

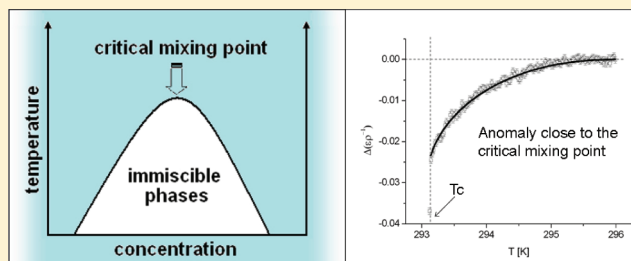
# Electric Permittivity Anomaly Close to the Critical Consolute Point of a Nitrobenzene + Octane Liquid Mixture

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**S** Supporting Information

**ABSTRACT:** Electric permittivity and density were measured in a nitrobenzene and octane mixture in the vicinity of the upper critical consolute point. Measurements were conducted in the one-phase region, at the critical concentration. The possibility of stirring in the course of measurements allowed us to check if the density and concentration gradients had any influence on the obtained results. No signs of the presence of the gradients mentioned above were found. Using the data obtained in the reported measurements, different methods of the fitting of the equation describing the permittivity anomaly were tested. The calculation of a reliable value of the critical amplitude, used to estimate the critical temperature shift under the influence of the electric field, was of particular interest. The derivative  $(\partial T_c / \partial E^2)$  was found to be  $(-3.9 \pm 0.3) \times 10^{-16} \text{ K m}^2 \text{ V}^{-2}$ .



## INTRODUCTION

The upper critical consolute point is the maximum of the phase coexistence curve in mixtures of limited solubility liquids. Macroscopic properties of a mixture in the vicinity of the critical point are different from those observed far from it. The so-called critical anomalies are caused by large and long-lived concentration fluctuations.

Electric permittivity ( $\epsilon$ ) anomalies close to the upper critical consolute point have been investigated for a long time. The first experiments would often give conflicting results. Some of them showed a strong increase in  $\epsilon$  close to  $T_c$ , whereas the others demonstrated only a small decrease in  $|\mathrm{d}\epsilon/\mathrm{d}T|$ . The reason for this controversy was explained by Thoen et al.<sup>1–4</sup> They found that large and long-lived concentration fluctuations caused a low-frequency dispersion and absorption, known in inhomogeneous systems as a Maxwell–Wagner effect. It is the reason why the character of the permittivity anomaly depends on frequency.

The electric permittivity anomaly measured at the frequencies higher than the dispersion range of the Maxwell–Wagner effect, but in the low-frequency range of dipolar or structural relaxation, is called an “inherent” critical anomaly of  $\epsilon$ . Far from the critical point,  $\epsilon$  is almost a linear function of temperature. Close to the critical point ( $T - T_c = 1 \div 3 \text{ K}$ ;  $x = x_c$ ), a change of the slope of  $\epsilon(T)$  is detected. In most of the examples investigated so far, the  $\mathrm{d}^2\epsilon/\mathrm{d}T^2$  derivative was negative in the vicinity of  $T_c$ ; even the maximum of  $\epsilon(T)$  was observed.<sup>2</sup> The maximum was found also by Rzoska et al. in measurements of permittivity as a function of pressure at the temperature close to the critical one.<sup>5,6</sup> However, just recently, Leys et al.<sup>7</sup> found a different curvature of  $\epsilon(T)$  dependence in a mixture with an upper critical consolute point. In the

nitromethane + 3-pentanol system, the  $\mathrm{d}^2\epsilon/\mathrm{d}T^2$  derivative was found to be positive in the vicinity of  $T_c$ .

Theoretical models, both microscopic<sup>8</sup> and thermodynamic<sup>9</sup> ones, predict a weak critical anomaly of electric permittivity. A description based on the scaling<sup>9</sup> and complete scaling<sup>10,11</sup> theory leads to the following  $\epsilon(T)$  dependence under critical conditions in the one-phase region

$$\epsilon \hat{\rho}^{-1} = \epsilon_c + C_1 t + C_{1-\alpha} t^{1-\alpha} + C_{1-\alpha+\Delta} t^{1-\alpha+\Delta} + \dots \quad (1)$$

where  $\epsilon$  is the electric permittivity,  $\hat{\rho}$  is the reduced density ( $\hat{\rho} = \rho/\rho_c$ , where  $\rho$  and  $\rho_c$  are the density and the critical density, respectively),  $C_i$  are dimensionless system-dependent constants,  $t = (T/T_c - 1)$  is the dimensionless temperature critical deviation,  $\alpha$  is the critical exponent of heat capacity, and  $\Delta$  is the correction-to-scaling critical exponent. The binary liquid mixtures with the critical consolute point belong to the 3D-Ising universality class, and the theoretical values of  $\alpha$  and  $\Delta$  are 0.109 and 0.5, respectively.<sup>12</sup>

