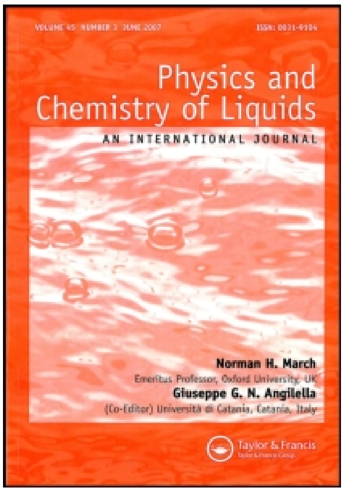

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Coexistence curves of electrical conductivity in critical solution: isobutyric acid-water with added ions

Emna Cherif[a]; Moncef Bouanz[a]
[a] Laboratoire de Physique des Liquides et d'Optique non Linéaire, 1060 Tunisia

To cite this Article Cherif, Emna and Bouanz, Moncef(2006) 'Coexistence curves of electrical conductivity in critical solution: isobutyric acid-water with added ions', Physics and Chemistry of Liquids, 44: 4, 419 — 429
To link to this Article: DOI: 10.1080/00319100600801900
URL: http://dx.doi.org/10.1080/00319100600801900

Physics and Chemistry of Liquids
Vol. 44, No. 4, August 2006, 419–429

Coexistence curves of electrical conductivity in critical solution: isobutyric acid–water with added ions

EMNA CHERIF and MONCEF BOUANZ*

Laboratoire de Physique des Liquides et d'Optique non Linéaire, Département de Physique,
Faculté des Sciences de Tunis, 1060 Tunisia

(*Received 2 May 2006; in final form 12 May 2006*)

Comprehensive results of temperature (T) studies of electrical conductivity (σ) in the one-and-two phase regions of the binary fluid mixture of isobutyric acid–water (IBAW) with X M[KCl] at various critical concentrations are presented. A strong asymmetry of the coexistence curves as determined causes a strong violation of the law of rectilinear diameter. The obtained critical anomalies in the homogeneous phase $\sigma_{\text{crit}}(T)$ or the diameter of the $\sigma_{\text{d}}(T)$ are associated with the same critical exponent $\theta = 1 - \alpha \approx 0.88$, where α is the specific heat critical exponent. For the mixture with critical composition, the two phase regions show a concentration behavior with $\sigma_{\text{l}} - \sigma_{\text{u}} \approx |-t|^{\beta}$. The phase transition region shifts as a function of the salt concentration. The effective critical exponent $\beta^* = (0.264–0.296)$ is neither compatible with the Ising value $\beta = 0.325$ nor with the Fisher renormalized value ~0.365.

Keywords: Electrical conductivity; Coexistence curves; Electrolytes; Critical point and critical exponents; Isobutyric acid

1. Introduction

The transport properties of ionic binary liquids exhibit intriguing anomalies near a consolute point [1–3], which are presumably due to the presence of large critical fluctuations in the concentration. However, these ions can be considered as impurities which behave as a third component in the liquid mixture. The influence of such impurities is known to significantly affect both the temperature and the concentration of the critical point [4, 5]. It modifies the behavior of several thermodynamic and transport properties. Researchers have also used impurities to shift the critical point when measuring surface wetting [6, 7].

In the field of phase transitions, most of the liquid mixture near the consolute point, belongs to the universality class of three-dimensional (3D) Ising model. The critical exponent β is predicted to be 0.325 from renormatization group theory [8], 0.328 from series expansion [9] and 0.500 from mean-field theory [10].

---

*Corresponding author. Email: Moncef.Bouanz@fsb.rnu.tn

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100600801900

When the salt is added to the binary mixture of isobutyric acid–water (IBAW), the exponent β of the coexistence curve is not compatible with the Ising model [11,12]. The coexistence curve in mass densities takes a new shape and is characterized by a new effective critical exponent $\beta^* = 0.266$ [12].

The determination of critical conductivity σ ($\Omega^{-1}\,\mathrm{cm}^{-1}$) of electrolytes was developed in our laboratory for an ionic critical mixture. Our experiments have been made both in the vicinity of, and far away from, the critical point. The critical behavior of binary mixtures with added ions is an area of active experimental [13] and theoretical [14,15] research. The experimentally investigated binary ionic mixtures show either a 3D Ising criticality [16, 17], a mean-field critical behavior [18], or a crossover from mean-field to Ising type criticality [19, 20].

The purpose of this work is to confirm the existence of a singular contribution to σ [21], and to measure the critical exponent θ [22], which characterizes this singularity. We find that in the one-phase region, the conductivity of these mixtures does indeed contain a term of the form $\sigma_{\mathrm{sig}} = t^{\theta}$, where $t = (T - T_{\mathrm{c}})/T_{\mathrm{c}}$ and T_{c} is the critical temperature.

