

Pressure and temperature studies of dielectric permittivity in the homogeneous phase of nitrobenzene–dodecane binary mixture

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Abstract

Results of isothermal high-pressure (up to 120 MPa) and isobaric ($P = 0.1$ and 51 MPa) temperature studies of dielectric permittivity in nitrobenzene–dodecane binary solution are presented. The dependencies of $\varepsilon(P)$ and $\varepsilon(T)$ obtained can be well portrayed by isomorphic relations with the same value of the critical exponent $\phi = 1 - \alpha \approx 0.88$. The influence of correction-to-scaling terms for the temperature and pressure paths is shown. It has been found that the strength of the pretransitional anomaly of the isothermal pressure path is definitely larger than that of the isobaric temperature path. The influence of the Maxwell–Wagner effect was found to be insignificant in the isothermal pressure studies even for a frequency of 100 Hz. Data were completed by the results of low-frequency (250 kHz) measurements of the shift of dielectric permittivity due to application of a strong electric field (the non-linear dielectric effect). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Critical phenomenon; Dielectric permittivity; High pressure

1. Introduction

Dielectric permittivity ε is a basic physical quantity which characterises a dielectric located between the plates of a capacitor, generally in liquids [1],

$$\varepsilon^E = \varepsilon + \varepsilon_1 E^2 + \dots, \quad (1)$$

where ε and ε_1 are dielectric permittivities in a weak and a strong electric field E , respectively. The measure of a shift of dielectric permittivity in a strong electric field is the coefficient: $\varepsilon_1 = \Delta\varepsilon/E^2 = (\varepsilon^E - \varepsilon)/E^2$ known as the non-linear dielectric effect (NDE).

Until the late 1970s there was no theoretical model to describe the critical anomaly of dielectric permittivity upon approaching the critical consolute point in binary liquid systems [2,3]. However, in the second part of the 1980s, the anomaly of dielectric permittivity was successfully tested experimentally [4–6]. It is interesting that until recently the same situation existed for NDE [7–9]. In 1980 Sengers et al. [3] obtained a functional form for the dielectric constant in the homogeneous phase of critical solutions:

$$\varepsilon = \varepsilon_c (1 + Ct + C_1 t^{1-\alpha} + C_2 t^{1-\alpha+\Delta_1} + \dots) \quad (2)$$
$$T > T_c,$$

where $t = |T - T_c|$ or $t = |(T - T_c)/T_c|$ is the distance from the critical consolute temperature T_c . In these

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studies the first definition was applied; ε_c is the value of dielectric permittivity at the critical point, C is the amplitude associated with the behaviour remote from T_c , C_1 is the critical amplitude, and C_2 is the amplitude of the first correction-to-scaling term. The critical exponent $\alpha \approx 0.11$ [10] describes the singularity of the specific heat, and $\Delta_1 \approx 0.5$ [10] is the first correction-to-scaling exponent.

In 1987 Thoen et al. [4,11] showed that the critical behaviour of the dielectric permittivity additionally depends on the frequency of the measuring electric field. They found a low-frequency dispersion of the dielectric permittivity in the immediate vicinity of T_c and interpreted this phenomenon in terms of Maxwell–Wagner (MW) polarisation. It has been found that the theoretically predicted temperature (relation (2)) dependence of ε describes $\varepsilon(T)$ only if $f \gg f_{MW}$, where f_{MW} is the characteristic frequency of MW polarisation.

There is a visible difference between the $\varepsilon(T)$ and NDE(T) anomalies in critical solutions. Contrary to the $\varepsilon(T)$ dependency, the critical anomaly of NDE is strongly influenced by pretransitional relaxation processes even remote from T_c [8,9]. In critical solutions theoretical models predicted $NDE(T) \approx (T - T_c)^{-\psi}$ [7–9], where $\psi = \gamma - 2\beta$, γ is the exponent of the osmotic compressibility and β of the order parameter. As was shown in Ref. [7] the strong electric field induces partially classical (mean-field) properties so that $\gamma = 1$ and the order parameter exponent can be equal $\beta = 0.5$ or 0.33 , depending on the relationship between time scales involved by the relaxation time and the frequency of the measuring field [8].

