

Evidence of a Critical Anomaly of the Electrical Conductivity in Highly Concentrated Nonaqueous Ionic Mixtures

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We present the first electrical conductivity measurements performed in highly concentrated electrolyte solutions near a critical consolute point. The critical binary mixtures studied are tetra-*n*-butylammonium picrate in 1-dodecanol and 1,4-butanediol solvents. An accurate determination of the regular conductivity in the one-phase region indicates the presence of a critical anomaly in the electrical conductivity for $\tau < 10^{-2}$, where τ is the reduced temperature. The nature of the anomaly does not correlate with the values of the viscosity, the dielectric constant, or the free ion concentration of the mixtures.

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At present, a theory that describes the critical behavior of highly concentrated electrolyte solutions and molten salts is not yet available [1]. The mechanism of corrosion in supercritical water is a subject of growing scientific interest due to new technological applications such as the oxidation of organic wastes [2]. At high temperature and pressure, supercritical water becomes self-ionized and behaves quite like a highly conducting medium, resembling molten salts [3]. Highly concentrated binary ionic mixtures, made of an organic salt in a low dielectric-constant organic solvent with an upper critical consolute point near room temperature, have been recently investigated [4–8]. These systems belong mostly to the 3D Ising universality class, possibly with some weak crossover from Ising-like to mean-field criticality [Ref. [4(b)]];]. The transport properties in such systems have not been studied yet, except for the shear viscosity that shows a weak anomaly similar to that observed in pure fluids or in neutral binary mixtures [8].

This Letter presents the first electrical conductivity measurements in highly concentrated nonaqueous electrolytes near a critical consolute point. The conductivity has been studied in the past in aqueous and poorly conductive nonaqueous critical solutions, as well as in ion-doped solutions [9–15]. The critical exponent θ of the conductivity anomaly is found experimentally between 2β and $(1 - \alpha)$ [9–14], where $\beta = 0.326$ and $\alpha = 0.109$ are the usual 3D Ising-like exponents [16]. A $\theta = (1 - \alpha)$ exponent should be attributed to short-range fluctuations [17] or should be found in a proton hopping mechanism [13]. A percolation model for the transport of the ions would yield $\theta = 2\beta$ [10,11]. Scattering of ionic impurities by concentration fluctuations should give a $\nu = 0.630$ singularity [9].

We have measured the electrical conductivity of the salt tetra-*n*-butylammonium picrate (TBAP) in two different solvents: 1-dodecanol (DD) (static dielectric constant $\epsilon = 4.6$ at $T = 61^\circ\text{C}$) and 1,4-butanediol (BD) ($\epsilon = 25.9$ at $T = 59^\circ\text{C}$). Mixtures of TBAP in solvents with composition (92.5% DD + 7.5% BD) and (85% DD +

15% BD) have been also studied. The coexistence curve of these binary mixtures is described by the 3D Ising β exponent with almost no crossover to mean field [7].

The low-frequency electrical impedance was measured between two parallel vertical platinized platinum electrodes [18]. The conductivity cell is enclosed in a hermetically sealed copper container with two transparent windows to allow for the simultaneous measurement of the turbidity through the 2 cm sample thickness. The container is earth-grounded and immersed in a temperature regulated water bath with temperature stability better than ± 2 mK over several hours [6]. The complex impedance Z is measured with a four terminal auto balancing LCR bridge (HP 4284A) in the frequency range $\Delta f = 100$ Hz–300 kHz. Calibration of the cell was made with a standard reference solution with conductivity comparable to that of the sample. Open-circuit (empty cell) and short-circuit (cell filled with mercury) compensations were performed to eliminate the cell and the electrical wiring impedances. Typically, before compensation the real part of the impedance differs by no more than 0.3% from $|Z|$ and after compensation by no more than 0.001%. To correct the data for the double-layer capacitance due to the electrode polarization, the conductivity is extrapolated to infinite frequency using a sixth-order $1/f$ polynomial, assuming that the electrode polarization impedance is in series with the sample one [19]. Each conductivity measurement is carried out at thermal equilibrium. The dissipated electrical power with a 50 mV excitation amplitude is less than $2 \mu\text{W}$ and does not modify the sample temperature over the measuring time. At thermal equilibrium, no temporal drift of the conductivity was observed over periods of at least one hour. The absolute precision of the measurements is 0.1%. The reproducibility was found to be better than 0.001%. The studied temperature range was $1 \times 10^{-5} < \tau < 3 \times 10^{-2}$ with $\tau = (T - T_c)/T_c$, the reduced temperature (Table I). The critical temperature T_c was determined as the temperature at which the transmission of the laser beam falls to zero. Below T_c , a