The critical exponent θ of the conductivity anomaly is found experimentally between $(1-\alpha)$ and 2β [23–26] where $\beta = 0.326$ and $\alpha = 0.11$ are the usual 3D Ising-like exponent [27]. A $\theta = (1-\alpha)$ exponent should be attriuted to short-range fluctuations [28].

A percolation model for the transport of the ions would yield $\theta = 2\beta$ [13, 14] scattering of ionic impurities by concentration fluctuations should give the critical exponent ν of the correlation length; $\nu = 0.630$ [23].

2. The coexistence curves

In binary mixtures, the order parameter M can be chosen as the difference $\mathrm{M}_{\mathrm{u,l}} = \sigma_{\mathrm{u,l}} - \sigma_{\mathrm{c}}$ of the electrical conductivity $\sigma_{\mathrm{u,l}}$ of one component and its critical value σ_{c}. The subscripts (u) or (l) refer to the phase above or below the meniscus in gravity.

The electrical conductivity of the upper and lower phases can be written as [29]:

$$\sigma_{\mathrm{u,l}} = \sigma_{\mathrm{c}} \pm B_{\sigma} t^{\beta}\left(1 + b_{\sigma} t^{\Delta}\right) + F_{\sigma} t + G_{\sigma} t^{1-\alpha} + H_{\sigma} t^{2\beta} + \cdots \tag{1}$$

The sign ± corresponds to the upper (+) or lower (−) phases. In equation (1), t is the reduced temperature, while $\beta = 0.325 \pm 0.002$, and $\Delta = 0.52 \pm 0.03$ are universal critical exponents of the 3D Ising-model universality class [30–32].

The fraction σ_{c} is the first critical composition, B_{σ} is the coexistence curve amplitude, b_{σ} is the first order correction to scaling amplitude. F_{σ}, G_{σ}, and H_{σ} are nonuniversal amplitudes.

Generally, the accuracy is not good enough to distinguish between the behaviors of t, $t^{1-\alpha} = t^{0.89}$ and $t^{2\beta} = t^{0.65}$.

Therefore, one can introduce an effective exponent ω with amplitude E_{σ}, whose range will be $\omega = [0.5, 1]$. The equation (1) can be rewritten as:

$$\frac{1}{2}(\sigma_{\mathrm{u}} - \sigma_{\mathrm{l}}) = B_{\sigma} t^{\beta}\left(1 + a_{\sigma} t^{\Delta}\right) \tag{2}$$

$$\frac{1}{2}(\sigma_{\mathrm{u}} + \sigma_{\mathrm{l}}) = \sigma_{\mathrm{c}} + E_{\sigma} t^{\omega} \tag{3}$$

In a previous work [33], we studied extensively the critical behavior of the binary-fluid (IBAW) with added (K^+, Cl^-) ions. We have performed the first precise measurement of the coexistence curve of this mixture (IBAW) near its consolute point in the precise of various amounts of KC1 salt. We have detected a difference in the critical temperature T_c when the salt is added, the shift of T_c is positive and is dependent on the number of KC1 moles per kilogram of mixture (M). The coexistence curve of the electrolyte mixture takes a new shape and is characterized by a new effective critical exponent β_{eff} of the order parameter σ. The value obtained for:

$$\beta_{\text{eff}} = \frac{\partial \log \Delta\sigma}{\partial \log t} \tag{4}$$

is outside of the field of the Fisher renormalized value. It has been found to show a sharp and nonmonotonic crossover from Ising to mean-field behavior [34, 35].

The purpose of this work is to carry out an exhaustive electrical conductivity σ study of the highly concentrated critical binary ionic mixtures of the IBAW + KCl system, in the one and two phase regions, and for three different salt concentrations.

The article is organised as follows: section 2 shows a rapid survey of the theoretical situation of coexistence curves. The experimental methods used in this work are discussed in section 3. The data collection and analysis techniques we used are treated in section 4, and conclusions are given in section 5.

3. Experimental

The isobutyric acid (IBA) was purchased from Riedel de Haën (Germany). The purity was stated to be 99.99 mol%.The main impurity is probably water. The water used was purified by deionization and triple distillation and had a specific conductivity of about $10^{-6}\,\Omega^{-1}\,\text{cm}^{-1}$. This gave a critical separation temperature, which is a good indication of purity, of 26.945°C which compares favorably with 26.948°C for the data of [11]. The guaranteed purity of the KCl salt (Merck, Germany) is better than 99.5%. In this mixture, this salt can be totally dissolved. All electrolytes were prepared from weighed amounts of the pure components. The weight was obtained with a resolution of 0.1 mg.

