Critical anomaly of dielectric permittivity for the temperature and pressure paths on approaching the critical consolute point

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The experimental results of isothermal pressure dielectric permittivity ε studies in a critical mixture characterized by a negative shift of critical temperature induced by pressure ($dT_C/dP<0$) are presented. The critical effect is portrayed by the same relation as in previous $\varepsilon(T)$ and $\varepsilon(P)$ studies, with the critical exponent $\alpha=0.12\pm0.03$. The advantage of pressure studies is the negligible influence of the correction-to-scaling term and the low-frequency Maxwell-Wagner effect. This conclusion is supported by the distortion-sensitive derivative analysis of the experimental data. In contrast to previous $\varepsilon(P)$ studies, carried out in mixtures with $dT_C/dP>0$, the critical effect manifests by the *bending-up* behavior near the critical point. It is suggested that signs of the critical amplitudes of $\varepsilon(P)$ and $\varepsilon(T)$ anomalies may be related to the excess volume V^E and the excess enthalpy H^E, respectively.

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INTRODUCTION

In 1932, Piekara [1] studied the temperature behavior of dielectric permittivity ε in the homogeneous phase of a nitrobenzene-hexane critical mixture. On approaching the consolute temperature T_C he noted a small *bending down* of $\varepsilon(T)$ from the nearly linear behavior remote from T_C. It was not until 1979/1980 that the theoretical models describing this phenomenon, based on the modern theory of critical phenomena, were proposed [2,3],

$$\varepsilon(T)=\varepsilon_C+a_T\theta+A_T\theta^{1-\alpha}(1+b\,\theta^{0.5}), \tag{1}$$

where $\theta=T-T_C$ or $\theta=(T-T_C)/T_C$ describes the distance from T_C, $\alpha\approx0.115$ is the specific heat critical exponent, ε_C denotes the value of the dielectric permittivity at the critical point, a_T and A_T are constant coefficients: A_T is the critical amplitude. The bracket contains the correction-to-scaling term, important on moving away from T_C. Noteworthy is the agreement with the dependence proposed by Mistura in the early 1970s [4],

$$\frac{d\varepsilon}{dT}\propto C_p\propto\theta^{-\alpha}, \tag{2}$$

where C_p is the heat capacity.

However, the straightforward experimental verification of the latter was only possible [5,6]. In decades following the finding of Piekara the experimental situation was puzzling. On approaching T_C both the *bending-up* and *bending-down* behavior of the dielectric permittivity was observed [6–17]. In the late 1980s, Thoen *et al.* [18] showed that for lower frequencies the dielectric response of critical fluctuations is associated with the Maxwell-Wagner (MW) effect, which can dominate the *static* critical effect described by relation (1). It induces the additional, positive contribution described by [18],

$$\Delta\varepsilon_{\mathrm{MW}}=\varepsilon_{1\ \mathrm{kHz}}-\varepsilon_{1\ \mathrm{MHz}}\propto(T-T_C)^{\varpi}=(T-T_C)^{\beta-\nu}\approx(T-T_C)^{-0.3}, \tag{3}$$

where $\beta\approx0.325$ is the order parameter critical exponent and $\nu\approx0.625$ describes the critical behavior of the correlation length.

The existing experimental data give $\varpi=0.3$–0.4 [18–26].

In the following years a series of experiments in mixtures with the upper critical temperature showed that the static critical effect follows Piekara's bending-down critical behavior [16–27] portrayed by relation (1). To the best of the authors' knowledge only one mixture (triethylamine-water [20]) with a lower critical temperature was examined. It showed the *bending-up* critical effect of the static. The resulting opposite sign of the critical amplitude did not influence the value of the critical exponent $\phi=1-\alpha$. The lowest value of the frequency for the *static* critical effect [relation (1)] depends on the electric conductivity of the mixture [6,18,22,24]. In practice the validity of relation (1) was shown for frequencies spanning from 100 kHz to 10 MHz [6,18–27]. When discussing the *static* critical behavior of $\varepsilon(T)$ it is worth stressing the weakness of the critical anomaly. This is probably the main reason for the significant error of the fitted exponent $\phi=1-\alpha$. In the opinion of the authors it can be estimated as ±0.2 [6,25,26].

