Critical Behavior of the Dielectric Modulus in Nitrobenzene-Dodecane Mixture

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The dielectric properties of a homogenous critical mixture of nitrobenzene-decane were studied in the range $1 \text{ Hz} < f < 1 \text{ Mz}$. The temperature dependences of the “static” dielectric permittivity $\varepsilon'$ (1 MHz) and the electric conductivity $\sigma(1 \text{ Hz})$ exhibit pretransitional anomalies which may be associated with the same critical exponent $\phi = 1 - \alpha \approx 0.88$, where $\alpha$ is the critical exponent of the specific heat. The same data were analyzed using the dielectric modulus representation. They show loss curves for the imaginary part of the modulus $M''(f)$, the temperature evolutions of the peak frequency $\tau = 1/2\pi f_p$ and the peak maximum of $M'' = M''(f_p)$ also exhibit critical anomalies. Their forms resemble anomalies obtained for the imaginary part of the dielectric permittivity $\varepsilon''(f)$, carried out for $40 \text{ MHz} < f < 1 \text{ GHz}$, in an ethanol-dodecane critical mixture [S. J. Rzoska, K. Orzechowski, and A. Drozd-Rzoska, Phys. Rev. E \textbf{65}, 042501 (2002)]. – PACS: 64.70.Ja, 77.20.+y, 64.60.Fr

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1. Introduction

In 1932 Arkadiusz Piekara studied the temperature behavior of the static dielectric permittivity $\varepsilon'(T)$ in the homogeneous phase of a nitrobenzene-hexane critical mixture [1]. He noted a linear dependence of $\varepsilon'(T)$ remote from the critical consolute temperature $T_C$ and a small bending down from this behavior on approaching $T_C$. However, only in 1979/1980 a theoretical relation describing this phenomenon was proposed [2, 3]:

$$\varepsilon'(T) = \varepsilon_C + \alpha T_t + \Lambda T_t^{1-\alpha} + b T_t^{1-\alpha+\Delta},$$  \hspace{1cm} (1)

where $t = (T - T_C)/T_C$ describes the distance from $T_C$, $\phi = 1 - \alpha$ and $\alpha \approx 0.12$ is the critical exponent of the specific heat. The last term (1) is associated with the correction-to-scaling, important when moving away from the critical point. The exponent $\Delta \approx 0.5$ is the first correction-to-scaling critical exponent [4].

The experimental evidence for the $\varepsilon'(T)$ behavior remained puzzling till the late eighties [5 – 11]. It was shown in [5, 6] that the “static” critical anomaly of $\varepsilon''(T)$, predicted by (1), can only be detected at high enough frequencies, in practice for $f > 100 \text{ kHz}$ [5 – 11]. It was found that for lower frequencies a parasitic contribution from the Maxwell-Wagner (MW) effect may dominate the critical, pretransitional behavior [5, 6]. In practice, frequencies $f = 1 - 10 \text{ kHz}$ are most often used as the MW critical effect reference frequency. It is noteworthy that this factor can be significantly reduced by pressure [10 – 13]. Worth recalling are also comprehensive pressure and temperature studies in critical solutions, characterized by the positive and negative signs of the pressure induced shift of the critical consolute temperature $(dT_C/dP)$ [14, 15]. They gave the dependence of the critical amplitude $A_C(T, P)$ on the volume excess and the enthalpy excess of the tested mixture [13].

Instead of the temperature behavior of the imaginary component of the dielectric permittivity $\varepsilon''$, the electric conductivity $\sigma(T)$ is usually tested [5, 6, 16 – 19]. Regarding the theoretical predictions of the critical effect of the $\sigma(T)$ dependence they are still puzzling [20 – 23]. Only recently experimental evidence for a relation resembling (1) for $\varepsilon'(T)$ was obtained [18, 19]:

$$\sigma(T) = \sigma_0 + C_T t^{1-\alpha}(1 + cr^2),$$  \hspace{1cm} (2)

where $\sigma_0$ denotes the non-critical background term on moving away from $T_C$. 

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For the background term, the polynomial \( \sigma_B(T) = (C_1 + C_2T + C_3T^2)B \) was successfully used in [18] and the Arrhenius dependence in [19]. For the electric conductivity the validity of (2) may be expected for lower frequencies [5, 6, 18, 19]. Only for critical mixtures with a large residual ionic conductivity this frequency may increase up to \( f = 1 - 10 \text{ kHz} \) [18]. To our knowledge the evidence for the critical anomaly of \( \sigma(T) \) in mixtures of low electric conductivity, preferably used in \( \varepsilon''(T) \) studies, remains very poor.

