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

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(Received 7 December 2000; revised manuscript received 6 June 2001; published 20 November 2001)

The experimental results of isothermal pressure dielectric permittivity \( \varepsilon \) 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 \( \alpha = 0.12 \pm 0.03 \). 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.

DOI: 10.1103/PhysRevE.64.061104

PACS number(s): 64.70.Ja, 77.22.Ch

\[ \Delta \varepsilon_{MW} = \varepsilon_{1 \text{ kHz}} - \varepsilon_{1 \text{ MHz}} \cdot (T - T_c)^{\alpha} = (T - T_c)^{\beta - r \approx (T - T_c)^{-0.3}}, \]

where \( \beta \approx 0.325 \) is the order parameter critical exponent and \( r \approx 0.625 \) describes the critical behavior of the correlation length.

The existing experimental data give \( \alpha = 0.3-0.4 \) [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 \( \pm 0.2 \) [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].

\[ A_T \approx -C \left( \frac{2}{\varepsilon_0} \frac{dT_c}{dE^2} + \varepsilon C \frac{dT_c}{dP} \right), \]

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

INTRODUCTION

In 1932, Piekara [1] studied the temperature behavior of dielectric permittivity \( \varepsilon \) 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].

\[ \varepsilon(T) = \varepsilon_c + a \theta + A \theta^{1-a} (1 + b \theta^{0.5}), \]

where \( \theta = T - T_c \) or \( \theta = (T - T_c)/T_c \) describes the distance from \( T_c \), \( a \approx 0.115 \) is the specific heat critical exponent, \( \varepsilon \) denotes the value of the dielectric permittivity at the critical point, \( a \) and \( A \) are constant coefficients: \( A \) 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],

\[ \frac{d\varepsilon}{dT} \approx C_p \varepsilon^{-\alpha}, \]

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].
This relation put forward the question of the influence on the critical amplitude of the implicit \((dT_C/dP)\) and the intrinsic \((dT_C/dE^2)\) 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 \(\varepsilon\) \((A_T>0)\) 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],

\[
\varepsilon(P) = \varepsilon_C + A_P[P - P_C] + A_P[P - P_C]^{1 - \alpha} + \cdots, \quad T = \text{const}, \quad x = x_C, \quad (5)
\]

\[
\frac{d\varepsilon}{dP} \propto (P - P_C)^{-\alpha}, \quad (6)
\]

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 \(\phi = 0.88 \pm 0.04\) [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:

\[
\left(\frac{A_P}{A_T}\right)^{1 - \alpha} \approx \frac{dT_C}{dP} \quad (7)
\]

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 \((dT_C/dP = -0.16 \, \text{K/MPa})\) and nitropropane-dodecane \((dT_C/dP = 0.1 \, \text{K/MPa})\) [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]

\[
\frac{dT_C}{dP} \approx T_C \frac{V_E}{H_E}. \quad (8)
\]

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 spectrometer is equipped with 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-\(\mu\)m Teflon film. Temperature was measured by a copper-constantan thermocouple placed inside the chamber with precision \(\pm 0.02 \, \text{K}\). Pressure was measured using a Novocontrol tensiometric pressure meter with accuracy \(\pm 0.1 \, \text{MPa}\). 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 \(P = 100 \, \text{MPa}\). Next, the chamber was cooled down to \(T = 15.4 \, \text{°C}\) 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 \(\varepsilon(P)\)
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: \(A^E(H^E)\) (temperature studies) and \(A^E(V^E)\) (pressure studies). This property reflects the well-known differ-