The electrical conductivity measurements were carried out using a (Konductometer 702 and cell type ZU 6985) conductometer, with a conductivity cell consisting of fixed spacing stainless steel circular electrodes. The cell had a conductivity constant of $41\,\text{cm}^{-1}$ when filled with 100 mL of the sample. The cell constant changed by no more than 0.1%. The calibration of the cell was made by using liquids of known electrical conductivity with NaCl solution. The relative measurement of temperature in the cell can be verified as the second electrode which detected the numerical value within 0.02°C. The temperature difference between the cell and the bath does not exceed 0.03°C. The temperature of the cell was varied from to $T - T_{\text{PS}} = 0.05°\text{C}$ in steps of 0.20°C and the overall accuracy of the temperature determination was 0.02°C where T_{PS} is the phase separation temperature along phase diagram of the critical mixture. The critical temperature T_C is the top of T_{PS}. The conductivity measurements are believed to be reproducible up to 0.01% $10^{-3}\,\Omega^{-1}\,\text{cm}^{-1}$. The cell containing the solution was immersed in a thermally stabilized water bath with good thermal regulation. The long-term stability of the cell was better than 20 mK. The temperature was measured using a quartz thermometer (HP 2804 A) giving a resolution of ±0.1 mK, and which was calibrated on an absolute scale within 0.01 K.

4. Data collection and analysis

We measured the electrical conductivity of three different solutions: IBAW, IBAW $+ 5 \cdot 10^{-4}$ M [KCl], IBAW $+ 5 \cdot 10^{-3}$ M [KCl], with versus temperature above and below the separation temperature T_t at each concentration X of (IBA) along the coexistence curve. The conductivity data for these solutions are shown in figure 1a, b, c. The data cover a good range of temperature above and below T_t. The lower limit was considered adequate for the main purpose of this study. Data were taken at the higher temperature in order to establish the temperature dependence of these transport properties well away from Tc, the separation temperature for the critical concentration X_c, $T_c = T_t$ ($X = X_c$, X_c is the critical mole fraction of IBAW + KCl):

$$\text{IBAW}: X_c = 38.89\%;\ T_c = 26.945^\circ\text{C}$$

$$\text{IBAW} + 5.10^{-4}\,\text{M[KCl]}: X_c = 39.90\%;\ T_c = 27.085^\circ\text{C}$$

$$\text{IBAW} + 5.10^{-3}\,\text{M[KCl]}: X_c = 42.63\%;\ T_c = 28.488^\circ\text{C}$$

The critical temperature Tc and the critical composition Xc increased linearly with the salt concentration. The effect of KCl salt on the shift of the critical point of this mixture (IBAW), was extensively studied in a previous work [12].

4.1. *β determination*

According to the theory of critical phenomena, the difference in the order parameter along the coexistence curve can be expressed as:

$$(\sigma_u - \sigma_l) = B_\sigma t^\beta \left(1 + B_1 t^\Delta + B_2 t^{2\Delta} + \cdots .\right) \tag{5}$$

where β denotes the critical exponent of the order parameter in the limit $t \to 0$ and Δ is the Wegner correction exponent.

The experimental data were analyzed using equation (5) in the temperature range where Wegner expansion is considered as valid, to determine the limiting value of the universal exponent β and the system dependent parameters B, B_1, and B_2.

A. The pure IBAW mixture. In order to determine the effect of salt (ions) on the critical behavior of the mixture, it is necessary to investigate the coexistence curve of the pure IBAW mixture.

The difference in electrical conductivity of coexisting phases in the restricted range $t < 10^{-2}$ was first fitted to equation (5) by adjusting the parameters Tc, B, and, with all $B_i = 0$ (no Wegner corrections). The results are listed as fit A in table 1. A good representation, $\chi^2 = 10^{-3}$, was obtained in that restricted temperature range, despite the approximation of neglecting Wegner corrections. The optimized adjustable parameter

Table 1. Parameters determined from analyzing the coexistence curve of isobutyric acid and water (IBAW pur). The electrical conductivity is fitted to equation (5).

Fits	T_c^{exp} (K)	T_c^{fit} (K)	β	B (mS/cm)	B$_1$ (mS/cm)	B$_2$ (mS/cm)	$\chi^2 \cdot 10^3$
A	300.110	300.041	0.325	2.805	–	–	1.07
B	300.110	300.116	0.326	1.981	2.001	–	2.1
C	300.11	300.116	0.326	2.441	9.230	−5.106	3.4

Table 2. Parameters in equation (5) deduced for the electrolyte "IBAW + KCl" salt "at different concentrations.

