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The super- and sub-critical effects for dielectric constant in diethyl ether

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Results of dielectric constant (ε) studies in diethyl ether for the surrounding of the gas–liquid critical point, $T_C - 130 \text{ K} < T < T_C + 50 \text{ K}$, are presented. The analysis recalls the physics of critical phenomena for portraying $\varepsilon(T)$ evolution along branches of the coexistence curve, along its diameter ($d(T)$) and in the supercritical domain for $T > T_C$. For the ultrasound sonicated system, the split into coexisting phases disappeared and dielectric constant approximately followed the pattern of the diameter. This may indicate the possibility of the extension of the “supercritical technology” into the ultrasound “homogenized” subcritical domain: the “strength” and the range of the precritical effect of $d(T)$ are ca. $10\times$ larger than for $\varepsilon(T > T_C)$. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4953616>]

INTRODUCTION

The gas–liquid critical point has attracted researchers since the 19th century.¹ However, the nature of observed behavior was explained only due to the physics of critical phenomena, few decades ago.^{2,3} The power-type pretransitional behavior of various physical properties, similar in qualitatively different systems, was linked to the appearance of critical fluctuations whose size (correlation length $\xi(T)$) and life time ($\tau(T)$) increase infinitely on approaching the critical temperature T_C :³

$$\xi(T) = \xi_0(T - T_C)^{-\nu} + \dots, \quad \tau(T) = \tau_0(T - T_C)^{-z\nu} + \dots, \quad (1)$$

where ν and $z\nu$ are critical exponents and z is the dynamic exponent; ξ_0 and τ_0 are for critical amplitudes.

All these lead to the “critical” behavior of such basic physical properties as the specific heat (c), compressibility (susceptibility χ), or the order parameter (M),³

$$\begin{aligned} c(T) &= A_0|T - T_C|^{-\alpha} + \dots, \\ \chi(T) &= \chi_0|T - T_C|^{-\gamma} + \dots, \\ M(T) &= B_0|T - T_C|^\beta + \dots. \end{aligned} \quad (2)$$

The physics of critical phenomena showed that values of critical exponents and ratios of critical amplitudes depend solely on the dimension of the order parameter (n) and the space dimensionality (d). Consequently, all near-critical systems can be assembled into universality classes (d, n).³ The surrounding of the gas–liquid critical point belongs to ($d = 3, n = 1$) universality class, together with the basic paramagnetic–ferromagnetic transition, 3-dimensional Ising model, and the critical consolute point in binary mixtures of limited miscibility. For this universality class critical exponents $\alpha \approx 0.115$, $\chi \approx 1.23$, $\beta \approx 0.625$, and $\nu \approx 0.63$.³ Notwithstanding, the case of the gas–liquid critical point remains unique. First, recent studies showed that in the supercritical domain, above the critical temperature, there

are still unexpected fundamental phenomena.^{4–8} Second, the pretransitional behavior of some basic physical properties, such as dielectric constant, remains surprisingly weakly experimentally evidenced. Third, there is a great interest in supercritical fluid technologies associated with precritical phenomena for the supercritical region $T > T_C$, $P > P_C$, particularly regarding the possibility of highly tuned and selective solubility and extraction. In fact, this technology is considered as one of the most promising “green technology” for 21st century industries.^{9–12} However, for practical implementations the knowledge of the evolution of dielectric constant (ε) is essential due to the postulated direct link to the solubility: $s \propto \exp(A/\varepsilon)$.⁹

The description of the pretransitional anomaly of dielectric constant on approaching the gas–liquid critical point and the critical consolute point was first predicted, using a heuristic reasoning, by Mistura¹³ who indicated the possible link to the specific heat critical behavior: $\varepsilon(T)/dT \propto c_p(T) \propto (T - T_C)^{-\alpha}$. The precise formula was derived by Goulon, Greffe, and Oxtoby,¹⁴ using the droplet model, Sengers *et al.*¹⁵ and Losada-Perez *et al.*¹⁶ using thermodynamics and critical phenomena physics,

$$\begin{aligned} \varepsilon(T) &= \varepsilon_C + A_C(T - T_C)^{1-\alpha} + A_{corr.}(T - T_C)^{1-\alpha+\Delta} \\ &+ a(T - T_C) \dots, \quad T > T_C, \end{aligned} \quad (3)$$

where the second term is for the first correction-to-scaling, significantly remote from the critical point. The first correction-to-scaling exponent $\Delta_1 \approx 0.5$.

