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High-pressure behavior of dielectric constant in a binary critical mixture

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An alternative design of the measurement capacitor for high-pressure studies of complex liquids or soft matter systems is presented. Subsequently, results for the precritical anomaly of dielectric constant in 1-nitropropane–octane critical mixture are reported. First, the pressure dependence of the critical consolute temperature T_C up to $P = 0.55$ GPa was determined and portrayed using the derivative-based analysis. Second, temperature and pressure evolutions of dielectric constant on approaching the critical consolute point at ($T_C = 304.1$ K and $P_C = 403$ MPa) were studied. They revealed that the pretransitional anomaly $\varepsilon(P \to P_C)$ is notably more pronounced than for $\varepsilon(T \to T_C)$. For both paths, the static domain extends even to as low frequency as $f = 100$ Hz, whereas for tests under atmospheric pressure, they require at least $f = 100$ kHz. The discussion of the impact of correction-to-scaling terms, including the unique case of the pressure paths, is also presented.

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I. INTRODUCTION

High-pressure studies of soft matter [1] constitute a challenging area of research, enabling the insight related to the density and free volume changes, whereas temperature investigations are coupled to the activation energy shift [2,3]. For soft matter systems, compressing, even below 1 GPa, can create a significant change of properties [2,3], whereas, for the classical hard matter systems, tens or even hundreds of GPa are required [4–6]. For soft matter systems, critical liquids constitute a unique category, for which the sensitivity to external disturbations, including compressing, increases infinitely on approaching the critical point. In one-component liquids, there is a single gas-liquid critical point, defined by the critical temperature (T_C) and pressure (P_C). Unique properties in the surrounding of the critical point are associated with multimolecular critical fluctuations, where size (correlation length ξ) and lifetime ($\tau_{fl.}$) increase infinitely for $T \to T_C$ or $P \to P_C$ [7–10]:

$$\xi(T) = \xi_0|T - T_C|^{-\nu}, \quad \tau_{fl.}(T) = \tau_0|T - T_C|^{-z\nu}, \tag{1}$$

$$\xi(P) = \xi_o^P|P_C - P|^{-\nu}, \quad \tau_{fl.}(P) = \tau_o^P|P_C - P|^{-z\nu}, \tag{2}$$

where ν denotes the critical exponent of the correlation length and z is the dynamical exponent. For critical mixtures of limited miscibility, discussed below, $\nu \approx 0.625$ and $z = 3$, what yields $z\nu \approx 1.875$; ξ_0 and τ_0 are critical amplitudes.

The similarity of Eqs. (1) and (2) is related to the isomorphism postulate of critical phenomena [10], i.e., the parallel description of the precritical behavior for temperature and pressure paths of approaching the critical point. Such origins of the precritical behavior led to extraordinary changes of susceptibility to external perturbations (compressibility) $\chi(P) \propto |T - T_C|^{-\gamma} + \cdots$ ($\gamma \approx 1.23$), the specific heat $c_p(T) \propto |T - T_C|^{-\alpha} + \cdots (\alpha \approx 0.115)$, or the order parameter $\Delta M(T) \propto |T - T_C|^{\beta} + \cdots (\beta \approx 0.325)$. The order parameter is related to the appearance/disappearance of an element of symmetry: in the given case, related to the difference of density, refractive index, or dielectric constant between two phases [9,10].

The *Physics of Critical Phenomena* explained that the gas-liquid critical point and binary mixtures of limited miscibility with the critical consolute point belong to the same universality class ($n_{OP} = 1$, $d = 3$), where n_{OP} and d are for space and order parameter dimensionalities [7–11]. Simple magnetic systems with the Curie point and three-dimensional Ising model associated with the one-component order parameter also belong to this universality class. All systems within a given universality class are described by the same (universal) values of critical exponents, and ratios of critical amplitudes for different physical properties, and linked via scaling equations [9–11]. However, there is a notable difference between the gas-liquid critical point and the liquid-liquid critical consolute point in binary mixtures of limited miscibility. The latter is associated with the continuous curve of critical points, emerging as the function of pressure [8,11]. It yields a unique possibility of adjusting the critical consolute temperature and properties of the tested mixture to experimental or application requirements.