Systems	T_c^{fit} (K)	β	B (mS/cm)	B$_1$ (mS/cm)	B$_2$ (mS/cm)	$\chi^2 \cdot 10^3$
IBAW + 5.10^{-4} M [KCl]	300.119	0.264	1.999	–	–	1
	299.892	0.312	2.414	1.388	−7.017	2
IBAW + 5.10^{-3} M [KCl]	301.504	0.296	4.495	–	–	3
	301.594	0.534	8.828	15.270	−116.950	8

$T_c^{fit} = (300.041 \pm 0.006)$ K was very close to the corresponding experimental value, $T_{exp}^{c} = (300.110 \pm 0.010)$ K, and consistent with a slightly off-critical sample. The value obtained for the critical exponent $\beta = 0.329 \pm 0.010$ shows consistency with its Ising value $\beta = 0.325$. Since the limiting asymptotic behavior is undoubtedly nonclassical, $\beta = 0.326$, $T_c^{fit} = (300.116 \pm 0.014)$ K were fixed in fits B and C, and one and two Wegner terms were included, respectively, in an unsuccessful attempt to describe the whole experimental range. Both fits give very strong systematic deviation and high χ^2 values, as shown in table 1.

B. Coexistence curve of isobutyric acid–water with (KCl) salt. The results of the fits to the difference in the electrical conductivity of coexisting phases $\Delta\sigma = \sigma_u - \sigma_l$; where σ_u and σ_l are electrical conductivity of the upper and lower coexisting phases at each temperature, are given in table 2.

Two series of fits have been performed to determine β, either with a_σ imposed ($B_i = 0$) or with B_i free in equation (5).

The fit of the simple scaling form, equation (5), where B, T_c, and β are free, yields an effective critical exponent β of 0.264 and 0.296. The values are lower than we expect for the Ising model. When the correction term is added (B_i free in equation 5), a significantly better fit is obtained but the value of β^* is higher than the values of β^*obtained when B_i is set to zero (0.312, 0.534 and), see table 2.

Contrary to the theoretical expectation, we did not find renormalized Ising values for β^*. This exponent is slightly smaller than the theoretical Ising value and the Fisher renormalized exponent. However, the KCl salt is not to be considered as a third component in the mixture of IBAW.

The binary mixture with added salt belongs to a new class of universality related to the effects of the electrostatic field of the ions [12].

4.2. *Diameter of coexistence curve*

For the diameter of coexistence curve, the theory of critical phenomena predicts a temperature dependence given by:

$$\sigma_{\mathrm{d}} = \frac{\sigma_{\mathrm{l}} + \sigma_{\mathrm{u}}}{2} = \sigma_{\mathrm{c}} + D_1 t + D_2 t^{1-\alpha}\left(1 + D_3 t^{\Delta} + \cdots\right) + D_4 t^{2\beta} \tag{6}$$

The second term on the right-hand side is the regular linear dependence while the third represents the nonregular contribution, with its correction to simple scaling as given by a Wegner expansion. The last term in equation (6) takes into account the effect on the diameter of an incorrect choice of order parameter.

In the present analysis, the nonlinearity of the diameter, as shown in figure 1a, b, c, imposes of a nonregular contribution into equation (6), either a $1-\alpha$ or 2β term.

A. The pure IBAW mixture without ion. Therefore, the simples representations (fits I and II) included one singular term. The critical temperature was fixed to its experimental value and the 3 parameters (σ_{c}, D and D_2 for fit I and σ_{c}, D and D_4 for fit II) were adjusted to minimize χ^2. A slightly better performance was obtained for fit I, with a $(1-\alpha)$ term, than for fit II, according to the values of χ^2. As a consequence, the choice of the electrical conductivity as the parameter for representing the critical behavior seems to be justified.

Fit III was performed leaving the value of the exponent (either $1-\alpha$ or 2β) as a free parameter. In accordance to the results of fits I and II, the obtained value matches very closely the value of $1-\alpha=0.88$. In fit IV, both nonregular terms were included, and the values of D_2 and D_4 were adjusted (together with σ_{c} and D), without any improvement in the goodness of the fit.

Finally, fit V explores the possibility of improving fit I by adding a Wegner correction term, introducing the D_3 coefficient in equation (6) as an adjustable parameter.

The results of the fits (I, II, III, IV, V) obtained from equation (6) for coexisting phase are given in table 3.

B. Systems IBAW with KCl salt. The results of the fits to the diameter in the electrical conductivity of coexisting phases are given in table 4.

Two series of fits have been performed to determine α, with all imposed ($D_3=0$ and $D_4=0$) in equation (6).

The fit of the equation (6) shows that the exponent $\alpha=0.11$ is compatible with the renormalized group theory.

The factor D_2 that measures the amplitude of the critical anomaly in the electrical conductivity increases when the concentration of the added salt increases.