For $T < T_C$ the system splits into coexisting gas- and liquid-phases. For their description one can consider the evolution of the order parameter ($M(T)$) and the diameter of the coexistence curve ($d(T)$),¹⁷

$$\begin{aligned} d(T) &= \frac{\varepsilon_L + \varepsilon_U}{2} = \varepsilon_C^d + B_d(T_C - T)^{2\beta} + A_d(T_C - T)^{1-\alpha} \\ &+ C_d(T_C - T), \end{aligned} \quad (4)$$

$$M(T) = \varepsilon_U(T) - \varepsilon_L(T) = B_\varepsilon(T_C - T)^\beta + \dots, \quad (5)$$

where $\varepsilon_U(T) = \varepsilon_{gas}$ and $\varepsilon_L(T) = \varepsilon_{liquid}$ are for the upper (gas) and lower (liquid) coexisting phases and $d(T)$ denotes the diameter of the coexistence curve (binodal).

Regarding critical amplitudes in the above relations,¹⁷ $A_C \propto A_o(d\mu_C/dE^2)$, $B_\varepsilon \propto -B_0(d\mu_C/dE^2)$, $B_d \propto -A^{(-)}B_0^2(d\mu_C/dE^2)$, $A_d \propto [dT_C/dE^2 + b(d\mu_C/dE^2)] \times [A^{(-)}/(1 - \alpha)]$, where μ_C is the critical part of the chemical potential and E is for the intensity of the electric field. These relations are for the isochoric approaching the gas–liquid critical point (the change of density $\Delta\rho = 0$).¹⁷ For binary mixtures of limited miscibility with the critical consolute point, the pressure (P) evolution of the critical consolute temperature (T_C) via the coefficient dT_C/dP has to be taken into account.^{16,17}

The first clear experimental validation of Eq. (3) for the gas–liquid critical point was obtained in supercritical CO¹⁹ and SF₆.²⁰ In 1989 Thoen *et al.*²¹ reported results of studies in the homogeneous phase of nitroethane–isooctane critical solution of limited miscibility showing the significance of the low frequency Maxwell-Wegner (MW) effect. For lower frequencies, in practice $f < 100$ kHz, the MW effect can completely mask the basic critical contribution described via Eq. (3). In subsequent decades studies of $\varepsilon(T)$ focused mainly on the homogeneous phase of binary mixtures of limited miscibility. This can be linked to the fact that they can be conducted under atmospheric pressure and for near-room temperatures.^{16,21–33} Relations analogous to Eqs. (3)–(5) can be also expected for the isothermal, pressure path of approaching the critical point.^{31–33} This was first shown for nitrobenzene–hexane critical mixtures ($dT_C/dP > 0$)³¹ and subsequently for the homologous series of mixtures where $dT_C/dP > 0$ and $dT_C/dP < 0$.³² The latter revealed the link between the critical amplitude and excesses of volume and enthalpy. Studies of dielectric constant and electric conductivity in the two-phase region focusing both on $M(T, P)$ and $d(T, P)$ behavior were carried out for the nitrobenzene–heptane critical mixture.³³ These studies also showed notably larger pretransitional amplitudes of $d(T)$ than ones noted in density or refractive index studies. It is worth stressing that for the pressure path of approaching the critical consolute point the impact of the MW effect appeared to be negligible even for as low frequencies as $f < 100$ Hz.