TABLE I. Critical coordinates of the ionic mixtures studied and the parameter values of the fits to the VFT regular conductivity $\Lambda_{\text{VFT}} = A \exp[-B/(T - T_0)]$. x_m : critical salt mole fraction; T_c : critical temperature; Λ_c : conductivity value at T_c ; $\Delta\Lambda_c = \Lambda_c - \Lambda_{\text{VFT}}(T_c)$.

Mixture	x_m	T_c (K) (± 2 mK)	Λ_c (mS cm $^{-1}$) ($\pm 4 \times 10^{-2}$)%	$-\Delta\Lambda_c/\Lambda_c$ (%)	A (ms cm $^{-1}$) ($\pm 1\%$)	B (K) ($\pm 1\%$)	T_0 (K) ($\pm 1\%$)	VFT temperature range $\Delta T = T - T_c$ (K)
TBAP + DD	0.147	334.384 ₂	0.4946 ₀	1.42	7.91 ₉	160.15	276.34	3.5 < ΔT < 8.9
TBAP + (92.5% DD + 7.5% BD)	0.149	325.656 ₅	0.4265 ₀	2.15	33.97 ₅	389.49	236.25	6.4 < ΔT < 17.7
TBAP + (85% DD + 15% BD)	0.150	317.782 ₀	0.3549 ₅	2.65	81.87 ₀	560.34	214.30	9.3 < ΔT < 25.5
TPAP + BD	0.145	331.901 ₅	0.9232 ₁	0.42	152.51 ₀	520.96	229.81	2.8 < ΔT < 11.4

change of the electrical conductivity due to the phase separation is observed. To reduce the concentration gradients in the sample, the fluid height was kept to ≈ 1 cm. No concentration gradient induced by gravity or convection was noticed within the measuring accuracy down to $T_c + 2$ mK. In this temperature range, the measurements are reproducible by either increasing or decreasing the temperature [20].

In an extended temperature range above T_c , a pure Arrhenius law fails to describe the measured specific conductivity Λ . The Vogel-Fulcher-Tammann (VFT) law [21] $\Lambda_{\text{VFT}} = A \exp[-B/(T - T_0)]$, valid for highly concentrated electrolytes [22], fits well the conductivity data far from T_c (Table I). Figure 1 shows the linearized VFT equation [23] $(d \ln \Lambda_{\text{VFT}}/dT)^{-1/2} = B^{-1/2} (T - T_0)$ versus temperature together with the experimental data. Deviations from the VFT temperature dependence can be seen clearly for $T < T_c + 3$ K to $T_c + 10$ K. The amplitude of the deviation depends on the solvent and increases as