The factor D_1 can have also anomaly due to the importance of the size of the fluctuations concentration.

The factor D_1 is compatible in absolue value to the thermal variation for the case of all electrolyte systems. In the literature, the factor D_1 can present only a fraction of $(\delta\,\sigma/\delta\,T)$ (equation 7).

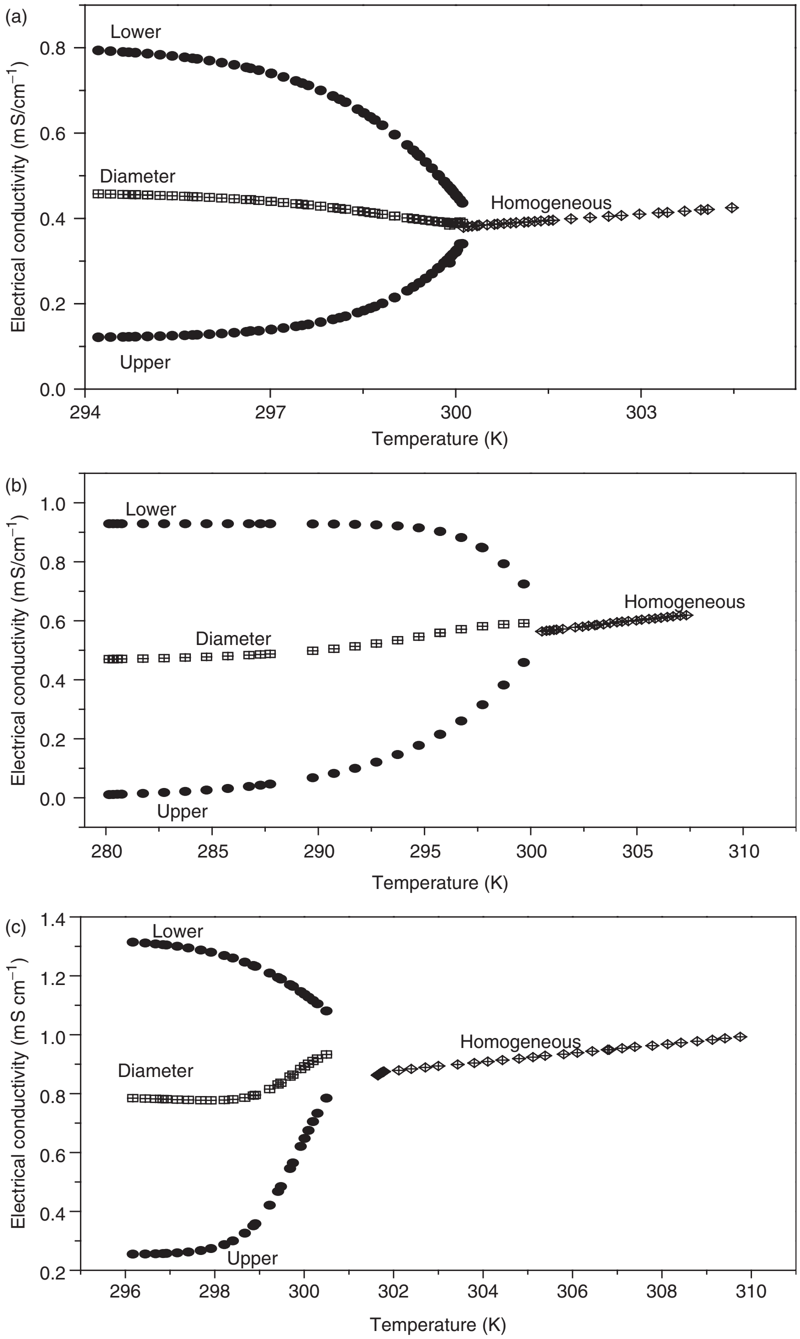

Figure 1. Coexistence curve in electrical conductivity for IBAW with successive amounts of a salt (KCl) added. (a) (IBAW) pure; (b) IBAW + $5 \cdot 10^{-4}$ M [KCl]; (c) IBAW + $5 \cdot 10^{-3}$ M [KCl]. The diameter is the average of electrical conductivity above and below the meniscus.

Table 3. Results to the fit of equation (6) for the coexistence curve diameter of IBAW.

Fits	σ_c (mS/cm)	D_1 (mS/cm)	D_2 (mS/cm)	D_3 (mS/cm)	D_4 (mS/cm)	$1-\alpha$	2β	$\chi^2 \cdot 10^3$
I	0.381	−11.163	9.523	–	–	0.88*	–	8
II	0.380	−0.429	–	–	1.175	–	0.65*	10
III	0.381	−0.601	0.106	–	1.212	0.88	0.65	10
IV	0.395	−70916	64.163	–	−7.253	0.88*	0.65*	1
V	0.390	70.982	−27.937	3.645	–	0.88*	–	0.9

Table 4. Results to the fit of equation(6) with all imposed ($D_3 = 0$ and $D_4 = 0$) of the coexistence curve diameter of IBAW + XM [KCl].