Amongst the variety of properties tested on approaching the critical consolute point, dielectric constant occupies a unique position [11–33]. This is the basic and classical dielectric property, established previously by Faraday [34]. Studies focused on the precritical anomaly of dielectric constant in binary critical mixtures appeared surprisingly puzzling [11–33], and refs. therein, if comparing with similar research for other physical properties. The first clear indications for the decisive role of the measurement frequency and the biasing impact of the low-frequency Maxwell-Wegner effect asso-

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ciated with residual ionic contamination, and indicating the agreement with the model relation derived by Oxtoby *et al.* (1979, Ref. [11]) and Sengers *et al.* (1980, Ref. [12]), were published by Thoen *et al.* already in the years 1980 [13] and 1981 [14]. In the opinion of the authors, the ultimate experimental breakthrough can be linked to state-of-the-art extensive analysis by Thoen *et al.* published in the years 1989 [15] and 1990 [16]. These results showed that the description derived in Refs. [11,12] can appear only for the frequency increased up to $\sim f = 100\,\text{kHz}$, where the impact of the ionic contaminations can be neglected [13–16]:

$$\varepsilon(T) = \varepsilon_c + A(T - T_C)^{1-\alpha}[1 + a(T - T_C)^{\Delta} + \ldots] + b(T - T_C). \tag{3}$$

For the success of the mentioned model validation, despite the weakness of $\varepsilon(T)$ precritical anomaly, it was important to take into account the correction-to-scaling term, significant when shifting away from T_C. This term is shown in the square bracket, with the exponent $\Delta \approx 0.5$ [35]. For the gas-liquid critical point (diethyl ether), the validation of Eq. (3) was reported by the authors of the given report only recently [32]. Previously mentioned experimental problems are worth recalling when considering the significance of $\varepsilon(T, P)$ behavior for the supercritical extraction technologies [34], developed from five decades, and being one of the key green technologies for the 4th Industrial Revolution [36,37].

The evidence for the pressure-related changes of the dielectric constant on approaching the critical consolute point under pressure is still minimal. The first results were reported in the year 1999 [20]. It shows the following portrayal of the precritical effect in 1-nitropropane–hexadecane mixture:

$$\varepsilon(P) = \varepsilon_c + A_P(P_C - P)^{1-\alpha} + b_P(P_C - P), \tag{4}$$

where $T = \text{const}$ and $P \rightarrow P_C = 140\,\text{MPa}$.

Notable was the lack of the correction-to-scaling term and the negligible impact of the Maxwell-Wegner ionic effect.

This report presents a design of the measurement capacitors for dielectric studies with the reliable isolation between the tested sample and the pressurized medium. Subsequently, the results for the application of such a device for studying the precritical anomaly in the critical mixture, a system extremely sensitive even to the slightest contaminations [38], are presented. They cover both temperature and pressure related studies, and includes the discussion of the impact of the correction-to-scaling, limited so far. For the tested 1-nitropropane–octane critical mixture preliminary $T_C(P)$ studies were also carried out.

II. EXPERIMENTAL

The dielectric constant was measured using the Novocontrol Alpha impedance analyzer. Tests were carried out for a few frequencies ranging between 100 Hz and 100 kHz, with five digit resolution. The temperature was stabilized with the accuracy $\pm 0.02\,\text{K}$ and measured via the Copper-Constantan thermocouple placed within the high-pressure chamber. Additionally, two Pt100 resistors monitored a possible temperature gradient along the high-pressure chamber: it was always lesser than $\pm 0.02\,\text{K}$. The chamber was surrounded by a special jacket enabling the permanent flow of a temperature-stabilized liquid using Julabo thermostat with the external circulation and the volume $V = 20\,\text{L}$. Generally, there are different methods applied in high-pressure studies, depending on the temperature and pressure range. For pressures up to ∼1 GPa and temperatures, $-50\,^{\circ}\text{C} < T < 150\,^{\circ}\text{C}$ experiments can be carried out in relatively large volumes, reaching even 1 L, and precise pressure control via the external pump and the intermediate liquid transferring pressure (Plexol in the given case) is possible. Such conditions open possibilities for designing modules for the precise monitoring of physical properties *in situ* under high pressure. The following features for their optimal design are expected [2,3]:

(1) The tested sample should be in contact only with inert materials. In the given case, there are Invar, Teflon, and quartz.