Nowadays, there is broad experimental evidence regarding dielectric constant behavior in the surrounding of the critical consolute point in binary mixtures of limited miscibility but it remains very limited for the gas–liquid critical point. This constitutes a considerable problem for the fundamental insight, which constitutes the *sine non qua* condition for the development of supercritical fluid technologies.^{5–12}

This report presents results of isochoric studies of dielectric constant in diethyl ether in the supercritical and subcritical regions for $T_C - 130$ K $< T < T_C + 50$ K. When applying the ultrasound sonication, the split into coexisting phases virtually disappeared and dielectric constant followed the pattern for the diameter.

EXPERIMENTAL

The high pressure chamber (inner diameter 40 mm, length 80 mm) was placed within $V = 20$ l thermostat bath (filled

with a special mixture of oils), whose temperature could be changed and controlled. The special design of fit-through made it possible to carry out dielectric measurements *in situ* within the pressure chamber. Two flat-parallel capacitors, made from Invar and gold coated, were located within the chamber: diameter $2r = 30$ mm and the distance between plates $d = 1$ mm. Capacitors were spaced by ca. 3 cm. The chamber was oriented vertically. The free volume within the chamber (V) with capacitors was precisely estimated prior to the experiment. Subsequently, the chamber was filled in with diethyl ether to such a proportion that $V_{dee} = V(T = T_C)$. During experiment isochoric simultaneous changes of pressure (P) and temperature (T) on heating took place. Below (T_C, P_C) capacitors were in the liquid and gaseous phase, respectively. Above (T_C, P_C) both capacitors were in the same supercritical domain. Measurements of dielectric constant were carried out using Solartron 1260 impedance analyzer, enabling a permanent 5 digit resolution, for $f = 100$ kHz measurement frequency and voltage $U = 1$ V. Within the limit of the experimental error only negligible changes of dielectric constant for shifting frequencies between 1 kHz and 10 MHz were detected. The sonication was carried out by placing the chamber in the ultrasound cleaner, with $f = 50$ kHz ultrasound frequency.

Temperature was monitored via three constantan–copper thermocouples, giving ± 0.03 K resolution. One of them was located within the pressure chamber. Other thermocouples were placed on the outer wall of the pressure chamber, at positions reflecting locations of measuring capacitors. The difference between indications of thermocouples, depending on the range of temperatures, was not greater than ± 0.1 K. This value was also assumed as the accuracy of temperature determining in the given experiment. The sonication was carried out by locating the chamber (external diameter 80 mm) in the center of Elmasonic ultrasound cleaner, with $30 \times 25 \times 30$ cm dimensions of the tank.

The strong precritical increase of compressibility (Eq. (2)), in the presence of gravity, causes that in the immediate vicinity of the gas–liquid critical point some gradient of density is evidenced.^{34–36} This can induce the convection of heat and mass, disturbing results. In the opinion of the authors, this effect may be present in the given experiment since starting from $T - T_C < 3$ K some prevalence of values detected by the lower capacitor in the pressure chamber was detected: it reached $\Delta\varepsilon \approx 0.003$ at $T - T_C \approx 0.2$ K. However, the character of this shift was not regular enough for an analysis. In the given report the average of dielectric constant for both capacitors was taken into account. Notwithstanding, the analysis based on the average or on values separately detected for the upper or lower capacitor yielded approximately the same fitting results for the pretransitional anomaly. The authors cannot also exclude some fluxes within the pressure chamber associated with the gradients mentioned above. When discussing these issues we would like to stress that the given experiment was not focused on “gravity effects” near the gas–liquid critical point which requires extreme temperature stability ($\Delta T < 0.01$ K) and focused experiment design. The target of the reported studies was the lacking “critical” in the broad surrounding of the gas–liquid critical point. The

selection of diethyl ether for studies facilitated the dielectric insight.