Systems	σ_c (mS/cm)	D_1 (mS/cm)	D_2 (mS/cm)	$1-\alpha$	$\chi^2 \cdot 10^3$
IBAW + 5.10^{-4} M [KCl]	0.624	11.173	−9.914	0.884	4
IBAW + 5.10^{-3} M [KCl]	1.284	273.240	−185.701	0.880	4

4.3. *($1-\alpha$) determination*

A. Electrical conductivity near the critical point. In this work, we present the results of the electrical conductivity of the binary system (IBAW) in the presence of the (K^+, Cl^-) ions to the neighborhood of the critical region in the homogeneous phase of the systems.

Along a path of constant critical concentration, the temperature dependence of the electrical conductivity in the homogeneous phase may be written as [21]:

$$\sigma(t) = \sigma_{\text{crit}}(t) + \sigma_{\text{reg}}(t) \tag{7}$$

where $t = (T - T_c)/T_c$ is the reduced temperature, σ_{reg} is the regular part of the electrical conductivity for which we assume a Vogel–Fulcher–Tammann (VFT) temperature dependence down to T_c,. σ_{crit} is the critical term of conductivity.

Figure 2 presents the critical conductivity σ_{crit} as a function of the reduced temperature (t) for the four electrolytes studies: (IBAW), (IBAW + $5 \cdot 10^{-4}$ M [KCl]), (IBAW + $5 \cdot 10^{-3}$ M [KCl]), the one-region phase presents a critical anomaly in keeping with [21].

B. Determination of the critical parameters. This anomaly can be explained by the critical exponent $(1-\alpha)$ where α is the heat capacity exponent [22].

The electrical conductivity to the neighborhood of the critical point can be written as:

$$\sigma_{\text{crit}} = \sigma_{\text{cr}} + \sigma_1 t + \sigma_2 t^{1-\alpha}\left(1 + a\, t^{\Delta} + b t^{2\Delta} + \cdots\right) \tag{8}$$

where σ_{cr} is the critical conductivity limit. σ_1 and σ_2 are the amplitudes induced by the critical fluctuations [22] and that are comparable to the thermal variation ($\delta\sigma_{\text{crit}/}\delta t$) for the case of all the studied systems. To the immediate neighborhood of the critical point, the thermal coefficient σ_2 can also have an anomaly because of the important size of the concentration fluctuations. a and b are the amplitudes of the correction to simple scaling terms, and α is the critical exponent that characterizes the divergence of the heat