(2) The module should enable several cycles of compressing and decompressing without a risk of the parasitic contamination.

(3) Complete and reliable isolation between the tested sample and the intermediate fluid transferring pressure.

Unfortunately, the typically used experimental solutions only partially fulfilled the above features, including: (i) containers made from a relatively soft material, like indium, for instance, crashed during compressing, (ii) a module with a piston shifting to increase the compression, (iii) two electric capacitor plates, separated by Teflon film or special spacers (typical gap 10–100 μm), and surrounded several times using the plastic, deformable Teflon tape [2,3].

The first case (i) is the one-usage solution, destroyed during the experiment. The second one (ii) requires the seal of the piston, which does not introduce the high resistance to its movement, and the subsequent compressing after decompression is not possible because of the contamination caused by the film from the intermediate pressurized liquid. The third solution is excluded for contaminations-sensitive systems, for instance, critical liquids. Notwithstanding, the latter is often applied in broadband dielectric spectroscopy studies in ultraviscous glass-forming systems [2,3].

In the past, the authors of the given report developed two constructions in which pressure was transmitted into the tested sample via the deformation of the Teflon film (20–50 μm), which formally fulfilled ideal conditions indicated above [39,40]. However, in the practical usage, bothersome problems with microholes in the Teflon film appeared, especially after the necessary stretching of the film to avoid the formation of a pressure gradient.

Figure 1 shows the design of the measurement capacitor for high-pressure studies, with the innovative way of transferring pressure changes into the sample. It is realized via the deformation of a tube made from Teflon or any flexible plastic material neutral for the tested sample, containing 30–40% of the volume of the sample. This solution is reliable, simple for assembling, and also cheap in usage. The results presented below, for the critical liquid mixture extremely sensitive for impurities, confirmed all these favorite features.

Studies were carried out in 1-nitropropane–octane (1-np–oct) critical mixture, for which the critical consolute temperature and pressure were determined using the photo-analysis of the fractional meniscus heights changes [41,42] yielding: $T_C = 275.5\,\text{K}$ and $x_C = 0.535$ mole fraction of 1-np. Both components were distilled twice under vacuum, directly

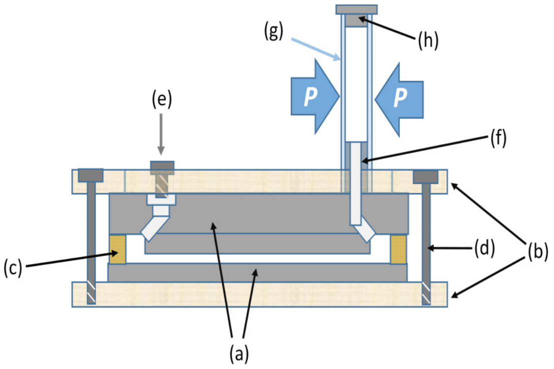

FIG. 1. Capacitor for dielectric studies under pressure, with the effective isolation between the tested sample and the pressurized medium: (a) capacitor plates (Invar, diameter $2r = 16$ mm), (b) clamp (PTFE (poli(tetrafluoroetylne, Teflon) or PVDF (polyvinylidene fluoride) (c) spacer between plates (the ring ∼3-mm wide and 4–5 mm high; made from quartz, PTFE, …), (d) screws linking clamps assembling plates of the capacitor, (e) the screw closing the channel for introducing of the sample, (f) the sleeve for fixing the flexible/elastic tube, (g) the elastic/flexible tube (Teflon or other elastic and resistant to the tested sample plastic); it transmits pressure to the sample, (h) the stopper closing the flexible tube. There are 20-μm film washers (Teflon) between capacitor plates (a) and the spacer (c). For the screw (e) 1-mm-thick washer is required. Arrows with the letter P show how pressure is transmitted to the sample.

before the preparation of samples. Studies of the pressure dependence of the critical consolute temperature showed that even 10+ cycles of compressing and decompressing, associated with the shift to the next isotherm, did not contaminate the sample.