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

<table>
<thead>
<tr>
<th>(P) (MPa)</th>
<th>1 kHz</th>
<th>10 kHz</th>
<th>100 kHz</th>
<th>1 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.0</td>
<td>10.7067</td>
<td>10.7135</td>
<td>10.7066</td>
<td>10.7009</td>
</tr>
<tr>
<td>30.4</td>
<td>10.7005</td>
<td>10.7079</td>
<td>10.7019</td>
<td>10.707</td>
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<td>31.8</td>
<td>10.703</td>
<td>10.710</td>
<td>10.7064</td>
<td>10.7096</td>
</tr>
<tr>
<td>33.20</td>
<td>10.708</td>
<td>10.7164</td>
<td>10.709</td>
<td>10.7123</td>
</tr>
<tr>
<td>34.20</td>
<td>10.7155</td>
<td>10.7258</td>
<td>10.7175</td>
<td>10.7206</td>
</tr>
<tr>
<td>35.05</td>
<td>10.7203</td>
<td>10.7311</td>
<td>10.7224</td>
<td>10.7269</td>
</tr>
<tr>
<td>36.0</td>
<td>10.7274</td>
<td>10.7355</td>
<td>10.7286</td>
<td>10.7314</td>
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<tr>
<td>36.9</td>
<td>10.7361</td>
<td>10.7429</td>
<td>10.7351</td>
<td>10.7386</td>
</tr>
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<td>38.55</td>
<td>10.7492</td>
<td>10.7557</td>
<td>10.7434</td>
<td>10.7478</td>
</tr>
<tr>
<td>39.7</td>
<td>10.7604</td>
<td>10.7666</td>
<td>10.7547</td>
<td>10.7612</td>
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<tr>
<td>42.4</td>
<td>10.7894</td>
<td>10.7906</td>
<td>10.7839</td>
<td>10.7823</td>
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<tr>
<td>45.4</td>
<td>10.8222</td>
<td>10.8255</td>
<td>10.8236</td>
<td>10.8206</td>
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<tr>
<td>47.9</td>
<td>10.8488</td>
<td>10.8555</td>
<td>10.8453</td>
<td>10.8434</td>
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<tr>
<td>49.9</td>
<td>10.8738</td>
<td>10.8806</td>
<td>10.8705</td>
<td>10.8666</td>
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<td>52.2</td>
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<td>54.75</td>
<td>10.9352</td>
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<td>10.9288</td>
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<td>57.75</td>
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<td>60.6</td>
<td>11.0111</td>
<td>11.0128</td>
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<tr>
<td>62.8</td>
<td>11.0943</td>
<td>11.0511</td>
<td>11.0461</td>
<td>11.0387</td>
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<td>66.5</td>
<td>11.093</td>
<td>11.0882</td>
<td>11.0834</td>
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<td>69.2</td>
<td>11.1222</td>
<td>11.1198</td>
<td>11.1162</td>
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<td>73.21</td>
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<td>77.81</td>
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<td>11.2283</td>
<td>11.2248</td>
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</tr>
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<td>81.55</td>
<td>11.2775</td>
<td>11.2694</td>
<td>11.2689</td>
<td>11.2691</td>
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<tr>
<td>85.65</td>
<td>11.3238</td>
<td>11.3125</td>
<td>11.3044</td>
<td>11.3023</td>
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<tr>
<td>89.8</td>
<td>11.3719</td>
<td>11.352</td>
<td>11.3531</td>
<td>11.352</td>
</tr>
</tbody>
</table>

### Table II. Results of fitting of data from Fig. 1 using relation (5) for various frequencies.

<table>
<thead>
<tr>
<th>(f) (kHz)</th>
<th>(\varepsilon_C)</th>
<th>(a_P) (MPa)</th>
<th>(A_P) (MPa)</th>
<th>(\phi)</th>
<th>(P_C) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 kHz</td>
<td>10.741 ± 0.007</td>
<td>0.044 ± 0.006</td>
<td>−0.0543 ± 0.002</td>
<td>0.881</td>
<td>28.85</td>
</tr>
<tr>
<td>10 kHz</td>
<td>10.739 ± 0.005</td>
<td>0.0459 ± 0.002</td>
<td>−0.0545 ± 0.005</td>
<td>0.871</td>
<td>28.9</td>
</tr>
<tr>
<td>100 kHz</td>
<td>10.738 ± 0.005</td>
<td>0.045 ± 0.005</td>
<td>−0.054 ± 0.005</td>
<td>0.882</td>
<td>28.89</td>
</tr>
<tr>
<td>1 MHz</td>
<td>10.738 ± 0.005</td>
<td>0.05 ± 0.005</td>
<td>−0.53 ± 0.005</td>
<td>0.88</td>
<td>28.9</td>
</tr>
</tbody>
</table>
stressing again that the universal features of the temperature latter may be related to a shift in the free volume. It is worth is mainly due to change of the activation energy, whereas the 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 univer-
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 criti-
cal 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 differ-
ent $dT C/dP$ signs [33,38,39] appearing in critical mixtures may be of particular significance [38,39]. Another prelimi-
nary tested question concerns the behavior associated with the imaginary part of dielectric permittivity, i.e., the conduc-
tivity [40] and the dielectric relaxation time [41].

FIG. 2. Results of derivative analysis of dielectric permittivity critical effects in nitrobenzene-hexane ($dT C/dP \approx -0.17 \text{K MPA}^{-1}$) 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.

ACKNOWLEDGMENT

The authors wish to thank the Polish Committee for Scientific Research for support through Grant No. 2PO3B 020 15.