Despite the clear experimental evidence of the influence of critical fluctuations on the static dielectric permittivity and electric conductivity, only preliminary and qualitative statements of such an influence on the dielectric spectrum could be found until recently [16] and refs. therein. Probably the only clear experimental result was obtained for the ethanol-dodecane critical mixture [16]. Due to the selection of the tested mixture, the analysis of the frequency behavior of the imaginary part of the dielectric permittivity could be reduced to frequencies lower than 1 GHz [16]. It was shown that the temperature dependencies of the maxima of loss curves \( (\varepsilon''_p) \) and dielectric relaxation times taken as reciprocals of frequencies \( (\tau = 1/2\pi f_p) \) of loss curves peaks exhibit clear critical anomalies.

This paper presents results of dielectric studies on the nitrobenzene-decane critical solution, which belongs to the group of critical mixtures composed of a dipolar component, such as nitrobenzene, nitroethane or benzonitrile, and a non-dipolar solvent (alkane), which are most often used in studies on the \( \varepsilon'(T) \) critical behavior. High-resolution studies were conducted for frequencies in the range of \( 1 \text{ Hz} < f < 1 \text{ MHz} \). A clear quantitative evidence of the influence of critical fluctuations on \( \sigma(T), \varepsilon'(T) \) and the dielectric relaxation, tested by means of the modulus representation, was obtained.

2. Experimental

The measurement set-up was the same as described in [10–13]. The measurements were conducted in a flat parallel capacitor made from Invar (gap 0.5 mm, diameter 20 mm) using a Solartron 1260A impedance analyzer. That the temperature was stabilized using a Julabo HD 45SP thermostat with external circulation (temperature stabilization \( \pm 0.02 \text{ K} \)). It was measured by a platinum resistor placed in one of the capacitor covers by means of Keithley 195 multimeter. Analyses were made applying Origin 6.1 software. The components of the tested mixture \( (T_C \approx 25 \text{ °C} \text{ and } x_C = 0.64 \text{ mole fraction of nitrobenzene [14]}) \) where purchased from Fluka. Decane was used without purification. Nitrobenzene was distilled immediately prior to the measurements.

3. Results and Discussion

Figure 1 presents examples of the obtained behavior of the dielectric permittivity \( (\varepsilon', \varepsilon'') \) for three temperatures. There is no visible manifestation of dielectric relaxation on the \( \varepsilon'(f) \) and \( \varepsilon''(f) \) behavior, even in the immediate vicinity of \( T_C \). This agrees with the expectation that for the tested mixture such phenomena occur only if the range of frequencies is extended up to at least a few GHz [9, 16]. A weak pretransitional dependence occurs only for \( \varepsilon'(T)_{f=\text{const}} \). The dependence of \( \varepsilon'(T) \) for \( f = 1 \text{ MHz} \) corresponds to (1), predicted for the ’static’ dielectric permittivity (shown by the solid curve in Figure 2). On decreasing the frequency below \( f = 10 \text{ kHz} \), the contribution from the residual ionic dopants boosts the value of to the real part of the dielectric permittivity. Figure 2 presents also the temperature behavior of the electric conductivity, which for \( f = 1 \text{ Hz} \) can be portrayed by

\[
\sigma(T) = \sigma_C + at + C_d t^{-\alpha}(1 + ct^\beta).
\]

Fitted parameters are given in the legend capture of Figure 2. The results suggest that both the \( \varepsilon'(T) \) and \( \sigma(T) \) critical anomalies may be associated with the
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Fig. 2. Critical “static” anomalies of the dielectric permittivity ($\varepsilon'$) and electric conductivity ($\sigma$). The solid curves are parameterized by (1) and (2):

$$\varepsilon'(T) = 16.3 - 0.34(T - T_C) + 0.32(T - T_C)^{0.88}[1 + 0.06(T - T_C)^{0.5}], \sigma(T) = 2.91 - 0.06(T - T_C) + 0.09(T - T_C)^{0.88}[1 + 0.0004(T - T_C)^{0.5}]$$

The error for critical exponent is about 20%. The dashed arrow shows the critical temperature.

same critical exponent $\phi = 1 - \alpha \approx 0.88$. The relatively large error of fitting is caused by the weakness of these anomalies and the number of fitted parameters. It should be stressed that (3) and (1) the linear terms cannot be considered as non-critical background terms. They do not describe experimental data at any distance from the critical temperature.

In ionically conducting complex liquids, for instance glassformers, some of arguments speak for a presentation of the experimental data by means of the dielectric modulus $M^*(f)$:

$$M^* = \frac{1}{\varepsilon} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + i\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}. \quad (4)$$

Except of the form of the distribution, the spectra of $M''(f)$ show a similar temperature behavior as $\varepsilon''(f)$, although for much lower frequencies $f$, [26] and refs. therein. In glassforming liquids the so-called ionic conductivity relaxation time $\tau_\sigma(T)$, taken as the reciprocal of the $M''(f)$ peak frequency, is often found to follow the structural (alpha) relaxation time $\tau_\alpha(T)$ derived from the $\varepsilon''(f)$ loss curves peak frequency. Although values of $\tau_\sigma(T)$ and $\tau_\alpha(T)$ for the same temperature differ strongly, they can be often superposed into the same curve by appropriate scaling. This suggests that they may be described by the same function with different pre-factors $\tau_\omega$. Hence, the modulus representation may be a significant research tool for materials without accessible loss peak. However, the decoupling between $\tau_\sigma(T)$ and $\tau_\alpha(T)$ was also noted, particularly on approaching the glass temperature.