III. RESULTS AND DISCUSSION

Figure 1 shows the pressure dependence of the critical consolute temperature for 1-nitropropane – octane critical mixture of limited miscibility. It was determined via isothermal, pressure-related measurements, for which a sharp change of dielectric constant when passing the critical consolute point occurs. This was associated with fact that the gap of the measurement capacitor was in the lower coexisting phase after the pressure-induced phase separation. Subsequently, the system was suddenly decompressed by 20–30 MPa and heated up to the next isotherm. About 1 h was needed to reach the required temperature stabilization. In the meantime, the application of the series of strong electric pulses, lasting ∼1 ms, with voltage up to ∼1000 V, was used to support the homogenization of the mixture. The latter explored the high voltage system used for nonlinear dielectric effect studies [43]. The application of pulses of the strong electric to the inhomogeneous mixture, especially in the presence of the meniscus, causes sudden changes of the registered electric capacitance and facilitates mixing. Such shifts of the electric capacitance disappear when the tested mixture becomes finally homogeneous, and the system stabilizes.

Simon and Glatzel (SG) introduced the basic relation for describing the pressure evolution of the melting temperature [44,45]:

$$T_m(P) = T^0\left(1 + \frac{P}{a}\right)^{1/b}. \tag{5}$$

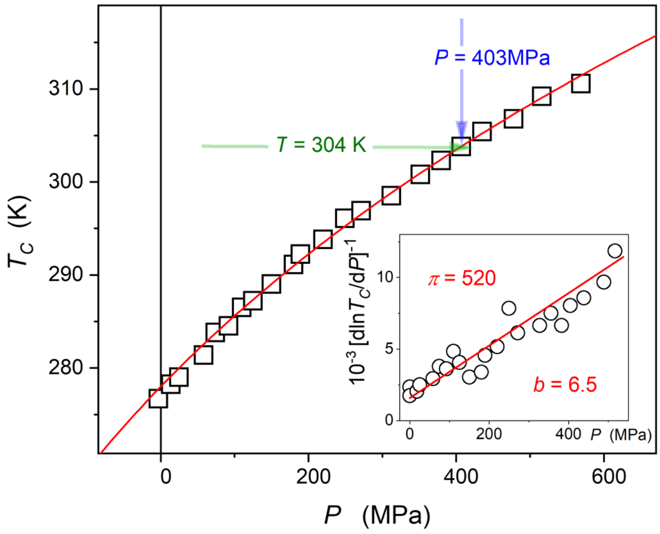

FIG. 2. Pressure dependence of the critical consolute temperature in 1-nitropropane–octane critical mixture. The curve portraying experimental data is related to Eq. (6), with the supported derivative-based analysis [Eq. (7)] shown in the inset.

Its parallel is a popular tool for describing the pressure evolution of the glass temperature, introduced by Andersson and Andersson (AA) [46]. Notable that for both the SG and AA relations, the strict condition is required for the reference pressure $T^0_{g,m} = T_{g,m}(P = 0) \approx T_{g,m}(P = 0.1\ \text{MPa})$ [47,48]. Other values of the reference temperature yield biased effective values of a and b coefficients. In Ref. [46] the extended version of Eq. (5), covering the negative pressure domain and valid for arbitrary reference temperatures, was introduced. In Refs. [22,28] it was applied to describe pressure changes of the critical consolute temperature:

$$T_C(P) = T^0\left(1 + \frac{\Delta P}{\Pi}\right)^{1/b} = T^0\left(1 + \frac{P - P^0}{P^0 + \pi}\right)^{1/b}, \tag{6}$$

where $(T_{0,} P_0)$ are the reference temperature and pressure, and $-\pi$ is for the asymptote hidden in the negative pressures domain.