Apart from the temperature, pressure is also a thermodynamic variable which has a significant influence on the critical anomaly of dielectric permittivity. For instance, dependence of the critical amplitude on the rate of the shift of T_c induced by the electric field (dT_c/dE^2) and by the hydrostatic pressure (dT_c/dP) [3,12] can be analysed:

$$C_1 = -S_c S_c^+ \rho_c \left(\frac{2}{\varepsilon_0} \frac{dT_c}{dE^2} + \varepsilon_c \frac{dT_c}{dP} \right), \quad (3)$$

where $S_c S_c^+$ is the critical amplitude in the expansion of the molar entropy.

According to the theory proposed by Sengers [3] the critical amplitude (C_1 in Eq. (2)) should be opposite in sign to (dT_c/dE^2). However, this derivative is extremely difficult to obtain experimentally. Values of (dT_c/dE^2) were reported by Debye and Kleboth for nitrobenzene–2,2,4-trimethylpentane [13] and by Beaglehole for cyclohexane–aniline [14]. In both these papers negative values of the derivatives were obtained, leading to positive C_1 values. It is noteworthy that the same sign of C_1 is found in solutions with positive [15,16] and negative [18] signs of (dT_c/dP).

To date, to the best of the authors' knowledge, almost all tests of ε were conducted under atmospheric pressure, as a function of temperature [11–20]. Only recently were preliminary measurements carried out at elevated pressure [21]. The basic difference between pressure and temperature paths for approaching the critical consolute point is that pressure changes the density of the system whereas temperature influences the activation energy. In this paper we report pressure and temperature studies of the dielectric permittivity in a near-critical nitrobenzene–dodecane binary solution. These studies have been conducted isothermally at high pressures (up to 120 MPa) and as a function of temperature ($P = 0.1$ and 51 MPa). Moreover, NDE studies were also performed.

2. Experimental

Studies were performed applying a pressure system with a specially designed flat-parallel capacitor (gap $d = 0.6$ mm and $C_0 \approx 8.5$ pF) described in detail in our previous paper [22]. The capacitor was constructed in such a way that the liquid tested was only in contact with stainless steel, quartz, and Teflon. Temperature stabilisation was about 0.02 K/24 h. The temperature was measured by means of a platinum resistor placed in the jacket of the pressure chamber (A1 class, DIN 40260) with a resolution of ± 0.002 K and an accuracy of ± 0.1 , using a Keithley 195 A multimeter. Pressure was measured by a Nova Swiss tensometric pressure meter, with a resolution of ± 0.1 MPa and an accuracy of ± 0.2 MPa. Measurements of the electric capacitance were

carried using a SOLARTRON 1260A impedance analyser. Appropriate averaging made it possible to receive the same 5-digit resolution in the range of frequencies (100 Hz to 1 MHz) tested. The critical concentration of the nitrobenzene–dodecane solution examined was determined earlier [23], $x_c \approx 0.63$ of mole fraction of nitrobenzene, and the critical temperature, $T_c \approx 27.4^\circ\text{C}$, was determined from the measurement of dielectric permittivity ϵ as a function of temperature at atmospheric pressure. Pressure may cause a shift in the critical concentration Δx_c . However, it was shown earlier that in the solution tested this fact is negligible [21,23]. The $T_c(P)$ dependence in nitrobenzene–dodecane solution [22] (inset, Fig. 1) may be approximated by a polynomial in the following form: $T_c = 300.26 + 0.007 \times P + (9.721 \times 10^{-5}) \times P^2$ [24]. Components for preparing the solution were purchased from FLUKA. Nitrobenzene was distilled four times and dried over molecular sieves. The last distillation was conducted immediately prior to preparing the solution. Dodecane