The critical amplitude  $C_{1-\alpha}$  allows one to calculate the shift of  $T_c$  under the influence of the electric field  $(\partial T_c / \partial E^2)_p$ . For the upper consolute temperature, the dependence is as follows (for details, please refer to the paper of Losada-Perez et al.<sup>10</sup>)

$$C_{1-\alpha} = -\frac{2k_B A_m^+ \rho_{\text{cnd}}}{\epsilon_0 (1 - \alpha)} \left( \frac{\partial T_c}{\partial E^2} \right) \quad (2)$$

**Received:** October 12, 2011

**Revised:** January 11, 2012

**Published:** January 25, 2012



where  $A_m^+$  is the critical amplitude of dimensionless isobaric heat capacity per molecule ( $\hat{C}_{p,E} = A_m^+ t^{-\alpha} + A_0$ ),  $k_B$  is the Boltzmann's constant,  $\epsilon_0$  is the electric permittivity of vacuum,  $E$  is the electric field strength,  $\rho_{\text{cnd}}$  is the critical number density ( $\rho_{\text{cnd}} = \rho_c N_A M^{-1}$ , where  $N_A$  is the Avogadro number and  $M$  is the mean molar mass of the mixture).

The applicability of the eq 1 for describing experimental results was proved many times; however, we should realize that the  $\epsilon\hat{\rho}^{-1} = f(T)$  dependence is almost linear, and a credible fitting of the equation parametrized by many variables is very difficult. Nevertheless, the question about the validity of a description employing the  $1-\alpha$  exponent and the value of critical amplitude  $C_{1-\alpha}$  responsible for the critical temperature shift under the influence of the electric field, is still interesting. Direct measurements of the  $(\partial T_c / \partial E^2)_p$  derivative are very difficult, and only few experiments aimed at its determination have been published to date.<sup>13–19</sup>

This paper presents precise measurements of electric permittivity and density in a nitrobenzene and octane mixture, in the vicinity of the upper critical consolute point. Measurements were conducted in the one-phase region, at the concentration equal to the critical one. The temperature was lowered toward the critical one with a constant rate (1.2 K/h). To check if the concentration and/or temperature gradients had any influence on the obtained results, the sample was continuously stirred during some experimental runs.

Using the data obtained in the reported measurements, different methods of fitting of the equation describing the permittivity anomaly were tested. A particular focus was given to the determination of a credible value of the critical amplitude  $C_{1-\alpha}$ , allowing us to estimate the critical temperature shift under the influence of the electric field.

## EXPERIMENTAL SECTION

**Permittivity Measurements.** Electric permittivity measurements were performed using the HP-4284A Precision LCR Meter in a two-electrode configuration with lead capacity compensation. Measurements were conducted at 800 kHz (available frequency range 0.02–1000 kHz). The capacitor consisted of two platinum electrodes (surface of approximately 1 cm<sup>2</sup>, distance between the electrodes of 1 mm) embedded in a glass pipe. One of the electrodes was slightly longer in order to improve the effectiveness of mixing. At the bottom of the glass sample holder, a small magnetic rod covered with Teflon was placed. Above the capacitor, a Teflon ring was mounted to reduce the impact of mixing (caused by vibrations of the liquid surface) on dielectric measurements. The sample holder was mounted on the top of the water turbine with a permanent magnet. The turbine was driven by a water pump stirring the water bath. The sample holder and turbine were immersed in the water bath. We checked in the preliminary measurements that the stirring did not produce any detectable heating and did not disturb the dielectric measurements. A scheme of the experimental setup is presented in Figure 1.

The geometrical capacity and the residual lead capacity were calculated on the basis of measurements of electric permittivity of an empty capacitor and a capacitor filled with 1,2-dichloroethane. The geometrical capacity thus determined was 0.977 pF. The capacity was measured with a resolution of  $7 \times 10^{-4}$  pF.

**Temperature Control and Reading.** The sample was immersed in the 60 dm<sup>3</sup> water bath, the temperature of which was stabilized by means of a thermostat. In all measurements,

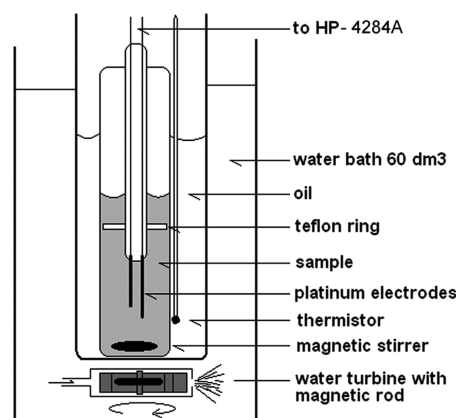


Figure 1. Scheme of the experimental setup.

the temperature was lowered from 300 to 290 K with a rate of 1.2 K/h. The temperature was measured by means of a thermistor. The resolution of temperature readings was 0.001 K, and an absolute error was 0.2 K.