The preliminary derivative-based and distortions-sensitive transformation can indicate the validity of using Eq. (6) for a given set of experimental data:

$$\ln T_C(P) = \ln T^0 + \frac{1}{b}\ln\left(1 + \frac{\Delta P}{\Pi}\right) \Rightarrow \left[\frac{d\ln T_C(P)}{dP}\right]^{-1}$$
$$= b\pi + bP = A + BP. \tag{7}$$

The linear regression fit can yield optimal values of $\pi(\Pi)$ and b coefficients. Subsequently, they can be substituted into Eq. (6), taking the arbitrary experimental value of $T_C(P_C) = T^0_C$ as the reference, and avoiding the uncertainty associated with the nonlinear fitting.

The solid (red) curve in the central part of Fig. 2 is related to Eq. (6), with parameters derived via Eq. (7), and given in

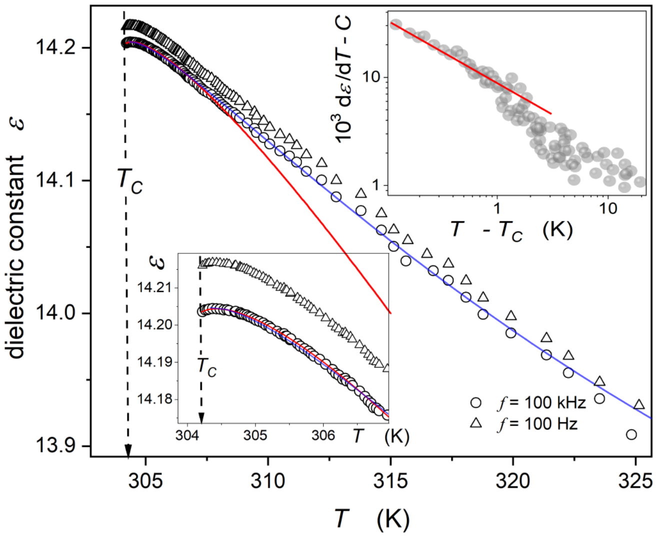

FIG. 3. Temperature changes of dielectric constant in 1-nitropropane–octane critical mixtures under pressure $P_{\text{path}} = 403\,\text{MPa}$: the critical consolute point is defined as $(T_C, P_C = P_{\text{path}})$. The inset shows the behavior near T_C. The results are for two measurement frequencies. The solid curve in blue is related to Eq. (3) and in red to Eq. (3) without the correction-to-scaling term (in the square bracket]. The lower inset shows the behavior in the immediate vicinity of T_C and the upper inset is for the derivative-based and distortions sensitive analysis defined by Eq. (9). The values of the fitted parameters are given in the Appendix.

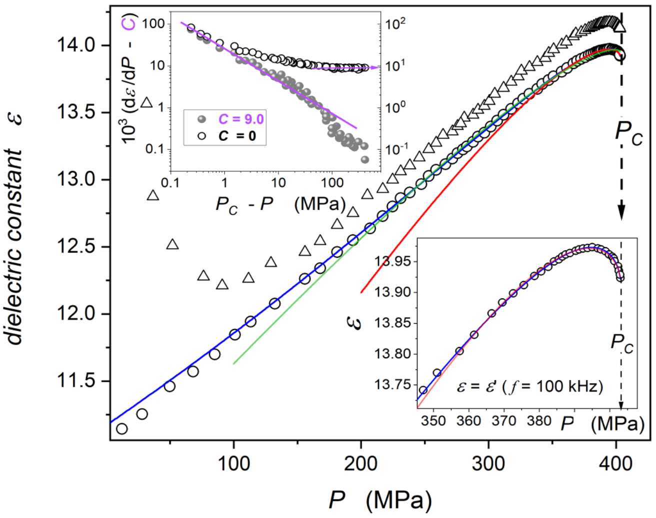

FIG. 4. Pressure changes of dielectric constant in 1-nitropropane–octane critical mixtures under temperature $T_{\text{path}} = 304.3\,\text{K}$: the critical consolute point is defined as $(T_{\text{path}} = T_C, P_C)$. The inset shows the behavior near P_C. The results are for two measurement frequencies. The solid curve in blue is related to Eq. (8) and in red to Eq. (8) without the correction-to-scaling term (in the square bracket]. The lower inset shows the behavior in the immediate vicinity of P_C and the upper inset is for the derivative-based and distortions sensitive analysis defined by Eq. (10). The values of the fitted parameters are given in the Appendix.

the inset in Fig. 2. Arrows in Fig. 2 show paths for which the pretransitional anomaly of dielectric constant was studied. They are related to the critical consolute point: $T_C = 304.1\,\text{K}$ and $P_C = 403\,\text{MPa}$.