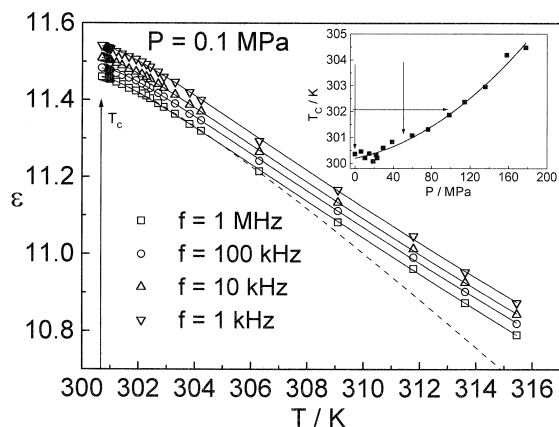


Fig. 1. Temperature dependence of dielectric permittivity in a near-critical nitrobenzene–dodecane solution under atmospheric pressure. Results are for: 1 kHz (∇), 10 kHz (Δ) (+0.025), 100 kHz (\circ) (+0.05), and 1 MHz (\square) (+0.07); ordinate displacements are in brackets. Solid lines are a guide for the eyes. The upper scale represents the pressure experimental scale transformed to a temperature scale: $\Delta T_p = dT_c/dP \times (P_c - P)$ to facilitate comparison with temperature studies under atmospheric pressure. The top-right inset shows the dependence of T_c on pressure P , and the arrows indicate the way of approaching the phase transition line. Dashed line represents the result of the fitting of the data near T_c without the correction-to-scaling terms which was then extrapolated on the whole data.

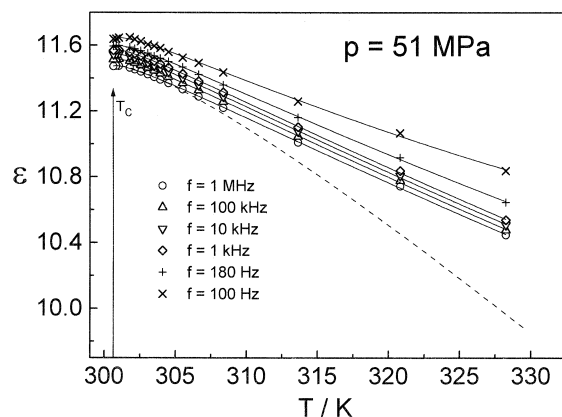


Fig. 2. Temperature dependence of dielectric permittivity in a near-critical nitrobenzene–dodecane solution under pressure of 51 MPa. Results are for: 100 Hz (\times), 180 Hz ($+$) (+0.03), 1 kHz (\diamond) (+0.06), 10 kHz (∇) (+0.09), 100 kHz (Δ) (+0.12), and 1 MHz (\circ) (+0.15); ordinate displacements in brackets. Solid lines are a guide for the eyes. Dashed line represents the result of the fitting of the data near T_c without the correction-to-scaling terms which was then extrapolated on all the data.

(FLUKA, HPLC class) was used without further purification.

The temperature measurements were conducted using a cylindrical capacitor similar to that given in Ref. [25]. Detailed description of the capacitor was given in our previous paper [16]. The sample inside the capacitor was only in contact with stainless steel and Teflon. The capacitor with a tested sample was placed in a continuously mixed silicone oil bath, in a thermostatted vessel. The temperature of the vessel was stabilised by a double-stage system of water-circulating thermostats. Temperature was measured by the same apparatus as in the pressure measurements. The dielectric permittivity was measured by means of an HP 4192A impedance analyser.

The NDE studies were conducted using an apparatus described in detail in Ref. [26]. There are two generators, a reference generator and one with the sample tested, connected in a differential system. Application of a strong electric field changes the difference of the frequency of generators. This shift, proportional to the change in capacitance ΔC of the sample, after detection, was recorded by means of a 12-bit digitizer with a computer system. The frequency of the measurement generator was 300 kHz