Diethyl ether (DEE, HPLC class) was purchased from Fluka. Reference coordinates of the critical point in DEE: 467 K (194 °C) \pm 1, 3.60 MPa.³⁷ It is notable that the molecule of DEE ((C₂H₅)₂O) has a permanent dipole moment $\mu \approx 1.15D$, which led to the relatively large dielectric constant at room temperature, $\varepsilon \approx 4.5$.³⁸ DEE is encountered as a model liquid in molecular and dielectric physics, since the liquid DEE can be analyzed by simple models with non-interacting permanent dipole moments.³⁸ DEE is also considered as the perspective material for supercritical fluid technologies.³⁷

RESULTS AND DISCUSSION

Results of measurements of dielectric constant for the selected near-critical isochore in diethyl ether are presented in Fig. 1. They were carried out using two capacitors, initially located in the liquid and the gas phase, respectively. When heating, the parallel change of pressure and temperature occurred and finally both capacitors were in the hypothetically homogeneous, supercritical region for $P > P_C$ and $T > T_C$. Measurements were carried out up to ca. $T_C + 50$ K in the supercritical domain and down to $T_C - 130$ K in the subcritical one. Changes of pressure (P) induced by heating can be estimated by the Antoine equation,³⁹ $\log_{10} P = A + B/(T + C)$, with $A = 44.6988$, $B = 13549.13$, and $C = -55.37$ for P in MPa. In the supercritical domain, for $T \rightarrow T_C$, an “anomalous” increase above the almost-linear ($\varepsilon_{linear}(T)$) evolution remote from the critical temperature is visible. The evolution of dielectric constant, including the critical effect, can be well portrayed by Eq. (3) with the following parameters: $\varepsilon_C = 1.495 \pm 0.01$, $A_C = -0.155 \pm 0.01$, $A_{corr.} = -0.0062 \pm 0.0007$, $a = 0.0118 \pm 0.01$, T_C

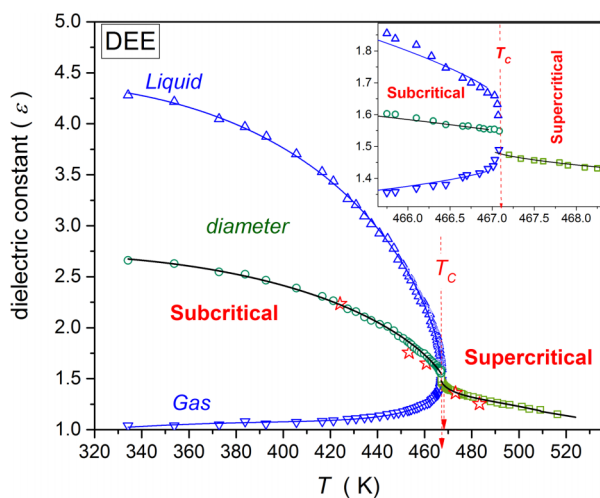


FIG. 1. Experimental results for dielectric constant behavior in the surroundings of the gas-liquid critical point for the critical isochore of diethyl ether (DEE): (i) the upper gas phase ($T < T_C$, triangles “down”), (ii) the lower liquid phase ($T < T_C$, triangles up), (iii) the supercritical phase (gas, $T > T_C$, squares), and (iv) the diameter of the bimodal defined by Eq. (5) ($T < T_C$, circles). Solid curves are portrayed by Eq. (3) for the supercritical state, Eq. (4) for the diameter, and Eqs. (9) and (10) for branches of the bimodal. The stars are for ultrasound sonicated samples.

$= 467 \text{ K} \pm 0.1$, and $\alpha = 0.12 \pm 0.02$. Results of the fitting are shown by the solid curve for $T > T_C$ in Fig. 1. Notable is the small impact of the correction-to-scaling term: $A/A_{corr} \approx 0.04$. Results of the fitting are visualized by the solid curve in Fig. 1.