**Procedure of Dielectric Measurements.** The capacitor was filled with a homogeneous mixture at 25 °C. To protect it from moisture, filling was carried out in a dry nitrogen atmosphere. Before each run of measurements, the sample holder was removed from the water bath and shaken vigorously. Manual shaking before measurements was necessary especially in the case when the sample was separated in the previous run. A magnetic stirrer was unable to mix the sample sufficiently due to the Teflon ring above the capacitor.

**Density Measurements.** The density was measured by means of a capillary pycnometer. The volume of the pycnometer ( $V [\text{cm}^3] = 1.8193 + 5.1 \times 10^{-5} \cdot (T - 273.15) + h$ , where  $T$  is the temperature in K,  $h$  is the reading from the capillary in cm<sup>3</sup>) was determined by calibration, using twice-distilled and degassed water. The density was measured with a resolution of 0.0001 g/cm<sup>3</sup> and an absolute error of 0.0005 g/cm<sup>3</sup>. In the course of the density measurements, the temperature was stabilized and read with a precision of 0.025 K.

**Chemicals and Sample Preparation.** Nitrobenzene (ABCR GmbH, 99%) was crystallized three times and stored above A3 molecular sieves. Octane (Sigma Aldrich, 99%) was used without additional purification. The sample was prepared by weighing in a dry nitrogen atmosphere. The critical composition was checked using the criterion of the equal volume of coexisting phases. The determined critical composition of the nitrobenzene and octane mixture was equal to  $0.511 \pm 0.005$  (mole fraction of nitrobenzene), the critical temperature being  $293.1 \pm 0.2$  K. The obtained values are close to the parameters cited in the literature:  $T_c = 293.1 \pm 0.2$ ,  $x_c = 0.505 \pm 0.001$ ;<sup>20</sup>  $T_c = 292.6$ ,  $x_c = 0.51$ ;<sup>21</sup>  $T_c = 293.22 \pm 0.01$ ;<sup>22</sup>  $T_c = 293.2$ .<sup>23</sup>

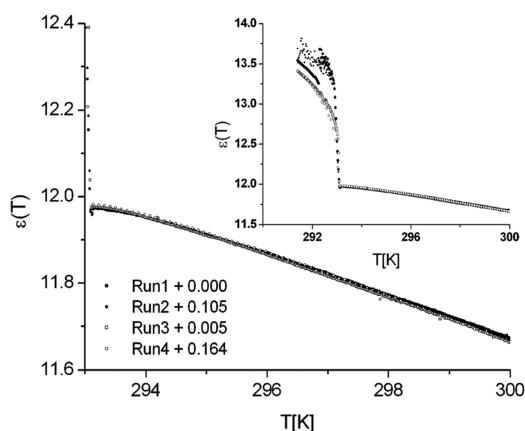
## RESULTS

Measurements were performed in the mixture of nitrobenzene and octane at the critical concentration. The temperature was reduced from 300 K (one-phase mixture) toward the critical point. In the vicinity of the critical consolute point, a low-frequency dielectric permittivity is characterized by dispersion linked to the Maxwell–Wagner effect caused by large and long-lived concentration fluctuations.<sup>1–4</sup> The dispersion area of  $\epsilon$  depends mainly on the specific conductivity of the analyzed mixture.<sup>1</sup> For example, a nitroethane and cyclohexane mixture

with the conductivity  $\sigma = 25 \mu\text{S/m}$  demonstrates  $f_{\text{MW}} \cong 10 \text{ kHz}$  (relaxation frequency of the Maxwell–Wagner effect);<sup>2</sup> ethanol and dodecane,  $\sigma = 17 \mu\text{S/m}$ ,  $f_{\text{MW}} \cong 100 \text{ kHz}$ ;<sup>24</sup> and nitrobenzene and isooctane,  $\sigma = 0.82 \mu\text{S/m}$ ,  $f_{\text{MW}} \cong 30 \text{ kHz}$ .<sup>25</sup> The conductivity of the nitrobenzene and octane mixture investigated in this paper is  $0.39 \mu\text{S/m}$  ( $T = 300 \text{ K}$ ). Dielectric measurements were conducted at a frequency of  $800 \text{ kHz}$ , which is far above the relaxation range of the expected Maxwell–Wagner effect. Consequently, the critical anomaly of  $\varepsilon$  investigated in the nitrobenzene and octane mixture at  $800 \text{ kHz}$  could be treated as an “inherent” anomaly of the permittivity.