Worth mentioning is also a still existing controversy of the physical meaning of the modulus representation in complex liquids, [26] and refs. therein.

Figure 3 shows data from Fig. 1 presented by means of the dielectric modulus loss curve maximum $M''_{\text{peak}}$ and of the peak frequency ($\tau = 1/2\pi f_{\text{peak}}(M''_{\text{peak}})$). The solid curves are parameterized by (7) and (6), respectively.

Fig. 3. Dielectric modulus representation of experimental data in the vicinity of the critical temperature.

Fig. 4. Temperature dependencies of the dielectric modulus loss curve maximum $M''_{\text{peak}}$ and of the peak frequency ($\tau = 1/2\pi f_{\text{peak}}(M''_{\text{peak}})$). The solid curves are parameterized by (7) and (6), respectively.

$$M''(f) \propto f^m \quad \text{with} \quad m = 1 \quad \text{for} \quad f < f_p, \quad (5a)$$

$$M''(f) \propto f^{-n} \quad \text{with} \quad n = 1 \quad \text{for} \quad f > f_p. \quad (5b)$$
It is noteworthy that for $\varepsilon''(f)$ in the ethanol-dodecane critical mixture a stretched relaxation with $m, n < 1$ was found. A similar decoupling of distributions of relaxation times manifested by $\varepsilon''(f)$ and $M''(f)$ was noted in supercooled liquids [24–26]. Figure 4 shows that the relaxation time $\tau_\sigma = 1/2\pi f_0$ exhibits a critical dependence, which can be approximated by

$$\tau_\sigma = \tau_0^{\text{ion}}(T - T_C)^{-\theta},$$

where $\tau_0 = 1/2\pi f_0$, $f_0$ is the peak frequency, $T_C = 25.3^\circ\text{C}$, $\tau_0^{\text{ion}} = 50\ \mu\text{s}$, $\theta = 0.06 \pm 0.03$.

The obtained value of the exponent is close to the one known for other transport properties: diffusion ($z_\eta = 0.054 - 0.066$) and shear viscosity ($\phi = z_\eta v = 0.033 - 0.044$, $v$ is the exponent for the correlation length) [27]. Figure 4 also shows that the maximum of the peak $(M''_\text{peak})$ exhibits a relatively strong pretransitional dependence. It can be portrayed by

$$\frac{1}{M''_\text{peak}} = a + b (T - T_C) + C (T - T_C)^{1 - \alpha} + d (T - T_C)^{1 - \alpha + \Delta},$$

where $a = 1.1 \pm 0.03$, $b = -0.06 \pm 0.01$, $A_C = 0.065 \pm 0.01$, $d = 0.003$ and $\phi = 1 - \alpha = 0.88 \pm 0.2$. This relation is associated with peak frequencies tested for $2\ \text{kHz} < f_\text{peak}(M'') < 20\ \text{kHz}$.

It is noteworthy that similar dependencies of (6) and (7), with approximately the same critical exponents $\theta$ and $\phi = 1 - \alpha$, were obtained for the temperature dependence of $\varepsilon''_0(T)$ and $\tau = 1/2\pi f_\text{peak}(\varepsilon'')$ for peak frequencies $40\ \text{MHz} < f_\text{peak}(\varepsilon'') < 0.5\ \text{GHz}$ in [16].

4. Conclusions

The obtained “static” critical anomalies of the dielectric permittivity $\varepsilon'$ and dielectric conductivity $\sigma$ are described by the same critical exponent $\phi = 1 - \alpha \approx 0.88$. These results were obtained for a critical mixture with relatively low electric conductivity. For such critical mixtures the evidence of both $\sigma(T)$ and $\varepsilon'(T)$ was limited up to now. Novel possibilities for studying dynamic properties in critical mixtures by means of dielectric measurements are presented due to the application of the dielectric modulus representation. Such tests involve measurement frequencies in an experimentally convenient range. The maxima of the dielectric modulus loss curves show a critical anomaly, also associated with the critical exponent $\phi = 1 - \alpha \approx 0.88$. This anomaly is relatively strong and not affected by the parasitic MW contribution to the critical behavior. The critical anomaly shows also the temperature evolution of relaxation times taken as reciprocals of the peak frequencies of dielectric modulus loss curves. Critical anomalies obtained in $M''(f)$ analysis are similar to ones found recently in the analysis of dielectric permittivity loss curves $\varepsilon''(f)$ [16]. However, the latter are associated with frequencies in the GHz domain. To the best of our knowledge there exist no theoretical predictions discussing the evolution of $\tau_\sigma(T)$ and $1/M''_\text{peak}(T)$ in critical mixtures.

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