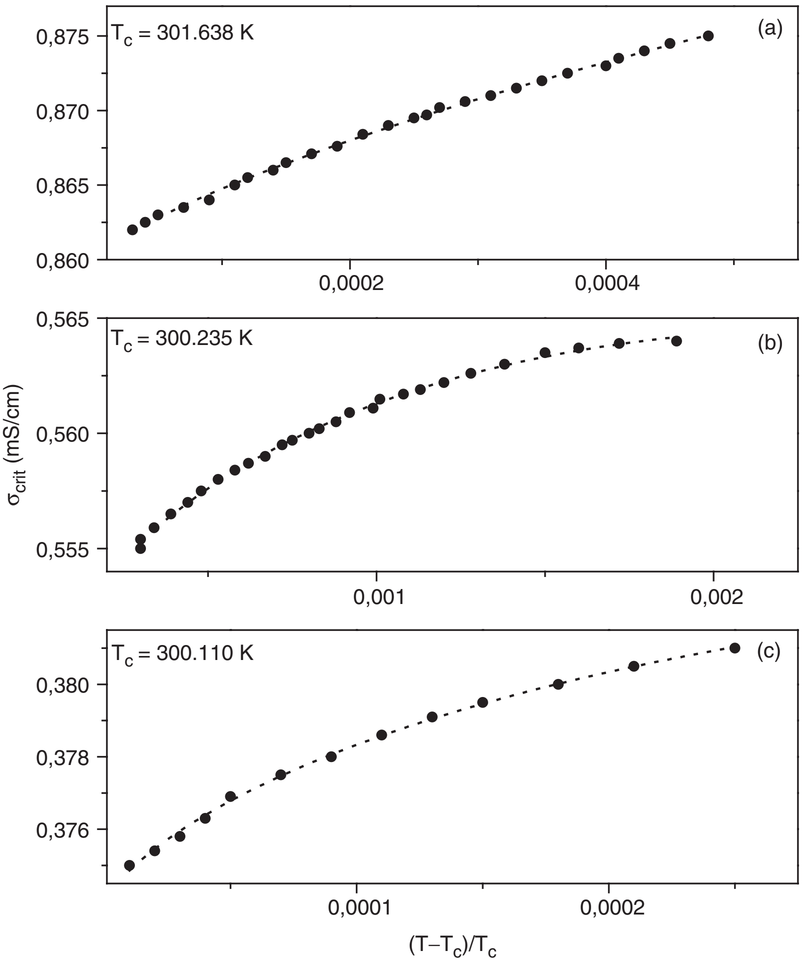

Figure 2. Variation of the critical conductivity σ_{crit} as a function to the reduced temperature $t = (T - T_c)/T_c$ for systems IBAW with successive amounts of a salt (KCl) added. (a) (IBAW) pure; (b) IBAW + $5 \cdot 10^{-4}$ M [KCl]; (c) IBAW + $5 \cdot 10^{-3}$ M [KCl].

Table 5. Parameters in equation (8) for the electrolyte "IBAW + KCl" salt "at different concentrations.

Systems	σ_{cr} (mS/cm)	$/\sigma_1/$(mS/cm)	σ_2(mS/cm)	$1-\alpha$	$\chi^2 \cdot 10^3$
IBAW pure	0.380	13.281	19.986	0.881 ± 0.09	1.7
IBAW + 5.10^{-4} M [KCl]	0.549	51.435	29.744	0.889 ± 0.2	1.6
IBAW + 5.10^{-3} M [KCl]	0.860	59.607	40.448	0.894 ± 0.2	1.2

capacity and the thermal expansivity near T_c. Table 5 gives the parameters of equation (8) that best fit the experimental results. Within the experimental uncertainty, we have been able to fit the experimental data using $\alpha = 0.11 \pm 0.01$, thus very close to the theoretical value for the Ising model. No correction-to-scaling terms were significant in equation (8). It must be stressed that obtaining α from electrical conductivity data is more difficult than from heat capacity, thus no firm conclusions can be obtained about any possible crossover behavior of this critical exponent over the temperature range studied. However, when the mean-field value of α is used, systematic residuals well beyond the experimental uncertainty are obtained in the fits.

Table 4 deserves some comments:

- The results of the work show that in the neighborhood of the critical temperature T_c, the electrical conductivity presents a critical anomaly, whereas the transport properties of ions in binary liquids exhibit intriguing anomalies near a consolute critical point.
- The fit of the equation (8) shows that the exponent α is compatible with the renormalized group theory.
- The factor σ_2 that measures the amplitude of the critical anomaly in the electrical conductivity, increases when the concentration of the added salt increases.
- When the KCl salt is added at the concentration $5 \cdot 10^{-4}$ and $5 \cdot 10^{-3}$ mol per kilogram of mixture,$/\sigma_1/$ is higher in the system without ions. This increase is due to the solvatation of ions by water. It is obvious that the electrical conductivity depends well of solvation phenomenon in binary fluid. However, the coefficient σ_1 can be determined by the derivation of σ_{crit}, according to: $\sigma_1 = (\partial\sigma_{crit}/\partial T)x$.

4.4. *Extrapolation of the diameter of the coexistence curves*

In all coexistence curves, the diameter and the curves of electrical conductivity in the one-phase region ($T > T_c$) do not meet, except for the coexistence curve of the pure system. The difference in electrical conductivity $\Delta\sigma_c$ at the transition phase depends well on the concentration of (K^+, Cl^-) ions added to the critical system. Using the fits of the data to equations (7) and (9), the difference $\Delta\sigma_c = \sigma_c – \sigma_{cr}$ was found to be:

$$\Delta\sigma_c(\mathrm{IBAW}) = 0.001(\mathrm{mS/cm})$$

$$\Delta\sigma_c(\mathrm{IBAW} + 5.10^{-4}\,\mathrm{M[KCl]}) = 0.075(\mathrm{mS/cm})$$

$$\Delta\sigma_c(\mathrm{IBAW} + 5.10^{-3}\,\mathrm{M[KCl]}) = 0.460(\mathrm{mS/cm})$$

The increasing separation between the diameters ($T < T_c$) and the one-phase at the critical temperature indicates an increase in the critical composition.

5. Conclusions

We have performed the first precise measurement of the coexistence curve in electrical conductivity of (IBAW) near its consolute point in the presence of various amounts of KCl salt. The coexistence curve of the electrolyte mixture, takes a new shape and is characterized by a new effective critical exponent $\beta^* = (0.264–0.296)$. The value obtained for β^* is outside of the field of the Fisher-renormalized value.

