *172*, 339−45.

(32) Kosmowska, M.; Orzechowski, K. Non-Linear Dielectric Effect in an Ethanol+Dodecane Critical Mixture With Minor Amounts of Ions. *J. Phys.: Condens. Matter* **2006**, *18*, 6225−36.

(33) Kosmowska, M.; Orzechowski, K. Non-Linear Dielectric Effect and Critical Phenomena in a Ternary Mixture Cyclohexane +Acetonitrile+p-Xylene. *J. Non-Cryst. Solids.* **2010**, *356*, 815−17.

(34) Goulon, J.; Greffe, J.-L.; Oxtoby, D. W. Droplet Model for the Analysis of the Dielectric Properties of Critical Binary Mixtures. *J. Chem. Phys.* **1979**, *70*, 4742−50.

(35) Piazza, R.; Bellini, T.; Degiorgio, V.; Goldstein, R. E.; Leibler, S.; Lipowsky, R. Stretched-Exponential Relaxation of Birefringence in a Critical Binary Mixture. *Phys. Rev. B* **1988**, *38*, 7223−26.

(36) Dutta, P.; Tominaga, K. Terahertz Time-Domain Spectroscopic Study of the Low-Frequency Spectra of Nitrobenzene in Alkanes. *J. Mol. Liq.* **2009**, *147*, 45−51.

(37) Thoen, J.; Kindt, R.; Van Dael, W. Measurements of the Temperature and Frequency Dependence of the Dielectric Constant near the Consolute Point of Benzonitrile-Isooctane. *Phys. Lett. A* **1980**, *76*, 445−48.

(38) Thoen, J.; Kindt, R.; Van Dael, W. The Dielectric Constant Anomaly of Nitroethane-Cyclohexane Near the Critical Solution Point. *Phys. Lett. A* **1981**, *87*, 73−77.

(39) Thoen, J.; Kindt, R.; Van Dael, W.; Merabet, M.; Bose, T. K. Low-Frequency Dielectric Dispersion and Electric Conductivity Near the Consolute Point in Some Binary Liquid Mixtures. *Physica A* **1989**, *156*, 92−113.

(40) Hamelin, J.; Bose, T. K.; Thoen, J. Dielectric Constant and the Electric Conductivity Near the Consolute Point of the Critical Binary Liquid Mixture Nitroethane−3-Methylpentane. *Phys. Rev. A* **1990**, *42*, 4735−42.

(41) Orzechowski, K. Electrical Properties of an Ethanol−Dodecane Mixture Near the Upper Critical Solution Point. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2757−63.

(42) Orzechowski, K. Dielectric Properties of Methanol plus Hexane Critical Mixtures Without and With Ionic Additives. *J. Mol. Liq.* **1997**, *73−4*, 291−303.

(43) Leys, J.; Losada-Pérez, P.; Cordoyiannis, G.; Cerdeiriña, C. A.; Glorieux, C.; Thoen, J. Temperature, Concentration, and Frequency Dependence of the Dielectric Constant Near the Critical Point of the Binary Liquid Mixture Nitrobenzene-Tetradecane. *J. Chem. Phys.* **2010**, *132*, 104508.

(44) Pyżuk, W.; Maka, E.; Podgajnik, K. Nonlinear Dielectric Effect of Critical Liquid Mixtures: Propylene Carbonate+ Monoalkylbenzene Systems. *Int. J. Thermophys.* **1990**, *11*, 911−22.

(45) Rzoska, S. J.; Degiorgio, V.; Bellini, T.; Piazza, R. Relaxation of Electric Birefringence Near a Critical Consolute Point. *Phys. Rev. E* **1994**, *49*, 3093−96.

(46) Rzoska, S. J.; Drozd-Rzoska, A.; Górny, M.; Ziolo, J. Time-Scale Dependence of the Critical Exponent for the Nonlinear Dielectric Effect in a Critical Binary Solution. *Phys. Rev. E* **1995**, *52*, 6325−28.