In the first part of the experiments, the influence exerted by the density (concentration) gradient on the dielectric properties was examined, especially in the vicinity of the consolute point. The densities of the liquids forming the mixture are significantly different (nitrobenzene,  $1.1985 \text{ g/cm}^3$ ; octane,  $0.6986 \text{ g/cm}^3$ ;  $T = 298 \text{ K}$ ).<sup>26</sup> When  $T > T_c$  the mixture is thermodynamically and diffusively stable ( $\Delta G^{\text{M}} < 0$ ,  $D_{12} > 0$ , where  $\Delta G^{\text{M}}$  is the free enthalpy of mixing and  $D_{12}$  is the mutual diffusion coefficient). However, when the temperature comes close to the critical value, both  $\Delta G^{\text{M}}$  and  $D_{12}$  approach zero.<sup>27,28</sup> Below  $T_c$  the mixture loses stability and forms two coexisting phases. Consequently, there arises a question of whether the density (as well as concentration) gradient could occur and influence the macroscopic properties of the mixture when the temperature approaches  $T_c$ . Close to the critical point of gases, the impact of the gravitational effect is very strong.<sup>29</sup> Experiments performed by Merabet and Bose<sup>25</sup> in a nitrobenzene and isooctane mixture using a multielectrode capacitor (electrodes were located at different heights in a sample) did not show any significant differences in the capacitance, which seems to contradict the occurrence of the said density gradient. To settle the problem definitively, a capacitor with a possibility of stirring a sample in the course of measurements was built. The data obtained in experiments when the mixture was continuously stirred (runs 1 and 2) and those gathered in experiments when the stirrer was switched off (runs 3 and 4) were compared.

Figure 2 presents the obtained data. Before each temperature run, the capacitor was pulled out from the thermostat and the

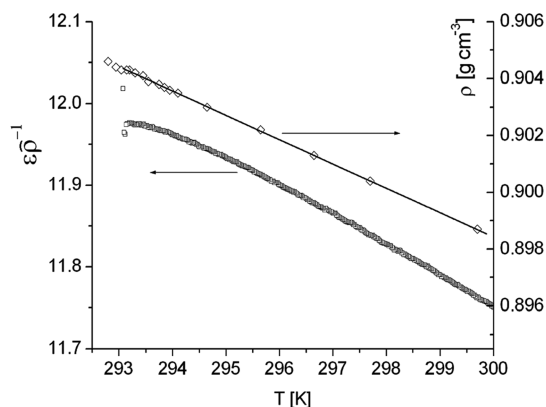


**Figure 2.** Comparison of the results obtained in runs 1–4. In runs 1 and 2, the stirrer was switched on; in runs 3 and 4, the stirrer was switched off.

sample was shaken vigorously. These operations resulted in slight changes in the lead capacity increasing an absolute error

of the obtained permittivity. These changes are marked in Figure 2 as a correction of the experimental results ( $\varepsilon + \delta\varepsilon$ ). In these measurements, the focus was on the  $\varepsilon(T)$  dependence, and a possible shift in the absolute value of  $\varepsilon$  was irrelevant. According to Figure 2, consecutive measurements follow the same curve in the one-phase region ( $T > T_c$ ). Relying on these results, it can be stated that neither the concentration gradient nor the density gradient had any effect on the obtained results. A large scatter of the experimental points obtained in the two-phase region reflects the differences in the kinetics of phase separation. The rotation speed of the magnetic root was small enough to limit the heat production by friction, but, as a consequence, the effectiveness of mixing was insufficient to provide a uniform spread of the two phases in the whole volume of the sample.

It is possible to analyze both the  $\varepsilon = f(T)$  and the  $\varepsilon\hat{\rho}^{-1} = f(T)$  dependences. However, the critical amplitude describing the  $\varepsilon(T)$  dependence is related to the  $dT_c/dp$  and  $dT_c/dE^2$  derivatives, whereas  $\varepsilon\hat{\rho}^{-1}$  to  $dT_c/dE^2$  only.<sup>10</sup> Since our intention was to estimate the  $dT_c/dE^2$  derivative, the analysis of  $\varepsilon\hat{\rho}^{-1} = f(T)$  was more convenient. Figure 3 shows the  $\varepsilon\hat{\rho}^{-1}$  as



**Figure 3.** The  $\varepsilon\hat{\rho}^{-1}$  vs temperature obtained in run 1 (stirrer was switched on) and the density vs temperature.

a function of temperature. A downward deviation close to  $T_c$  from a linear dependence, observed far from  $T_c$  allowed us to assume a positive value of the critical amplitude  $C_{1-\alpha}$ .