The model of Sengers and co-workers also suggested the dependence of the critical amplitude on thermodynamic properties of the critical mixture [3,21],

$$A_T\approx-C\left(\frac{2}{\varepsilon_0}\frac{dT_C}{dE^2}+\varepsilon_C\frac{dT_C}{dP}\right), \tag{4}$$

where dT_C/dE^2 and dT_C/dP are the electric-field- and pressure-induced shifts of critical temperature, C is a constant.

This relation put forward the question of the influence on the critical amplitude of the implicit (dT_C/dP) and the intristic (dT_C/dE^2) contributions [20]. It is probably the most successful attempt in showing the significance of both factors based on a comparison of $\varepsilon(T)$ behavior in a binary (methanol-cyclohexane) mixture and in a pseudobinary, isopycnic (methanol–cyclohexane–deuterated-cyclohexane) critical mixture [27]. It is noteworthy that there are only few experiments testing the dT_C/dE^2 dependence: in each case a small and negative value was obtained ([28–31] and references therein). The negative sign of dT_C/dE^2 coincides well with the *bending-down* behavior of ε $(A_T>0)$ mentioned above [19–21].

Recently, investigations of the anomaly of the dielectric permittivity were extended to the isothermal, pressure path of approaching the critical consolute point. The validity of dependencies isomorphic to relations (1) and (3) was shown [5,6,25,32],

$$\varepsilon(P)=\varepsilon_C+a_P|P_C-P|+A_P|P_C-P|^{1-\alpha}+\cdots,v$$

$$T=\text{const},\quad x=x_C, \tag{5}$$

$$\frac{d\varepsilon}{dP}\propto(P_C-P)^{-\alpha}, \tag{6}$$

where $P<P_C$ and A_p denotes the ''pressure'' critical amplitude.

The pressure critical anomaly of dielectric permittivity showed some unusual features. For instance, the correction-to-scaling term could be omitted even at large distances from P_C and the MW effect was absent even for frequencies as low as $f=100\,\text{Hz}$. Moreover, the pretransitional *bending down* was 30–60 times stronger than in $\varepsilon(T)$ studies. Owing to these features the estimation of the exponent $\phi=1-\alpha$ could be significantly simplified. The obtained value was $\phi=0.88\pm0.04$ [5,6,25,32].

The introduction of the pressure path to the studies recalls the question of the influence of the implicit contribution, related to dT_C/dP, to the critical amplitude [relation (4)]. Undoubtedly it is responsible for the mentioned differences in the behavior of $\varepsilon(T)$ and $\varepsilon(P)$. For the latter, tested mixtures were always characterized by the positive value of dT_C/dP (ranging from 0.07 to 0.11 K/MPa [5,6,25,32,33]) and the critical point was reached by increasing pressure, starting from the atmospheric pressure [22,31]. The small value of dT_C/dP caused the effective distance from the critical consolute point to be much smaller in pressure studies than in temperature tests. This factor is probably responsible for much greater ''strength'' of $\varepsilon(P)$ anomaly in comparison with the $\varepsilon(T)$ behavior. By comparing relations (1) and (5), the following relation may be deduced:

$$\left(\frac{A^P}{A_T}\right)^{1-\alpha}\approx\frac{dT_C}{dP} \tag{7}$$

in a reasonable agreement with experimental results [25].

The next question concerns the possible influence of the sign of dT_C/dP on the critical amplitude of the dielectric permittivity anomaly. Studies of $\varepsilon(T)$ were conducted at atmospheric pressure [1,6,12–27] and also at $P=50\,\text{MPa}$ [25]. They were conducted in mixtures with opposite signs of dT_C/dP, for instance, in nitrobenzene-hexane $(dT_C/dP\approx-0.16\,\text{K/MPa})$ and nitropropane-dodecane $(dT_C/dP\approx0.1\,\text{K/MPa})$ [6,25,26]. This fact does not influence the anomaly of $\varepsilon(T)$: for the upper critical point the *bending-down* behavior $(A_T>0)$ was always observed [14–26]. The same behavior was obtained in $\varepsilon(P)$ studies, however, all of them were carried out in mixtures with $dT_C/dP>0$ [5,6,25,32].