Results showing changes of dielectric constants along these paths are shown in Figs. 3 and 4. The portrayal of the full tested range of temperatures and pressures is possible when taking into account Eq. (3) and its pressure counterpart:

$$\varepsilon(P) = \varepsilon_c + A_P(P_C - P)^{1-\alpha}[1 + a_P(P_C - P)^{\Delta}] + b_P(P_C - P). \tag{8}$$

Results of the description of $\varepsilon(T)$ experimental data via Eq. (3) and $\varepsilon(P)$ via Eq. (8) are shown by blue curves in Figs. 3 and 4, respectively. The values of the fitted parameters are given in the Appendix.

Figure 4 shows evidence for the pressure-related impact of the correction-to-scaling under high pressure. Figures 3 and 4 also present the possibility of describing the pretransitional behavior of the critical consolute point solely by the single exponential term, i.e., neglecting the terms in the square bracket in Eqs. (3) and (8). Such behavior is shown via red curves. Notable is the clear manifestation of the pretransitional anomaly of dielectric constant even for the frequency as low as $f = 100$ Hz. This result shows the qualitative extension of frequency domain for the real part of dielectric permittivity in comparison to studies under atmospheric pressure [13–19]. For the latter, the ionic-related contribution cancels $\varepsilon(T)$ precritical anomaly already for $f = 1$ KHz [13–19]. It is notable that the manifestation of the pretransitional effect for the pressure path $(\varepsilon(P))$ is much stronger for the temperature one $(\varepsilon(T))$. This feature is particularly visible in lower insets in Figs. 3 and 4, respectively. The upper insets are related to derivatives of $\varepsilon(T)$ and $\varepsilon(P)$ experimental data. Considering derivatives of Eqs. (3) and (8) one obtains relations

$$\frac{d\varepsilon(T)}{dT} = A(1-\alpha)(P_C - P)^{-\alpha} + Aa(P_C - P)^{-\alpha+\Delta} + bT \approx A'(T - T_C)^{-\alpha} + C, \tag{9}$$

$$\frac{d\varepsilon(P)}{dT} = A_P(1-\alpha)(P_C - P)^{-\alpha} + A_P a_P(P_C - P)^{-\alpha+\Delta} + b_P P \approx A'_P(P_C - P)^{-\alpha} + C. \tag{10}$$

The results of such analysis are presented in the upper insets in Figs. 3 and 4. The additionally validated final (right-hand) approximation is applied in Eqs. (9) and (10).

Both insets show that the immediate vicinity of the critical point, i.e., the region where the correction to scaling terms can be neglected, occurs for $T - T_C < 2\,\text{K}$ (pressure path), and $P_C - P < 100\,\text{MPa}$ (temperature path), with the same value of critical exponent $\alpha = 0.12 \pm 0.015$. The comparison in the upper insets in Figs. 3 and 4 also confirms that the precritical anomaly for the pressure path is much stronger than for the temperature path. Precritical changes of $\varepsilon(P)$ extends for three decades whereas there is only one decade for the $\varepsilon(T)$ anomaly. Notable is that Eq. (9) resembles the relation known for temperature evolution of the specific heat under atmospheric pressure [9]. Such a link for the homogeneous phase of critical mixtures was indicated theoretically by Mistura in 1974 [49]:

$$d\varepsilon/dT \propto c_P(P) \propto (T - T_C)^{-\alpha}. \tag{11}$$

Recalling the definition of the specific heat [49] and the basic thermodynamic equation $H(T) = E(T) + PV(P)$, $c_P(T) = dE(T)/dT$ for $P =$ const, and that for the pressure path $V(P, T) = V(P) =$ const, one can associate the pretransitional anomaly of $\varepsilon(T)$ with the pretransitional behavior of $H(T)$ and for pressure related changes: $c_T(P) = V(T) + P(dV(P)/dP)$, and then the $\varepsilon(P)$ anomaly is linked to the activation volume. However, the pretransitional behavior for both ways is governed by the presence of critical fluctuations and described by the same value of the critical exponent $\alpha \approx 0.12$.