A similar pretransitional anomaly, associated with the critical exponent $\phi = 1 - \alpha$, was noted for the diameter of the coexistence curve (binodal). It could be portrayed by Eq. (4), with the additional $\Delta T^{2\beta}$ power term, yielding the following parameters: $\varepsilon_C = 1.525 \pm 0.01$, $B_{dia.} = -0.056 \pm 0.05$, $A_{dia.} = 0.149 \pm 0.03$, $a_{dia.} = -0.064 \pm 0.03$, and critical exponents $\phi = 1 - \alpha = 0.88 \pm 0.05$ and $2\beta = 0.65 \pm 0.05$. Results are shown via the solid curve in the subcritical region for 334 K $< T < T_C (= 467 \text{ K} \pm 0.1)$. Relative “critical changes” of dielectric constant in the supercritical domain can be estimated by $[\Delta\varepsilon(T_C)/\varepsilon_C] \times 100\% = [(\varepsilon_{linear}(T_C) - \varepsilon(T_C))/\varepsilon(T_C)] \times 100\% = 8\%$ with the gradual diminishing effect up to $T \approx T_C + 10$ K. The similar analysis for the diameter in the subcritical area yields: $[\Delta\varepsilon(T_C)/\varepsilon_C] \times 100\% = 45\%$, gradually diminishing down to $T \approx T_C - 80$ K.

It is notable that the discussion regarding the diameter of the coexistence curve dates back to Cailletet and Matthias report in the year 1886⁴⁰ and the empirical law of rectilinear diameter: $d(T) = a + bT$. It offered a convenient way for estimating critical density, concentration, etc.^{2,3} This “classical law” was finally questioned only a century later.^{41–44} Notwithstanding, for many physical properties (density, refractive index, concentration, etc.) deviation from the “law of rectilinear diameter” is relatively weak and notable only in the immediate vicinity of the critical point.^{33,41–44}

Fig. 1 shows that for the dielectric constant in DEE the distortion from the “rectilinear law” is particularly strong, and in fact extends down to $T_C - 130$ K from the gas-liquid critical temperature.

Figure 2 presents the evolution of the difference between dielectric constants in coexisting phases in the log-log scale, which can validate the simple power description via Eq. (5)

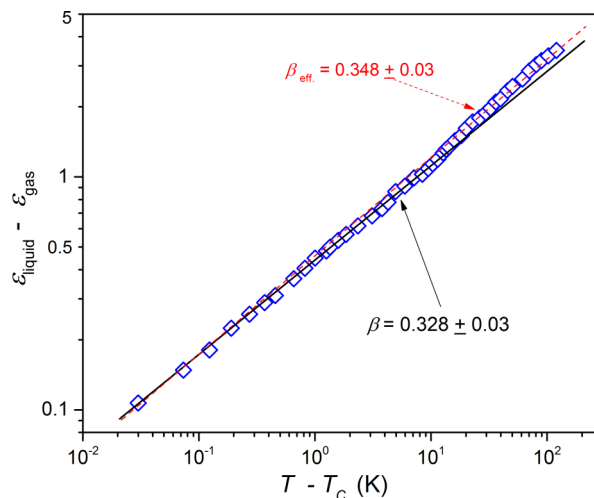


FIG. 2. The log-log plot of the difference between dielectric permittivities in coexisting phases ($T < T_C$) in diethyl ether for experimental data from Fig. 1. The solid line portrays results with the exponent $\beta \approx 0.328$ for $T - T_C < 15$ K. The red dashed line is for the approximate description of results via Eq. (4) up to $T - T_C \approx 130$ K with the effective exponent $\beta_{eff.} \approx 0.355$: see Eqs. (5) and (8).

with the following parameters: $\beta_{eff.} = 0.347 \pm 0.05$ and $B_{eff.} = 2.625 \pm 0.03$ in the temperature range $T_C - T < 130$ K (the dashed, red line in Fig. 1). However, this value is larger than $\beta \approx 325$ expected for the ($d = 3, n = 1$) universality class. It can be obtained for $T_C - T < 10$ K, as shown in Fig. 2 (the solid line).