Results presented below show that some new conclusions about the critical amplitude may be obtained by analyzing existing $\varepsilon(T)$ and $\varepsilon(P)$ results and by recalling the empirical dependence [33–35]

$$\frac{dT_C}{dP}\approx T_C\frac{V_E}{H_E}. \tag{8}$$

In the opinion of the authors, the missing link between relation (8) and experimental results is the lack of $\varepsilon(P)$ studies in the mixture with $dT_C/dP<0$ [5,6,25,32]. Such studies, in the nitrobenzene-hexane critical mixture, are presented below.

EXPERIMENT

To obtain high-resolution dielectric permittivity data the ''Alpha'' Novocontrol GmbH spectrometer was used. The pressure setup, with the measurement capacitor, is described in Refs. [5,6,25,32]. The capacitor was made from Invar, $d=0.5\,\text{mm}$ and $2r=16\,\text{mm}$. Its design is given in Ref. [33]. Pressure was transmitted to the tested mixture from pressurized liquid (silicone oil) by deformation of 50-μm Teflon film. Temperature was measured by a copper-constantan thermocouple placed inside the chamber with precision ±0.02 K. Pressure was measured using a Novocontrol tensometric pressure meter with accuracy ±0.1 MPa. The pressure chamber was surrounded by a special jacket fed from the Julabo HD 45S thermostat. Tested compounds were purchased from Fluka; hexane (HPLC grade) was used without purification and nitrobenzene was distilled three times, the last one immediately prior to measurements. Data were analyzed using ORIGIN 6.1 software. All errors are given as three standard deviations.

RESULTS AND DISCUSSION

The applied pressure path of the studies is shown in the inset of Fig. 1. The sample was placed in the pressure chamber heated well above $T_C(0.1\,\text{MPa})$. The pressure was increased up to $P\approx100\,\text{MPa}$. Next, the chamber was cooled down to $T=15.4\,^\circ\text{C}$ and the measurements of dielectric permittivity for gradually decreasing pressure were conducted. Results obtained are shown in the main part of Fig. 1 and collected in Table I. Remote from P_C, the value of the dielectric permittivity also decreases with decreasing pressure $(a_p>0)$. Near P_C the opposite tendency appears $(A_p<0)$: the critical *bending up* occurs. Hence, the behavior of $\varepsilon(P)$

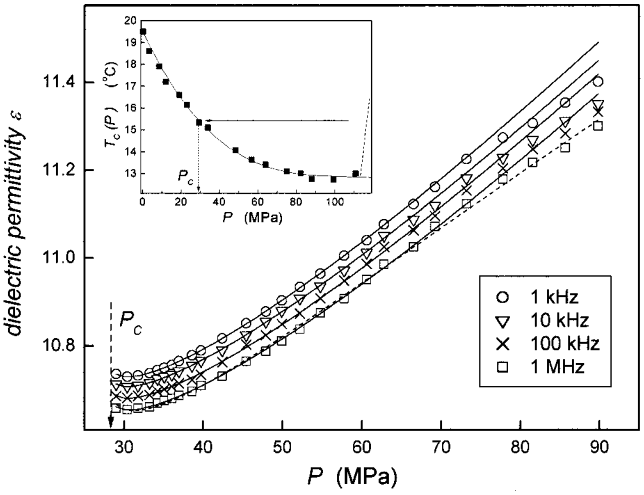

FIG. 1. Results of dielectric permittivity measurements in a nitrobenzene-hexane critical mixture for the pressure path of approaching the critical consolute point. Results presented are for following frequencies: 1 kHz (+0.03), 10 kHz, 100 kHz (−0.03), and 1 MHz (−0.06). Solid lines are parametrized by relation (5). For $f = 1$ MHz data are also fitted by relation (5) with the correction-to-scaling term (dashed line). The inset shows the dependence in the tested mixture and the applied path of studies (solid arrow). The dotted vertical arrow shows the value of P_C. The dashed line shows the crystallization of nitrobenzene. Pressure shift of T_C portrays the equation $T_C() = 19.5 - 0.18P + 0.0017P^2 - 6\times10^{-6}P^3$, T (°C), and P (MPa). The curve is plotted based on improved data of Ref. [33].