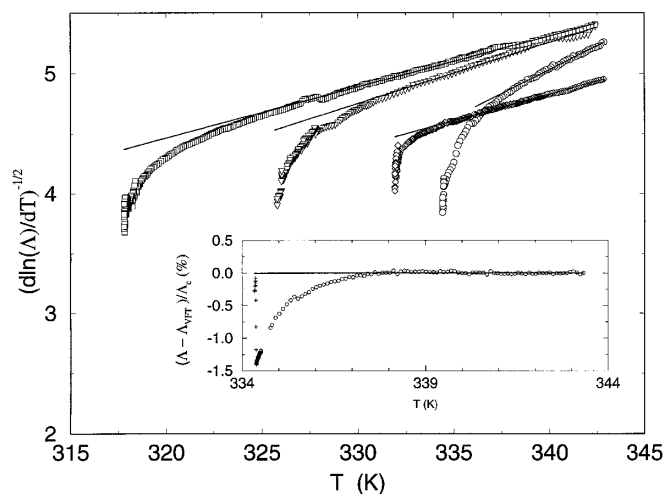


FIG. 1. Electrical conductivity Λ in a $(d \ln \Lambda / dT)^{-1/2}$ vs T representation for mixtures of tetra-*n*-butylammonium picrate (TBAP) in the following: (○) 1-dodecanol (DD); (◇) 1,4-butanediol (BD); (▽) mixture of (92.5% DD + 7.5% BD); (□) mixture of (85% DD + 15% BD). The salt concentrations are given in Table I. The straight lines are the VFT temperature dependent conductivities (see Table I). Inset: conductivity anomaly of TBAP in DD. (○) one-phase region; (+) phase-separated mixture. Λ_{VFT} : VFT temperature dependent conductivity; Λ_c : conductivity value at T_c .

T_c is approached. As shown in the inset, the amplitude $[(\Lambda_c - \Lambda_{\text{VFT}}(T_c))/\Lambda_c]$ is $\approx 1.4\%$ for TBAP in DD, where Λ_c is the finite value of the conductivity at T_c . The sharp increase of Λ below T_c corresponds to the phase separation of the mixture. A conductivity anomaly is observed for all the studied mixtures with an amplitude at T_c ranging from 0.4% to 2.7% (Table I). It might be attributed to a critical conductivity anomaly.

Along a path of constant critical concentration, the temperature dependence of the electrical conductivity may be written as $\Lambda = \Lambda_{\text{reg}}(\tau) + \Lambda_{\text{crit}}(\tau)$. $\Lambda_{\text{reg}}(\tau)$ is the regular part of the conductivity for which we assume a VFT temperature dependence down to T_c . $\Lambda_{\text{crit}}(\tau) = \Delta\Lambda(\tau) + \Lambda_0\tau^\theta$ is the critical contribution. $\Delta\Lambda(\tau)$ is an analytical term and $\Lambda_0\tau^\theta$ is the critical term with Λ_0 , the critical amplitude, and θ , the critical exponent. According to [17], $\Lambda_{\text{crit}}(\tau) = \Delta\Lambda_c + B_{\text{crit}}\tau + \Lambda_0\tau^{1-\alpha}$, where $\Delta\Lambda_c$ is the finite value of the critical part of the electrical conductivity at T_c (Table I), and B_{crit} is the amplitude of the linear term induced by the critical fluctuations [24].

The data have been fitted in the asymptotic range to $\Lambda = \Lambda_{\text{reg}}(\tau) + \Delta\Lambda_c + B_{\text{crit}}\tau + \Lambda_0\tau^\theta$, with the exponent θ free. When $B_{\text{crit}} = 0$, hence, without assuming the validity of [17], the asymptotic value of the effective exponent θ_{eff} computed as a function of the fitting temperature interval is found close to 2β in the range $\tau < 10^{-3}$ (see Fig. 2): For TBAP in BD, $\theta_{\text{eff}} = 0.61 \pm 0.05$ and,

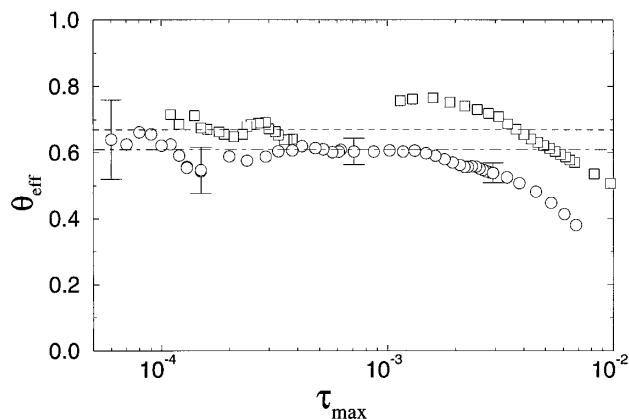


FIG. 2. Effective exponent θ_{eff} computed in the temperature interval $[\tau_{\text{min}} \approx 10^{-5}, \tau_{\text{max}}]$, as a function of τ_{max} : (○) TBAP in BD; (□) TBAP in DD.