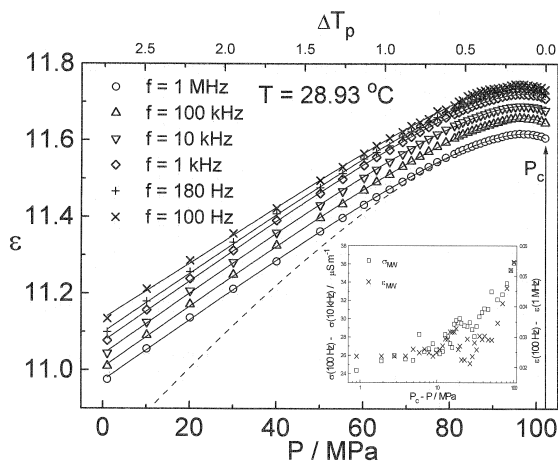


Fig. 3. Pressure dependence of dielectric permittivity in a near-critical nitrobenzene–dodecane solution for the isotherm remote from the critical temperature under atmospheric pressure by $\Delta T \approx 1.5$ K. Results are for: 100 Hz (x), 180 Hz (+) (+0.008), 1 kHz (\diamond) (+0.016), 10 kHz (∇) (+0.044), 100 kHz (Δ) (0.072), and 1 MHz (\circ) (0.107); ordinate displacements in brackets. The inset in the bottom-right corner shows the permittivity and conductivity increments versus reduced pressure. Solid lines are a guide for the eyes.

and the impulse length of the strong electric field ($U = 500$ – 1000 V DC) was 8 ms.

Data were analysed using ORIGIN 3.5 (Microcal) software.

3. Results and discussion

The inset in Fig. 1 shows the shift in temperature with a change in pressure in the solution tested. The arrows indicate applied paths of approaching the $T_c(P)$ line.

Isobaric temperature studies for $P = 0.1$ MPa (atmospheric pressure) (Fig. 1) and for $P = 51.2$

MPa (Fig. 2) were conducted. The anomaly obtained can be parametrized by means of relation (2). The results of fitting are collected in Tables 1 and 2. The dashed line shows the fit of the data near T_c ($T - T_c \approx 2$ K), also by means of relation (2) but without the correction-to-scaling term, and then the fit was extrapolated on all the data.

Under increasing pressure an isotherm, remote from critical temperature under atmospheric pressure by $\Delta T = 1.5$ K, was tested (Fig. 3). The isothermal pressure behaviour of ε can be portrayed by the pressure analogue of relation (2):

$$\varepsilon = \varepsilon_c + C^p \tilde{P} + C_1^p \tilde{P}^{1-\alpha} + C_2^p \tilde{P}^{1-\alpha+\Delta_1} + \dots$$

$$T = \text{const}, \quad (4)$$

where $\tilde{P} = P_c - P$ is the pressure distance from the phase transition point.

For all the fits (except for those obtained without the correction-to-scaling term, where at first the fits were calculated from a data subset near T_c and then extrapolated) all the data were used. For the first run T_c , P_c and ε_c were fixed to the values obtained from the experiment. During first run we also imposed $1 - \alpha = 0.88$ and $\Delta_1 = 0.5$. Next, all critical parameters (ε_c , T_c , P_c , $\phi = 1 - \alpha$), except Δ_1 , were set free. The correction exponent Δ_1 was always fixed at the theoretically predicted value of 0.50 [10]. Thus, all the parameters in Eqs. (2) and (4), except Δ_1 , were treated as adjustable. All fitted parameters, obtained by means of Eq. (4), are collected in Table 3.

It is noteworthy that the values of the critical amplitudes C_i^p are positive (Table 3), as it takes place in the temperature examinations (Tables 1 and 2), which means that, in both temperature and pressure studies, dielectric permittivity bends down in

Table 1

Fitted parameters ((relation (2)) of the temperature critical anomaly of dielectric permittivity in the nitrobenzene–dodecane binary solution under atmospheric pressure

Frequency	ε_c	T_c (K)	C (K ⁻¹)	C_1 (K ^{-(1-\alpha)})	C_2 (K ^{-(1-\alpha+\Delta_1)})	$\phi = 1 - \alpha$
1 MHz	$11.52_9 \pm 0.3$	300.63 ± 0.3	$-0.19_5 \pm 0.10$	$0.15_7 \pm 0.11$	$0.01_3 \pm 0.003$	$0.87_9 \pm 0.27$
100 kHz	$11.53_1 \pm 0.3$	300.60 ± 0.3	$-0.22_9 \pm 0.10$	$0.19_3 \pm 0.11$	$0.01_6 \pm 0.003$	$0.88_0 \pm 0.27$
10 kHz	$11.53_7 \pm 0.3$	300.60 ± 0.3	$-0.20_9 \pm 0.10$	$0.17_2 \pm 0.11$	$0.01_4 \pm 0.003$	$0.87_9 \pm 0.27$
1 kHz	$11.53_9 \pm 0.4$	300.60 ± 0.4	$-0.20_4 \pm 0.15$	$0.16_8 \pm 0.14$	$0.01_4 \pm 0.006$	$0.87_9 \pm 0.30$