TABLE I. Experimental results of isothermal pressure measurements of dielectric permittivity in nitrobenzene-hexane mixture of critical concentration.

P (MPa)	1 kHz	10 kHz	100 kHz	1 MHz
29.0	10.7067	10.7135	10.7066	10.7009
30.4	10.7005	10.7079	10.7019	10.707
31.8	10.703	10.710	10.7064	10.7096
33.20	10.708	10.7164	10.709	10.7123
34.20	10.7155	10.7258	10.7175	10.7206
35.05	10.7203	10.7311	10.7224	10.7269
36.0	10.7274	10.7355	10.7286	10.7314
36.9	10.7361	10.7429	10.7351	10.7386
38.55	10.7492	10.7557	10.7434	10.748
39.7	10.7604	10.7666	10.7547	10.7612
42.4	10.7894	10.7906	10.7839	10.7823
45.4	10.8222	10.8255	10.8236	10.8206
47.9	10.8488	10.8555	10.8453	10.8434
49.9	10.8738	10.8806	10.8705	10.8666
52.2	10.9044	10.9088	10.8946	10.8933
54.75	10.9352	10.9362	10.9288	10.9311
57.75	10.9752	10.9723	10.9688	10.9632
60.6	11.0111	11.0128	11.0076	11.0064
62.8	11.9472	11.0511	11.0461	11.0387
66.5	11.093	11.0882	11.0834	11.977
69.2	11.1222	11.1198	11.1162	11.1229
73.21	11.1956	11.1825	11.1744	11.1748
77.81	11.2444	11.2283	11.2248	11.2309
81.55	11.2775	11.2694	11.2688	11.2691
85.65	11.3238	11.3125	11.3044	11.3023
89.8	11.3719	11.352	11.3531	11.352

in critical mixtures with positive and negative dT_C/dP coefficients differs. This factor seemed to be absent in $\varepsilon(T)$ studies. Quantitatively, the obtained $\varepsilon(P)$ dependencies are well parametrized by Eq. (5) and show all specific features of the pressure critical effect mentioned above. Results of fitting are given in Table II and shown graphically as solid lines in Fig. 2.

Figure 2 presents results of the derivative analysis of the experimental data. The validity of the pressure version of Mistura's relation (6) is clearly visible. The distortion-sensitive derivative analysis shows also the negligible influence of the correction-to-scaling terms up to $P \approx 70$ MPa and the practical lack of MW critical effect in the tested range of frequencies.

Recalling relation (8), results for dT_C/dP, V^E, and H^E in nitrobenzene–*n*-alkanes critical mixtures [33], and results for critical amplitudes of dielectric permittivity, the following conclusions may be drawn.

(1) In $\varepsilon(T)$ tests in mixtures with an upper critical point, where $H^E|_{x=x_C} > 0$ [35], the *bending-down* ($A_T > 0$) behavior was always obtained [6,18–26,33].

(2) In $\varepsilon(T)$ tests in the mixture with a lower critical point, where $H^E|_{x=x_C} < 0$ [35], the *bending-up* ($A_T < 0$) behavior was noted [27,33].

(3) In $\varepsilon(P)$ tests in mixtures with an upper critical point, where $H^E|_{x=x_C} > 0$ [35], the *bending-down* ($A_T > 0$) behavior occurs if $V^E|_{x=x_C} > 0$ [5,6,25,32,33].

(4) In $\varepsilon(P)$ tests in mixtures with an upper critical point, where $H^E|_{x=x_C} > 0$ [35], the *bending-down* ($A_T < 0$) behavior occurs if $V^E|_{x=x_C} < 0$ (this paper and [33]).