IV. CONCLUSIONS

This report presents a solution for testing the dielectric properties of liquid and soft matter systems under pressure. Its features (i) reliable isolation between tested samples and the intermediate liquids transferring pressure, (ii) the possibility of multiple compressing -decompressing measurement cycles, and (iii) simple and easy assembling of the devices.

The measurement module was subsequently tested in studies of the pretransitional behavior of the dielectric constant in the homogeneous phase of a critical binary mixture of limited miscibility, the system extremely sensitive even to the slightest contamination.

Studies of $\varepsilon(T)$ and $\varepsilon(P)$ changes were carried out for 1-nitropropane – octane critical mixture on approaching ($P_C = 403$ MPa, $T_C = 304.0$ K) critical consolute point. The isomorphic forms of critical anomalies for both paths were found, including the impact of the correction-to-scaling terms, and with the negligible influence of residual ionic contaminations even for frequency as low as $f = 100$ Hz. Results obtained enabled the reasoning for the origins of the pretransitional anomaly of dielectric constant in critical mixtures of limited miscibility. It is notable that the critical anomaly of the dielectric constant for the pressure path is much stronger than the temperature path. In the opinion of the authors, this can be explained considering the model value for the critical amplitude in Eq. (3) describing the $\varepsilon(T)$ behavior [17]:

$$A \propto \left(\frac{2}{\varepsilon_0}\frac{dT_C}{dE^2} + \frac{dT_C}{dP}\right). \tag{12}$$

For the pressure paths $dT_C/dP = dT_C/dP_C \approx 0.05$ K/MPa for $T_C = 304$ K and $P_C = 403$ MPa critical point. One can expect that the critical amplitude for the $\varepsilon(P)$ path: $A_P \propto dP_C/dT_C \approx 20$ MPa/K.

In the opinion of the authors, the proposed experimental module can be considered as a convenient possibility for studying dielectric properties of liquids, complex liquids, or supercooled previtreous effects on approaching the glass transition point, i.e., issues for which high-pressure studies are still hindered by problems associated with measurement end modules.

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APPENDIX: PARAMETERIZATION OF PRECRITICAL EFFECTS

The temperature evolution of dielectric constant in Fig. 3, for the range $T - T_C < 20$ K is given by

$$\varepsilon(T) = 14.201 + 0.1045(T - T_C)^{1-\alpha} + 0.00853(T - T_C)^{1-\alpha+\Delta} - 0.1142(T - T_C). \tag{A1}$$

For $T - T_C < 2$ K reliable is the portrayal:

$$\varepsilon(T) = 14.201 + 0.0747(T - T_C)^{1-\alpha} - 0.07537(T - T_C), \tag{A2}$$

where $T_C = 304.1\ \text{K} \pm 0.02$ and critical exponents: $\alpha = 0.115$ and $\Delta = 0.5$.

The pressure evolution of dielectric constant in Fig. 3, for the range $P_C - P < 350$ MPa is given by

$$\varepsilon(P) = 13.96 + 0.01918(P_C - P)^{1-\alpha} + 0.000014(P_C - P)^{1-\alpha+\Delta} - 0.01717(P_C - P). \tag{A3}$$

For $P_C - P < 100$ MPa reliable is the portrayal:

$$\varepsilon(P) = 13.96 + 0.0538(P_C - P)^{1-\alpha} - 0.0373(P_C - P), \tag{A4}$$

where $P_C = 403.0$ MPa and critical exponents: $\alpha = 0.115$, and $\Delta = 0.5$.

Curves related to Eqs. (A1) and (A3) are shown in blue in Figs. 3 and 4, respectively. The curves associated with Eqs. (A2) and (A3) are shown in red in Figs. 3 and 4, respectively.

Note that linear terms in the above relations do not portray experimental data remote from the critical consolute point, and they cannot be considered as the noncritical background effect as often occurred for physical magnitudes directly coupled to critical fluctuations, for instance, nonlinear dielectric effect or the Kerr effect [2,3,40].

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