We have shown that the electrical conductivity exhibits a critical anomaly in a rather extended temperature range $t < 10^{-2}$. The critical anomaly is well described dy the exponent $(1-\alpha)$ predicted by the theory of short-range fluctuations. The diameter of the $\sigma_d\,(T)$ is associated with the same critical exponent $\theta = 1-\alpha \approx 0.88$, where α is the specific heat critical exponent.

References

[1] M. Bouanz. *Phys. Rev., A*, **46**, 4888 (1992).
[2] M. Bouanz, A. Gharbi. *J. Phys. Cond. Matter.*, **6**, 4429 (1994).
[3] M. Bouanz. *J. Phys. II.*, **6**, 1571 (1996).
[4] C.S. Bak, W.I. Goldburg. *Phys. Rev. Lett.*, **23**, 1218 (1969).
[5] E. Bloeman, J. Thoen, W. Van Dael. *J. Chem. Phys.*, **75**, 1488 (1981).
[6] M.R. Moldover, J.W. Cahn. *Science*, **207**, 1073 (1980).
[7] O'D. Kwon and al. *Phys. Rev. Lett.*, **48**, 185 (1982).
[8] J.C. Le guillou, J. Zinn-Justin. *Phys. Rev. B.*, **21**, 3976 (1980).
[9] B.G. Nickel. In *Phase Trans, Cargese*, 1980, M. Levy, J.C. Le guillou, J. Zinn-Justin (Eds), Plenum, New York (1981).
[10] D. Beysens, M. Gbadamassi, M. Bouanz. *Phys. Rev. A.*, **28**, 2491 (1983).
[11] M. Bouanz, D. Beysens. *Chem. Phys. Lett.*, **231**, 105 (1994).
[12] A. Toumi, M. Bouanz. *Eur. Phys. J. E.*, **2**, 211 (2000).
[13] J.M. H Levelt Sengers, J.A. Given. *Mol. Phys.*, **80**, 899 (1993).
[14] M.E. Fisher. *J. Stat. Phys.*, **75**, 1 (1994).
[15] G. Stell. *J. Stat. Phys.*, **78**, 197 (1995).
[16] M. Bonetti, A. Oleinikova, C. Bervillier. *J. Phys. Chem. B.*, **101**, 2164 (1997).
[17] M. Kleemeier, S. Wiegand, W. Schroer, H. Weigartner. *J. Chem. Phys.*, **110**, 3085 (1999).
[18] K.C. Zhang, M.E. Briggs, R.W. Gammon, J.M.H. Levelt Sengers. *J. Chem. Phys.*, **97**, 8692 (1992).
[19] T. Narayanan, K.S. Pitzer. *J. Chem. Phys.*, **98**, 9170 (1994).
[20] T. Narayanan, K.S. Pitzer. *J. Chem. Phys.*, **102**, 8118 (1995).
[21] A. Oleinikova, M. Bonetti. *Phys. Rev. Lett.*, **83**, 2985 (1999).
[22] A. Oleinikova, M. Bonetti. *J. Chem. Phys.*, **115**, 9871 (2001).
[23] J. Ramakrishnan and al. *J. Chem. Phys.*, **68**, 4098 (1978).
[24] S.C.H. Haw, W.I. Goldburg. *J. Chem. Phys.*, **65**, 4906 (1976).
[25] T. Narayanan, A. Kumar, E.S.R. Gopal. *Phys. Lett. A.*, **144**, 371 (1990).
[26] A. Stein, G.F. Allen. *J. Chem. Phys.*, **59**, 6079 (1973).
[27] R. Guida, Zinn-Justin. *J. Phys. A, Math. Gen.*, **31**, 8103 (1998).
[28] M.E. Fisher, J.S. Langer. *Phys. Rev. Lett.*, **20**, 665 (1968).
[29] M.S. Green, M. Ley-Koo. *Phys. Rev. A.*, **23**, 2650 (1981).
[30] C. Bagnuls, C. Bervillier. *Phys. Rev. B.*, **32**, 7209 (1985).
[31] J.C. Le guillon, J. Zinn-Justin. *J. Phys. (Paris).*, **48**, 19 (1987).
[32] S.Y. Zinn, M.E. Fisher. *Physica. A.*, **226**, 168 (1996).
[33] A. Toumi, M. Bouanz, A. Gharbi. *Chem. Phys. Lett.*, **362**, 567 (2002).
[34] J. Jacob, A. Kumar, M.A. Anisimov, A. Povodyrev, J.V. Sengers. *Phys. Rev. E.*, **58**, 2188 (1998).
[35] K. Gutkowski, M.A. Anisimov, J.V. Sengers. *J. Chem. Phys.*, **114**, 3133 (2001).