According to theoretical expectations,<sup>9</sup> the density has a similar critical anomaly as  $\varepsilon\hat{\rho}^{-1}$ . The density anomaly is much weaker,<sup>30–32</sup> but possible to observe. The critical amplitude of the density is proportional to the  $dT_c/dp$  derivative, which is usually much smaller than the  $dT_c/dE^2$  one.<sup>10</sup> In our investigations, the density measurements were performed in the temperature range of  $300\text{--}293 \text{ K}$ . The resolution of the density measurements was only  $0.0001 \text{ g/cm}^3$ , and no detectable anomaly of  $\rho(T)$  was found. The obtained density could be approximated as a linear function of temperature:  $\rho [\text{g/cm}^3] = 0.9044 - 8.57 \times 10^{-4} \cdot (T - 293.133)$  ( $T$  in Kelvin, equation applicable in the temperature range of  $293\text{--}300 \text{ K}$ ,  $T_c = 293.133 \text{ K}$ ). Experimental data of the density are presented in Figure 3.

## DISCUSSION

In accordance with theoretical expectations, the temperature dependence of  $\varepsilon\hat{\rho}^{-1}$  should be approximated by eq 1. However, eq 1 contains as many as seven selectable parameters ( $T_c$ ,  $\varepsilon_c$ ,  $C_1$ ,  $C_{1-\alpha}$ ,  $C_{1-\alpha+\Delta}$ ,  $\alpha$ ,  $\Delta$ ), and credible fitting of such an equation to

the almost linear dependence is very difficult. To limit the number of matched parameters, a few assumptions were made: (a) The critical temperature was fixed at the value calculated as the middle of the range bounded by the last point in the one-phase mixture (293.143 K) and the first point in the two-phase mixture (293.123 K, visible due to a permittivity jump). The critical temperature  $T_c$  obtained in this way was equal to 293.133 K. (b) The correction-to-scaling exponent  $\Delta$  was fixed at a theoretically predicted value of 0.5. (c) In most of the attempts, the critical exponent  $\alpha$  was fixed at a constant value. The quality of the fitting was controlled by the  $\chi^2$ , defined as

$$\chi^2 = \frac{1}{N - p - 1} \sum \frac{(y_i - f_i)^2}{\sigma_y^2 + \sigma_T^2 (\partial y / \partial T)^2}$$

where  $N$  is the number of data points,  $p$  is the number of fitted parameters,  $y_i$  is the  $i$ th measurement value,  $f_i$  is its corresponding fit value,  $\sigma_y$  is the measuring uncertainty of ( $\epsilon\bar{\rho}^{-1}$ ), and  $\sigma_T$  is the measuring uncertainty of the temperature. In the calculations, we assumed  $\sigma_y = 0.0008$  and  $\sigma_T = 0.001$  K. Fittings were performed using the SOLVER supplement in the EXCELL package. The results are presented in Tables 1–4.

**Table 1. Fitting of eq 1 to the Experimental Points Obtained in Run 1<sup>a</sup>**

$T_c$ [K]	$\epsilon_c$	$C_1$	$C_{1-\alpha}$	$C_{1-\alpha+\Delta}$	$1 - \alpha$	$\chi^2$
(293.133)	11.973	-15.43	2.16	-1.45	(0.700)	0.679
(293.133)	11.973	-19.35	3.57	1.90	(0.750)	0.679
(293.133)	11.973	-24.08	6.02	5.22	(0.800)	0.675
(293.133)	11.974	-29.18	10.19	6.65	(0.850)	0.665
(293.133)	11.974	-39.78	18.45	10.85	(0.891)	0.664
(293.133)	11.974	-72.45	47.38	18.88	(0.940)	0.683
(293.133)	11.974	-40.41	18.93	11.24	0.893	0.663

<sup>a</sup>The parameters presented in the parentheses were fixed in the course of the fitting.

**Table 2. Fitting of eq 3 to the Experimental Points Obtained in Run 1<sup>a</sup>**

$T_c$ [K]	$\epsilon_c$	$C_1$	$C_{1-\alpha}$	$1 - \alpha$	$\chi^2$
(293.133)	11.973	-16.08	2.18	(0.700)	0.590
(293.133)	11.973	-17.85	3.29	(0.750)	0.570
(293.133)	11.974	-20.49	5.17	(0.800)	0.560
(293.133)	11.974	-24.88	8.68	(0.850)	0.556
(293.133)	11.975	-31.38	14.39	(0.891)	0.559
(293.133)	11.975	-51.42	33.21	(0.940)	0.565
(293.133)	11.974	-24.88	8.68	0.850	0.556

<sup>a</sup>The parameters presented in the parentheses were fixed in the course of the fitting.