These facts suggest that the dependence of the critical amplitude on the coefficient dT_C/dP [relation (4)] should be decoupled: $A^T(H^E)$ (temperature studies) and $A^P(V^E)$ (pressure studies). This property reflects the well-known differ-

TABLE II. Results of fitting of data from Fig. 1 using relation (5). Graphically they are shown as solid lines in Fig. 2. The fit in the whole range of pressures with the correction-to-scaling term significantly influences the values of a_P and A_P amplitudes: $\varepsilon = 10.676 + 0.0098(P^* - P) - 0.113(P^* - P)^{0.88}[1 - 0.03(P^* - P)^{0.5}]$.

f (kHz)	ε_C (±0.07)	$a_P(\mathrm{MPa})^{-1}$ (±0.006)	$A_P(\mathrm{MPA})^{-\phi}$ (±0.002)	ϕ (±0.05)	P_C(MPa) (±0.3)
1 kHz	10.741	0.044	−0.0543	0.881	28.85
10 kHz	10.739	0.0459	−0.0545	0.871	28.9
100 kHz	10.738	0.045	−0.054	0.882	28.89
1 MHz	10.738	0.05	−0.53	0.88	28.9

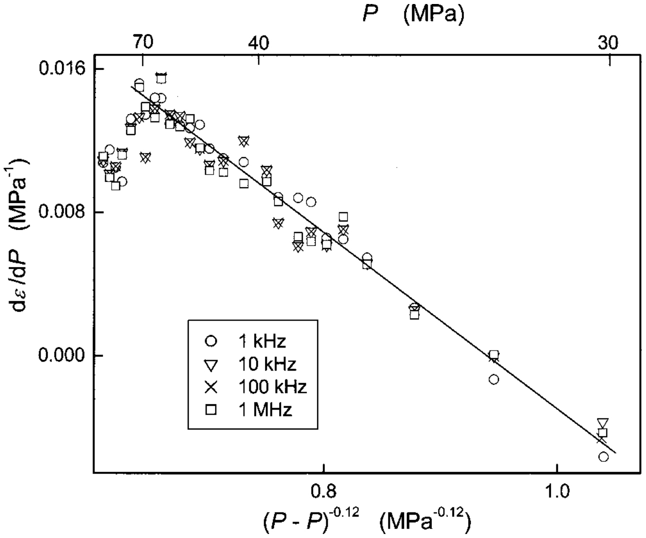

FIG. 2. Results of derivative analysis of dielectric permittivity critical effects in nitrobenzene-hexane ($dT_C/dP \approx -0.17\,\mathrm{K\,MPa}^{-1}$) critical mixture. The scale is transformed in a way to show clearly the value of the critical exponent $\alpha \approx 0.12$. The shown linear behavior for a few measurement frequencies and in a broad range of pressures shows the negligible influence of correction-to-scaling and the low-frequency MW effect.

ence between temperature and pressure studies. The former is mainly due to change of the activation energy, whereas the latter may be related to a shift in the free volume. It is worth stressing again that the universal features of the temperature and pressure critical anomalies, postulated by relation (4), remain the same. They yield the same values for the universal critical exponents $\phi = 1 - \alpha \approx 0.88$ and $\alpha \approx 0.12$. This result shows the validity of the postulate of the isomorphism of the critical phenomena for dielectric permittivity behavior in critical mixtures.

In the opinion of the authors, some basic questions still remain unanswered when discussing the anomaly of dielectric anomaly in critical mixtures. One of them is the influence of the factor dT_C/dE^2 on the critical anomaly. It is particularly puzzling that the semimicroscopic theoretical analysis yields $dT_C/dE^2 > 0$ [31], whereas experimental values always gave $dT_C/dE^2 < 0$ [30,31] and reference therein). Another problem is the relationship between the anomaly of dielectric permittivity and molecular properties of the mixture. Such a relationship is easily visible in the isotropic phase of nematogens, where relations (1) and (7) are also valid due to the supporting of the *fluidlike* and *critical* description proposed recently [36,37]. It locates the nematic clearing point on a branch of a hypothetical binodal curve. In this respect, a less empirical explanation of different dT_C/dP signs [33,38,39] appearing in critical mixtures may be of particular significance [38,39]. Another preliminary tested question concerns the behavior associated with the imaginary part of dielectric permittivity, i.e., the conductivity [40] and the dielectric relaxation time [41].

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