TABLE II. Results of the fit of the specific electrical conductivity for the critical binary mixtures (TBAP + BD) and (TBAP + DD) to Eq. (1). Data in parentheses are fixed in the fit. The uncertainties denote 1 standard deviation.

Fit	Mixture	θ	Λ_c (mS cm ⁻¹)	Λ_0 (mS cm ⁻¹)	B_{crit} (mS cm ⁻¹)	A (mS cm ⁻¹)	B (K)	T_0 (K)	Maximum deviation
1	TBAP + BD	(0.89)	(0.9232 ₁)	2.921 ± 0.06	3.371 ± 0.06	(152.51 ₀)	(520.96)	(229.81)	±0.02%
2	TBAP + BD	(0.89)	0.9234 ₈	2.787 ± 0.51	4.932 ± 0.50	158.65 ₅	519.94	230.09	±0.015%
3	TBAP + DD	(0.89)	(0.4946 ₀)	4.074 ± 0.07	5.137 ± 0.08	(7.91 ₉)	(160.15)	(276.34)	±0.07%
4	TBAP + DD	(0.89)	0.4944 ₃	4.822 ± 1.60	8.091 ± 3.0	9.11 ₆	161.88	278.67	±0.05%

for TBAP in DD, $\theta_{\text{eff}} = 0.67 \pm 0.05$. Variation of the critical parameters T_c and $\Delta\Lambda_c$ within the experimental uncertainty leads to a change of θ_{eff} within the errors bars. When the linear temperature dependent term $B_{\text{crit}}\tau$ is taken into account, an asymptotic value for θ_{eff} could not be determined accurately for $\tau < 10^{-3}$.

In the whole temperature range $1 \times 10^{-5} < \tau < 3 \times 10^{-2}$, corrections to scaling should be taken into account: Far from T_c , the critical part should vanish in order to recover only the regular contribution. To make this constraint somewhat in agreement with the theoretical knowledge on the corrections to scaling [25], the following relation has been used to describe the behavior of the conductivity in the whole temperature range,

$$\Lambda = \Lambda_{\text{reg}}(\tau) + \Delta\Lambda_c + \tau\{\Lambda_0\tau^{(\theta-1)}[(1 + \alpha_1\tau^\Delta)/(1 + \alpha_2\tau^{2\Delta})]^Y + B_{\text{crit}}\}. \quad (1)$$

The term $[(1 + \alpha_1\tau^\Delta)/(1 + \alpha_2\tau^{2\Delta})]^Y$ generates the usual confluent correction-to-scaling terms $\alpha_1\tau^\Delta$ and $\alpha_2\tau^{2\Delta}$ when $\tau \rightarrow 0$. $\Delta = 0.504$ is a universal exponent [16]. For $\tau \gg 1$, the critical contribution must vanish in order to obtain the regular part which has been shown to be well represented by the VFT law. Hence, in the limit $\tau \rightarrow \infty$, $\{\Lambda_0\tau^{(\theta-1)}[(1 + \alpha_1\tau^\Delta)/(1 + \alpha_2\tau^{2\Delta})]^Y + B_{\text{crit}}\} = 0$, from which follow the two conditions $Y = (\theta - 1)/\Delta$ and $\Lambda_0(\alpha_1/\alpha_2)^Y + B_{\text{crit}} = 0$. In Eq. (1), the critical exponent θ was fixed either to $(1 - \alpha)$ or 2β . The best fit is obtained with $\theta = (1 - \alpha)$ for both binary mixtures (Table II). No significant changes of the VFT parameters are observed when they are let free (fits 2 and 4). The homogeneously distributed residuals are shown in Fig. 3(a) from a fit of the conductivity data for the critical mixture (TBAP + BD). A fit with $\theta = 2\beta$ is less satisfactory as it can be seen from the larger deviations of the residuals [Fig. 3(b)].