In the first fitting step, we fitted eq 1 and four parameters were adjusted ( $\epsilon_c$ ,  $C_1$ ,  $C_{1-\alpha}$ ,  $C_{1-\alpha+\Delta}$ ). The critical exponent  $1-\alpha$  was fixed at a constant value, selected in the range (0.7–0.94), including the theoretically predicted one,  $1-\alpha = 0.891$ . A free adjustment of the  $1-\alpha$  exponent gave the value equal to 0.893. The obtained  $\chi^2$  was considerably lower than 1, which means that the differences between experimental and calculated values are generally smaller than the resolution of the measurements. Consequently, in the fitting, it is not possible to test the correctness of the exponent  $1-\alpha$ . The main difficulty in the fitting of eq 1 is a very similar temperature dependence of successive elements ( $t^1$ ,  $t^{0.891}$ ,  $t^{1.391}$ , respectively). It results in a

**Table 3. Fitting of eq 5 to the Experimental Points Obtained in Run 1<sup>a</sup>**

$T_c$ [K]	$C_{1-\alpha}$	$1 - \alpha$	$\chi^2$
(293.133)	2.27	(0.700)	0.614
(293.133)	3.33	(0.750)	0.578
(293.133)	5.02	(0.800)	0.575
(293.133)	8.32	(0.850)	0.602
(293.133)	13.56	(0.891)	0.641
(293.133)	30.22	(0.940)	0.707
(293.133)	5.09	0.800	0.575

<sup>a</sup>The parameters presented in the parentheses were fixed in the course of the fitting.

**Table 4. Fitting of eq 5 to the Experimental Points Obtained in Runs 1–4<sup>a</sup>**

series	$T_x$ [K]	$T_c$ [K]	$C_{1-\alpha}$	$1 - \alpha$	$\chi^2$
run 1	(296.0)	(293.124)	13.68	(0.891)	0.664
run 1	(296.0)	(293.133)	13.56	(0.891)	0.641
run1	(296.0)	(293.142)	13.44	(0.891)	0.626
run1	(296.5)	(293.133)	12.48	(0.891)	0.590
run 1	(295.5)	(293.133)	13.58	(0.891)	0.671
run 2	(296.0)	(293.133)	14.24	(0.891)	2.03
run 3	(296.0)	(293.133)	14.61	(0.891)	1.06
run 4	(296.0)	(293.133)	14.31	(0.891)	0.98

<sup>a</sup>In the performed fittings, we checked an effect of a selection of the critical temperature and the reference temperature on the fit results (run 1). The table presents also the fitting results of the data collected in runs 2–4. The parameters presented in the parentheses were fixed in the course of the fitting.

very strong correlation between the fitted parameters. To estimate the uncertainty of the fitted  $C_{1-\alpha}$  parameter, we repeated the fitting for the different (but fixed) values of  $C_{1-\alpha}$  allowing  $\epsilon_c$ ,  $C_1$ , and  $C_{1-\alpha+\Delta}$  to fit freely. We assumed that the  $C_{1-\alpha}$  parameter had an acceptable value if  $\chi^2 \leq 1$ . The exponent  $1-\alpha$  and the critical temperature were fixed (0.891 and 293.133 K, respectively). The fitted critical amplitude  $C_{1-\alpha}$  and its error were determined as  $C_{1-\alpha} = 18.45 \pm 10$ .

The analysis of the results of the fitting shows that the parameters  $C_1$  and  $C_{1-\alpha+\Delta}$  compensate each other. To diminish the correlation between the parameters, eq 1 was simplified by omitting the correction-to-scaling element:

$$\epsilon\bar{\rho}^{-1} = \epsilon_c + C_1 t + C_{1-\alpha} t^{1-\alpha} \quad (3)$$

This should decrease the correlation between the fitted parameters, but the equation is valid only in the vicinity of  $T_c$ . For this reason, the fitting range was limited to the temperature interval ( $T_c$ , 296 K). The results of the fitting are presented in Table 2. For all the tested  $1-\alpha$  exponents, the  $\chi^2$  was much smaller than 1; nevertheless, the best fit was found for  $1-\alpha = 0.85$ . When the exponent  $1-\alpha$  is fixed at  $1-\alpha = 0.891$ , the obtained  $C_{1-\alpha} = 14.65 \pm 4.0$ . The uncertainty was estimated in the same way as described before.