To explain this behavior, it is notable that on moving away from the critical point the impact of correction-to-scaling terms appears,^{45,46}

$$M(T) = Bt^\beta \left(1 + \sum_i b_i t^{\Delta_i} \right), \quad (6)$$

where b_i and Δ_i are correction-to-scaling amplitudes and exponents, $t = |T - T_C|/T_C = \Delta T/T_C$ is the dimensionless distance from the critical temperature.

Generally, it is expected that the scaling near critical point, related to the single term critical description with the critical exponent (index) for the given universality class (d, n), works only in the very vicinity of the critical point (1%-2% deviation from critical parameters). However, from the experimental (exp.) the “very vicinity” is related to the temperature range ΔT in which $\beta_{theor.} \approx \beta_{exp.}$. For the order parameter plot in Fig. 2 one can estimate $\Delta T \approx 10$, $\beta_{theor.} = 0.3264\dots$, and $\beta_{exp.} = 0.328 \pm 0.03$. The value of such experimental ΔT range depends on the type of critical system and on the physical magnitude monitoring its properties. On moving away from T_C , the impact of correction-to-scaling terms additionally appears. When using a single power term description in such an extended range of temperature one obtains “effective” description,⁴⁶⁻⁴⁹

$$\begin{aligned} \beta &= \frac{d \log_{10} M(T)}{d \log_{10} t} = \frac{d \log_{10} (Bt^\beta)}{d \log_{10} t}, \quad (7) \\ \beta_{eff.} &= \frac{d \log_{10} M(T)}{d \log_{10} t} = \frac{d \left[\log_{10} \left(Bt^\beta \left(1 + \sum_i b_i t^{\Delta_i} \right) \right) \right]}{d \log_{10} t} \\ &\approx \beta + \frac{d \left[\log_{10} \left(\sum_i b_i t^{\Delta_i} \right) \right]}{d \log_{10} t} = \beta + \sum_i \Delta_i b_i t^{\Delta_i}. \quad (8) \end{aligned}$$

The change $\beta (\approx 0.328) \rightarrow \beta_{eff.} (\approx 0.35)$ in Fig. 2 on moving away from the critical point can be linked to such behavior. Notwithstanding, from the canonical point of view any estimation of the critical exponent via the single power term beyond the very immediate vicinity of the critical point (usually 1%-2% deviation from critical parameters)³ should be formally also named pseudocritical exponents. However, 2% from of the value $T_C \approx 467$ K yielding $\Delta T \approx 10$ K. Hence, in the given experiment the “canonical” and the experimental immediate vicinity of T_C seem to be in fair agreement.

In the opinion of the authors, the impact of pressure is also important: in pressure studies on approaching the critical consolute point, the influence of correction-to-scaling can be even negligible.^{31,33} Linking Eqs. (4) and (5) for the domain below the critical point one obtains the following dependences

for portraying branches of the coexistence curve:

$$\varepsilon_L(T) = \varepsilon_{liquid}(T) = d(T) + \frac{M(T)}{2}, \quad (9)$$

$$\varepsilon_U(T) = \varepsilon_{gas} = d(T) - \frac{M(T)}{2}. \quad (10)$$

The application of these relations for experimental data in Fig. 1 shows that they yield a relatively fair portrayal of both branches of the coexistence curve.

It is notable that the evolution of dielectric constant is also associated with changes of density $\rho(T)$. This is most often shown via the Clausius – Mossotti relation. However, the local field model used for its derivation has limited validity for “dense” dipolar dielectrics, particularly in the near critical domain.³⁸ Two facts are worth stressing. First, “precritical” anomalies, $\rho(T)$ and $\varepsilon(T)$, are described by analogous relations, both for the coexistence curve and the supercritical region. Second, the pretransitional anomalies related to $\rho(T)$ are much weaker than for $\varepsilon(T)$ [Ref. 33 and references therein]. Sengers *et al.*,¹⁵ to reduce the impact of density on the pretransitional anomaly in the supercritical region, proposed to analyze ε/ρ . However, for DEE there are still no $\rho(T)$ experimental data with the evidence of precritical anomalies.