Table 2

Fitted parameters ((relation (2)) of the temperature critical anomaly of dielectric permittivity in the nitrobenzene–dodecane binary solution under pressure of 51 MPa

Frequency	ε_c	$T_c(K)$	C (K^{-1})	C_1 ($K^{-(1-\alpha)}$)	C_2 ($K^{-(1-\alpha+\Delta_1)}$)	$\phi = 1 - \alpha$
1 MHz	$11.62_3 \pm 0.3$	300.60 ± 0.4	$-0.17_9 \pm 0.16$	$0.16_2 \pm 0.20$	$0.00_9 \pm 0.006$	$0.88_0 \pm 0.33$
100 kHz	$11.63_4 \pm 0.3$	300.60 ± 0.4	$-0.18_1 \pm 0.16$	$0.16_3 \pm 0.20$	$0.00_9 \pm 0.006$	$0.88_0 \pm 0.33$
10 kHz	$11.63_4 \pm 0.3$	300.60 ± 0.4	$-0.17_9 \pm 0.16$	$0.16_0 \pm 0.20$	$0.00_9 \pm 0.006$	$0.88_0 \pm 0.33$
1 kHz	$11.63_0 \pm 0.3$	300.60 ± 0.4	$-0.17_9 \pm 0.16$	$0.16_2 \pm 0.20$	$0.00_9 \pm 0.006$	$0.88_0 \pm 0.33$
180 Hz	$11.62_6 \pm 0.4$	300.59 ± 0.5	$-0.18_7 \pm 0.18$	$0.17_1 \pm 0.22$	$0.01_1 \pm 0.007$	$0.88_0 \pm 0.38$
100 Hz	$11.63_8 \pm 0.5$	300.59 ± 0.6	$-0.22_1 \pm 0.28$	$0.20_9 \pm 0.29$	$0.01_5 \pm 0.012$	$0.88_0 \pm 0.40$

the vicinity of the critical point. Please note that in the solution tested, (dT_c/dP) is always greater than zero.

To facilitate comparison of the anomaly of dielectric permittivity in isothermal pressure and isobaric temperature studies, the pressure scale has been transformed into a temperature scale (Fig. 3) by means of relation $\Delta T_p = dT_c/dP \times (P_c - P)$, where $\Delta T_p = T - T_c$. The same procedure was previously used in dielectric studies of linear and non-linear dielectric permittivity, applying the fluid-like analogy in the isotropic phase of nematogens [26].

The influence of the correction-to-scaling terms is significant in temperature studies under atmospheric pressure (dashed line, Fig. 1). It is also visible in pressure studies (dashed line, Fig. 3). It is noteworthy that in 1-nitropropane–hexadecane solution omitting experimental data in the immediate vicinity of the transition point ($P_c - P < 20$ MPa) does not influence significantly the values of fitted parameters and the correction-to-scaling terms which do not

appear in relation (2) enabled a reliable estimation of the critical exponent $\phi = 1 - \alpha$ [21].

In temperature studies conducted to date under atmospheric pressure [20], upon decreasing the measurement frequency, a strong influence of the low-frequency MW effect appeared. Hence, on approaching the critical point the registered effect bends up, in comparison to the almost linear behaviour remote from the critical point. $f = 100$ kHz to 10 MHz was the frequency where its influence was completely negligible, and relation (2) was valid [27,28].

In the solution tested the MW effect in $\varepsilon(T)$ studies is small and it is not possible to perform a qualitative analysis. Surprising is the lack of this effect for the pressure path, even for $f = 100$ Hz (inset, Fig. 3). In temperature studies under atmospheric pressure, to the best of the authors' knowledge, such low frequency cannot be portrayed by means of relation (2). For the solution tested, the fit via relation (4) gives almost the same results for $f = 100$ Hz to 1 MHz.