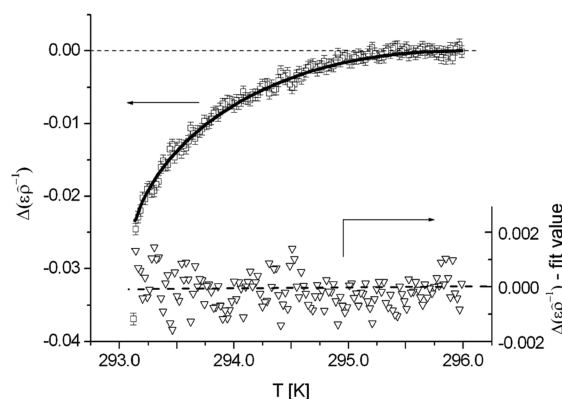
Recently a “critical increment” method has been proposed, convenient for an analysis of weak critical anomalies.<sup>33,34</sup> The method has its advantages: (a) it reduces the number of matched parameters, (b) it does not produce an increase in the error (like the derivative method), (c) it makes it possible to omit the correction-to-scaling element (analysis is performed in



the vicinity of  $T_c$  only), and (d) it makes it possible to avoid correlations between the critical amplitudes. The method consists of analyzing the differences between the experimental values and the tangent line calculated at some arbitrarily selected reference temperature  $T_x$  in the precritical region

$$\Delta(\varepsilon\hat{\rho}^{-1})_c = (\varepsilon\hat{\rho}^{-1}) - (B_0 + B_1T) \quad (4)$$

where  $(B_0 + B_1T)$  is the tangent to the  $\varepsilon\hat{\rho}^{-1}(T)$  calculated at  $T_x$ . In calculations,  $T_x = 296$  K was adopted; however, also  $T_x = 295.5$  and  $T_x = 296.5$  were tested. To calculate the tangent, a quadratic equation was fitted in the temperature range of  $(T_x - 1$  K,  $T_x + 1$  K), and the tangent was calculated in the middle of this range. Figure 4 presents the critical increment thus obtained.



**Figure 4.** Critical increment calculated according to eq 4 (experimental data were collected in run 1; the stirrer was switched on).

While analyzing the critical behaviors, only the temperature range ( $T_c$ ,  $T_x$ ) was considered. Because the analyzed range is close to the critical temperature, the correction-to-scaling element could be omitted. Consequently, the critical increment has the following form<sup>33</sup>

$$\Delta(\varepsilon\hat{\rho}^{-1})_c = -C_{1-\alpha}(\alpha \cdot t_x^{1-\alpha} + (1-\alpha) \cdot t_x^{-\alpha} \cdot t - t^{1-\alpha}) \quad (5)$$

where  $t_x = (T_x/T_c - 1)$  is the reduced reference temperature. The results of the fitting of eq 5 to the critical increment obtained in run 1 are presented in Table 3. The critical exponent  $1-\alpha$  was fixed at the values selected in the range  $\langle 0.7, 0.94 \rangle$ . The reference temperature  $T_x$  was equal to 296 K. The minimum of  $\chi^2$  was obtained for  $1-\alpha = 0.78$ , but for all the tested  $1-\alpha$  exponents, the  $\chi^2$  was much smaller than 1, which precluded a reliable test of the correctness of the  $1-\alpha$  exponent value. Similarly as before, the parameters  $C_{1-\alpha}$  and  $1-\alpha$  were strongly correlated. The main profit of the use of the increment method is a considerable decrease in the uncertainty of the  $C_{1-\alpha}$  parameter. When the  $1-\alpha$  exponent was fixed at 0.891 and  $T_c = 293.133$  K, the obtained  $C_{1-\alpha} = 13.6 \pm 0.9$ . The uncertainty was estimated in the same way as before, as a possible change of  $C_{1-\alpha}$  that gives  $\chi^2 < 1$ .

It is useful to check the influence of the critical temperature shift on the fitted parameters. Table 4 presents the results of additional fittings when the critical temperature was moved to the border of the temperature range bounded by the last point in the one-phase region and the first point in the two-phase

region. A change of the critical temperature influences the fitted parameters to a limited extent.

The increment method contains also an arbitrary choice of the reference temperature  $T_x$ . To check the effect of the  $T_x$  choice on the fit, we repeated the fitting with two different  $T_x$  temperatures (295.5 and 296.5 K). Table 4 presents the results of these fittings. It is visible that neither a change in the critical temperature nor a different selection of the reference temperature had any considerable effect on the fitted  $C_{1-\alpha}$  parameter.

Fittings of eq 5 were repeated for run 2 (stirrer was switched on) as well as for runs 3 and 4 (stirrer was switched off). The critical exponent was fixed at a theoretically predicted value. Fittings are consistent with the results obtained in run 1. The mean value of  $C_{1-\alpha} = 14.1 \pm 1.2$ . The fitting results are presented in Table 4.