In conclusion, we have shown that the electrical conductivity anomaly from two critical mixtures of tetra-*n*-butylammonium picrate in pure 1-dodecanol and 1,4-butanediol solvents, as well as in mixtures of both solvents, is well assessed and reproducible [26]. This anomaly is observable already at $\tau \leq 10^{-2}$ and tends to a finite value at T_c . A possible contribution to the conductivity of the Maxwell-Wagner frequency-dependent

dielectric dispersion effect induced by the concentration fluctuations [14] is estimated to be less than 3% of the critical contribution for $\tau < 10^{-5}$ and is assumed to be negligible. Close to T_c , quasistatic measurements of the shear viscosity in ionic mixtures show a divergence as large as 30% of the background value at $\tau = 10^{-5}$ [8] with a small value exponent $\cong 0.04$ [27]. These values would exclude a coupling between the conductivity anomaly and the divergence of the shear viscosity [15,28], although the regular conductivity should depend on the frictional resistance of the solvent molecules and the surrounding ions [29].

A simple asymptotic analysis including the VFT-like regular conductivity leads to a critical exponent θ close to 2β . However, when the analysis is performed in the whole temperature interval, a $\theta = (1 - \alpha)$ exponent fits better the data. The criticality of ionic systems might be described by the restricted primitive model (RPM) consisting of an ensemble of an equal number

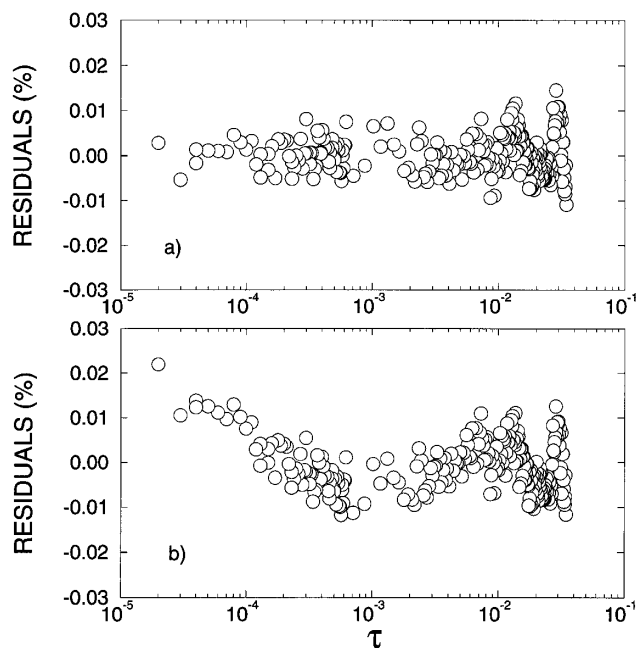


FIG. 3. Residuals of the fit in the whole temperature range of the specific electrical conductivity for the critical mixture (TBAP + BD) to Eq. (1). (a) $\theta = (1 - \alpha)$, fit 2, Table II; (b) $\theta = 2\beta$.

of positively (+ q) and negatively ($-q$) charged spheres of same size, in a medium with a dielectric constant ϵ , and interacting via a Coulomb potential. The RPM shows a critical point with reduced critical coordinates at $c_c^* \approx 0.028-0.070$ and $T_c^* \approx 0.049-0.057$ [30]. c_c^* is the critical concentration of free ions scaled by the ion diameter a , and T_c^* is the critical temperature scaled by the Coulomb energy $q^2/4\pi\epsilon_0\epsilon a$ between two ions in contact, where ϵ_0 is the vacuum permeability [30]. The reduced critical coordinates of (TBAP + DD) and (TBAP + BD) are $\{c_c^*, T_c^*\} = \{0.023, 0.05\}$ and $\{0.125, 0.335\}$, respectively [20]. Therefore, the system (TBAP + DD) would belong to the Coulombic class, whereas the mixture (TBAP + BD) should be similar to aqueous solutions of organic salts [31]. The similarity of the critical anomaly of the two binary mixtures might be attributed to the strong screening of the free ions as shown by the small value of the Debye length $\approx 2.1 \text{ \AA}$ in both systems [20].

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