Table 3

Fitted parameters ((relation (4)) of the pressure critical anomaly of dielectric permittivity in the nitrobenzene–dodecane binary solution, for the isotherm $\Delta T \approx 1.5$ K

Frequency	ε_c	P_c (MPa)	C^P (MPa^{-1})	C_1^P ($MPa^{-(1-\alpha)}$)	C_2^P ($MPa^{-(1-\alpha+\Delta_1)}$)	$\phi = 1 - \alpha$
1 MHz	$11.67_7 \pm 0.10$	104.32 ± 0.3	$-0.06_3 \pm 0.03$	$0.08_4 \pm 0.03$	$0.001_7 \pm 0.015$	$0.87_6 \pm 0.06$
100 kHz	$11.68_6 \pm 0.10$	103.91 ± 0.3	$-0.06_2 \pm 0.03$	$0.08_3 \pm 0.03$	$0.001_6 \pm 0.015$	$0.87_9 \pm 0.06$
10 kHz	$11.68_7 \pm 0.10$	104.15 ± 0.3	$-0.06_4 \pm 0.03$	$0.08_6 \pm 0.03$	$0.001_7 \pm 0.015$	$0.87_0 \pm 0.06$
1 kHz	$11.68_8 \pm 0.10$	104.16 ± 0.3	$-0.06_6 \pm 0.03$	$0.08_8 \pm 0.03$	$0.001_7 \pm 0.015$	$0.87_8 \pm 0.06$
180 Hz	$11.69_9 \pm 0.15$	103.69 ± 0.3	$-0.06_5 \pm 0.03$	$0.08_5 \pm 0.04$	$0.001_8 \pm 0.015$	$0.87_8 \pm 0.09$
100 Hz	$11.69_3 \pm 0.15$	104.07 ± 0.3	$-0.07_4 \pm 0.04$	$0.09_7 \pm 0.04$	$0.002_2 \pm 0.015$	$0.87_8 \pm 0.19$

In the isobaric temperature studies, the quality of the fit does not depend significantly on the form of the reduced temperature in the fitting function. Thus, the reduced temperature can be in the following forms: $(T - T_c)/T_c$, $(T - T_c)/T$ or $T - T_c$. In the isothermal pressure studies, in order to obtain a fit of a good quality, $P_c - P$ or $(P_c - P)/P_c$ can be applied. If in the fitting function $(P_c - P)/P$ is used, the quality of the fit is very poor. Introduction of unitless reduced variables makes it possible to compare isothermal and isobaric data. Noteworthy is the difference in the range of change of mentioned distances from the critical point: $0 \leq (P_c - P)/P_c \leq \infty$ (for $P \leq P_c$), $0 \leq (T - T_c)/T_c < \infty$ (for $T \geq T_c$), and $0 \leq (P_c - P)/P < \infty$ (for $P \leq P_c$), $0 \leq (T - T_c)/T < 1$ (for $T \geq T_c$).

Fig. 4 made it possible to compare the anomaly of dielectric permittivity presented above with the anomaly of its non-linear changes in a strong steady electric field (NDE). It can be seen that the pretransitional effect is much stronger. Their form is characterised by two different critical exponents, as was mentioned in Refs. [8,9].

$$\psi_{\text{NDE}} = 0.39 \pm 0.01, \quad \text{for } T - T_c < 2 \text{ K},$$

$$\psi_{\text{NDE}} = 0.61 \pm 0.02, \quad \text{for } T - T_c > 1 \text{ K}.$$

In the analysis of NDE, the critical effect has to be extracted from the total measured effect by taking

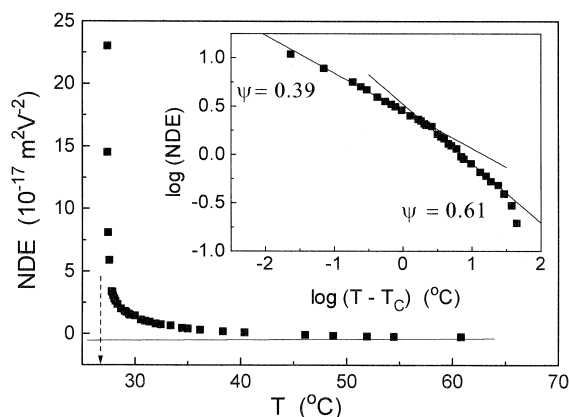


Fig. 4. The non-linear dielectric effect on approaching the critical consolute temperature. The solid line shows the non-critical background effect. The arrow denotes the critical temperature. The inset shows the critical effect of NDE versus the logarithm of temperature distance from the critical point for $f_m = 250$ kHz.

into account the non-critical background effect, marked as NDE_B . NDE_B was determined from measurements in a reference solution of unlimited miscibility nitrobenzene–benzene [7].