Equation 2 allows us to obtain the  $(\partial T_c/\partial E^2)$  derivative. However, in order to apply this equation, the critical amplitude of the dimensionless isobaric heat capacity per molecule  $A_m^+$  has to be known. The parameter  $A_m^+$  should be obtained from the measurements of the isobaric heat capacity critical anomaly. In the papers of Souto-Caride et al.<sup>22</sup> and Perez-Sanches et al.,<sup>35</sup> the isobaric heat capacity per unit of volume of a nitrobenzene + octane mixture was presented. The critical divergence of the obtained value was described by the  $A_V^+$  parameter, defined as follows:

$$\frac{C_p}{V} = \frac{C_p^{\text{mol}}}{V^{\text{mol}}} = \frac{A_V^+}{\alpha} t^{-\alpha} + A_1 \quad (6)$$

Hence, the dimensionless isobaric heat capacity per molecule (equal to the ratio of molar isobaric heat capacity to the gas constant  $R$ ) could be presented as

$$\begin{aligned} \hat{C}_{p,E} &= A_m^+ t^{-\alpha} + A_0 \\ &= \frac{C_p^{\text{mol}}}{R} \\ &= \frac{A_V^+ V^{\text{mol}}}{\alpha R} t^{-\alpha} + \frac{A_1 V^{\text{mol}}}{R} \end{aligned} \quad (7)$$

consequently

$$A_m^+ = \frac{A_V^+ V^{\text{mol}}}{\alpha R} \cong \frac{A_V^+ V_c^{\text{mol}}}{\alpha R} = \frac{A_V^+ M}{\alpha R \rho_c} \quad (8)$$

Using eq 2, we obtain

$$\begin{aligned} C_{1-\alpha} &= -\frac{2k_B \rho_c N_A}{\varepsilon_0(1-\alpha)M} \frac{A_V^+ M}{\alpha R \rho_c} \left( \frac{\partial T_c}{\partial E^2} \right) \\ &= -\frac{2A_V^+}{\varepsilon_0(1-\alpha)\alpha} \left( \frac{\partial T_c}{\partial E^2} \right) \end{aligned} \quad (9)$$

The value of  $C_{1-\alpha} = 13.6 \pm 0.9$ , obtained in run 1, and  $A_V^+ = 15 \times 10^3 \text{ J K}^{-1} \text{ m}^{-3}$ , available in the literature,<sup>22,35</sup> allowed us to estimate the expected critical temperature shift under the influence of the electric field as  $(\partial T_c/\partial E^2) = (-3.9 \pm 0.3) \times 10^{-16} \text{ K m}^2 \text{ V}^{-2}$ .

## CONCLUSIONS

The paper presents the measurements of electric permittivity and density in the nitrobenzene and octane mixture in the

vicinity of the critical consolute point. The critical amplitude responsible for the critical temperature shift under the influence of the electric field was of special interest to the authors. The experimental setup made it possible to stir the investigated mixture continuously during measurements. No effect of stirring on the produced results was observed. The obtained  $\varepsilon\hat{\rho}^{-1}$  dependence as a function of temperature was analyzed with reference to the theory of Sergers et al.<sup>9</sup> In the course of numerical analyses, the critical exponents and critical amplitudes were matched. Unfortunately, as the critical anomaly is very weak, the free fitting of the equation predicted by the theory was ineffective and showed a very strong correlation between the matched parameters. In our opinion, better results of the fitting can be obtained by employing the critical increment method, proposed by us for the description of weak critical anomalies.<sup>33,34</sup> In the performed fittings, we found that the critical anomaly of  $\varepsilon\hat{\rho}^{-1}$  could be properly described using the critical exponent predicted by the theory ( $1 - \alpha = 0.891$ ). Small differences between  $\chi^2$  errors did not allow us to discriminate in favor of either the theoretical critical exponent or the best fitted exponent. The critical amplitude  $C_{1-\alpha}$  strongly correlates with the  $1-\alpha$  exponent. If the exponent  $1-\alpha$  is equal to the value predicted theoretically, 0.891, then the critical amplitude  $C_{1-\alpha} = 13.6 \pm 0.9$ . Using this value, the calculated derivative ( $\partial T_c / \partial E^2$ ) is equal to  $(-3.9 \pm 0.3) \times 10^{-16} \text{ K m}^2 \text{ V}^{-2}$ . It is close to the value obtained in different mixtures.<sup>10</sup> On the basis of our experience, we estimate that the practically strongest electric field that can be applied to a nitrobenzene and hydrocarbon mixture is of the order of  $1.5 \times 10^7 \text{ V/m}$ . Under such conditions, the expected decrease in  $T_c$  is 0.09 K. It would be interesting to verify this prediction in the direct measurement of the impact of the electric field on the critical temperature in a mixture of nitrobenzene and octane.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information contains the data of the electric permittivity and the density of a nitrobenzene + octane critical mixture as a function of temperature. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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