When discussing the possible impact of density changes, it is notable that the pretransitional anomaly for density is much weaker than for dielectric constant, particularly for the diameter of coexistence.

Figure 1 also contains results for the ultrasound sonicated system (red stars). In the supercritical region the impact of the sonication is negligible. However, in the two-phase domain region the sonication causes changes of dielectric permittivity detected by both measurement capacitors following the same pattern determined by the diameter $d(T)$ (Eq. (4)). The split into $\varepsilon_{liquid}(T)$ and $\varepsilon_{gas}(T)$ associated with the coexisting phase disappears. These may suggest that the sonication converts the system into macro-homogeneous “critical composite,” composed of liquid and gas “critical droplets.”

CONCLUSIONS

There are continuous interests in the fundamental understanding of the surroundings of the gas–liquid critical point,^{5-7,16,50-52} supported by the boost of supercritical fluid technology implementations.⁹⁻¹² For both issues the behavior of the dielectric constant in the broad surrounding of the critical point constitutes the essential reference. Such evidence, in the broad temperature surroundings of the gas–liquid critical point in DEE, $T_C - 130$ K $< T < T_C + 50$ K (isochoric path), is presented in the given report. Diethyl ether is considered as an important model liquid for molecular and dielectric physics and the perspective solvent for supercritical fluid technologies.³⁷ It has been shown that relations derived on the base of the physics of critical phenomena¹⁵⁻¹⁷ offer a reliable parameterization in the whole tested range of temperatures, both in the supercritical and subcritical domains. Regarding the critical anomaly for $T \rightarrow T_C$, it manifests as the extra increase above the extrapolation of the linear

behavior obeying remote from T_C . Following the discussion related to Eq. (3) this can be associated with the coefficient $dT_C/dE^2 > 0$. In critical solutions of limited miscibility the anomalous decrease below the extrapolated linear dependence is observed.^{16,18–33} This can be associated with the fact that generally for critical mixtures $dT_C/dE^2 < 0$.⁵³ The only exception, still not explained ultimately, was obtained in nitromethane – 3-pentanol critical mixture.¹⁷ In the opinion of the authors the increase of the critical temperature due to the action of the electric field may suggest the dominance of the electrostriction, increasing the radius of critical fluctuations whereas the opposite sign may be linked to the elongation of fluctuations leading to the decrease of the correlation length. Such mechanisms appeared in the discussion of the critical behavior of the nonlinear dielectric effect (NDE), describing changes of dielectric permittivity due to the action of the strong electric field.^{54,55}

Worth stressing is the fact that the ultrasound sonication caused that both measurement capacitors detected approximately the same values of dielectric constant, located on the diameter of the coexistence curve. This may suggest that the macroscopic separation into two coexisting phase disappeared and a “micro-composite” consisting gas and liquid droplets appeared. So far, supercritical technologies focused on the homogeneous in the surroundings of the critical point, mainly for $T > T_C$ and $P > P_C$. They explore unique features of critical phenomena, including strong changes of relevant physical properties for relatively small shifts of pressure or temperature. Dielectric constant plays here a unique role due to its link to solubility. However, results of this report as well as Refs. 19–33 show that pretransitional “nonlinear” changes of dielectric constant in the supercritical domain ($T > T_C$) are relatively weak and take place only close to the critical point. It seems that the ultrasound sonication may create for $T < T_C$ the approximately macro-homogeneous critical system for which dielectric permittivity follows, $d(T) = (\epsilon_{liquid} + \epsilon_{gas})/2$. This indicates that the diameter of the coexistence curve may become directly available experimentally. It is notable that the pretransitional effect of $d(T)$ in the subcritical region is ca. $10\times$ larger than the one for $\epsilon(T)$ in supercritical domain. All these may indicate the new possibility of the extension of the supercritical technology into the two-phase based subcritical domain, additionally influenced by factors introduced by the ultrasound (frequency, intensity, and time-profile).

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