4. Conclusions

The results obtained show that, for the isothermal pressure path of approaching the critical consolute point, dielectric permittivity can be described by the relation analogue to that applied in temperature studies under atmospheric pressure (Eqs. (2) and (4)). The equivalence of the pressure and temperature paths of approaching the critical consolute point is known as the postulate of the isomorphism of critical phenomena and was experimentally verified for many thermodynamic properties [10]. The pretransitional anomaly of ϵ obtained in the isothermal pressure studies is stronger than the anomaly obtained in the isobaric temperature studies. This allowed for a reliable estimation of the critical exponents (Eq. (4)). However, it is important to note that two different critical points along the $T_c(P)$ line are compared (inset, Fig. 1). A difference in the strength of the pretransitional anomaly was also noted between the temperature isobaric studies at pressure of 51 MPa and at atmospheric pressure. It is possible that at the high pressure critical point the anomaly along a constant pressure line as a function of temperature could be larger than the anomaly obtained in the isothermal pressure studies.

The critical amplitudes C_1 obtained in the measurements at atmospheric pressure (Table 1) are smaller in value than those obtained in measurements at 51 MPa (Table 2). However, they are about 42 times smaller in value than those obtained in the pressure studies. For example, the critical amplitude in the pressure studies for the frequency of 1 MHz was found to be equal, after transformation, to about 6.616 whereas the critical amplitude in the temperature studies under atmospheric pressure was equal to 0.156. To compare the strength of the pretransitional anomalies, for pressure and temperature paths of approaching the critical point, the magnitude $\Delta\epsilon_{\text{avg}} = \epsilon_{\text{max}} - \epsilon_c$ can also be used (ϵ_{max} is the value of the dielectric constant extrapolated from the linear fit

of the data located away from T_c , ε_c is the critical dielectric constant): for the isotherm tested ($T = 28.93^\circ\text{C}$) $\Delta\varepsilon_{\text{avg}} = 0.15$, for temperature studies under atmospheric pressure $\Delta\varepsilon_{\text{avg}} = 0.02$, and for temperature tests ($P = 51.2 \text{ MPa}$) $\Delta\varepsilon_{\text{avg}} = 0.05$. Using this approach as a guide to the strength of the pretransitional anomaly, one can clearly see that the anomaly obtained in the isothermal high pressure studies is much stronger than that obtained in the isobaric temperature measurements.

Notable is that, in the pressure studies, the MW effect was found to be insignificant even for $f = 100 \text{ Hz}$ (inset, Fig. 3). This can be associated with a strong increase in viscosity of the tested liquid with pressure. It is noteworthy that, in the temperature tests under atmospheric pressure, the critical MW effect was also not too pronounced. In the analysis, the correction-to-scaling terms had a significant influence on the quality of the fit of the pressure measurements. Nevertheless, it is possible to obtain a good fit without the correction-to-scaling terms near T_c : $T - T_c \approx 2 \text{ K}$ and for the pressure path even far away from P_c : $P_c - P \approx 60 \text{ MPa}$.

This paper also presents results of $\varepsilon(T, P)$ and NDE(T) measurements which are described by different power laws. Noteworthy is the influence of relaxation processes of critical fluctuations on NDE(T) which does not appear in the dielectric permittivity measurements. This is related to the fact that NDE is sensitive to the relaxation of the critical fluctuations [7] and the dielectric measurements of ε are not [1].

In conclusion, it has been shown that the pressure path of approaching the critical consolute point reveals some new features not encountered in the temperature studies. The first feature is the strength of the pretransitional anomaly of ε which is stronger than in the temperature studies. The second feature is the absence of the MW effect in the pressure studies, even for a frequency of 100 Hz.

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