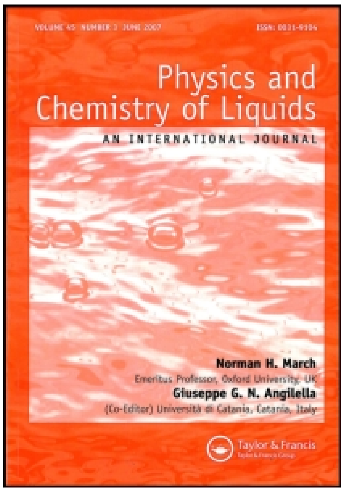

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Evidence of Vogel-Tamman-Fulcher behavior in ionic binary fluids

Emna Cherif[a]; Moncef Bouanz[b]
[a] Faculté des Sciences de Tunis, Laboratoire de Physique des Liquides et d'Optique non Linéaire, Tunisia [b] Faculté des Sciences de Bizerte, Laboratoire de Physique des Liquides critiques, Zarzonna, Tunisia

To cite this Article Cherif, Emna and Bouanz, Moncef(2007) 'Evidence of Vogel-Tamman-Fulcher behavior in ionic binary fluids', Physics and Chemistry of Liquids, 45: 6, 649 — 661, First published on: 07 July 2007 (iFirst)
To link to this Article: DOI: 10.1080/00319100701344644
URL: http://dx.doi.org/10.1080/00319100701344644

Physics and Chemistry of Liquids
Vol. 45, No. 6, December 2007, 649–661

Evidence of Vogel–Tamman–Fulcher behavior in ionic binary fluids

EMNA CHERIF† and MONCEF BOUANZ*‡

†Faculté des Sciences de Tunis, Laboratoire de Physique des Liquides et d'Optique
non Linéaire, Département de Physique, 1060 Tunisia
‡Faculté des Sciences de Bizerte, Laboratoire de Physique des Liquides critiques,
Département de Physique, 7021 Zarzonna, Tunisia

(*Received 6 October 2006; in final form 17 March 2007*)

The electrical conductivity σ of the six concentrated binary ionic mixtures of isobutyric acid–water with XM [KCl] at the critical concentrations was measured over an extended temperature range above the critical consolute point. Far from the critical temperature T_c, the electrical conductivity is accurately described by the Vogel–Fulcher–Tammann (VFT) law. However, in a temperature range $\Delta T = T - T_c \leq 2\,\mathrm{K}$, the electrical conductivity exhibits a monotonous deviation from the VFT behavior. This anomaly is finite at T_c. The asymptotic behavior of the electrical conductivity anomaly is described by a power law $(t)^{(1-\alpha)}$, with $t = (T - T_c)/T_c$, the reduced temperature, and α the critical exponent of the specific heat anomaly at constant pressure. This critical anomaly is similar to the one observed in other different concentrated critical electrolytes. The degree of dissociation α_{diss} of the salt for the critical mixture is estimated from the value of the Walden product computed at T_c. When the salt is added, the degree of dissociation α_{diss} shows dependence on the (K^+, Cl^-) concentrations: $0.15 < \alpha_{\mathrm{diss}} < 0.68$.

Keywords: Liquid–liquid critical mixture; Phase transition; Electrical conductivity; Viscosity; Activation energy

1. Introduction

This article represents another contribution to the study of the critical binary mixture of isobutyric acid + water (IBAW). We have been investigating and reporting data for this mixture for many years: transport phenomena [1], ionic structure [2], solvation phenomenon in a binary fluid [3], the effect of ions on the mixture (IBAW) [4], and the phase equilibrium properties occurring in the presence of added ions [5]. The electrical conductivity of (IBAW) mixtures has been also studied [6,7].

In previous work [7], we have studied extensively the coexistence curves in electrical conductivity (σ) in the one-and-two regions of three different solutions: isobutyric acid–water IBAW, IBAW $+ 5 \times 10^{-4}$ M [KCl], IBAW $+ 5 \times 10^{-3}$ M [KCl].

---

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

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100701344644

The coexistence curve of the electrolyte mixture, takes a new shape and is characterized by a new effective critical exponent $\beta^* = (0.264\text{–}0.296)$. The value obtained for β^* is outside of the field of the Fisher-renormalized value. Also, we have proved that the long-range coulombic interaction in such mixtures is significant and is caused by the potential of the ionic atmosphere. The electrical conductivity of the same electrolytic solution have been also studied and it shows that it's a temperature dependent parameter for ions, the adding of (K^+, Cl^-) ions have an important influence in the increasing of the electrical conductivity.

Here, we present the experimental measurements of the electrical conductivity and the shear viscosity *versus* temperature of the six concentrated binary ionic mixtures of (IBAW) with XM [KCl] at critical concentration. We determine the temperature effect in the Vogel–Fulcher–Tammann region $\Delta T = T - T_c \leq 2\,\mathrm{K}$, where T_c is the critical temperature.

From our study, we can deduce the thermodynamic properties of (IBAW) with XM [KCl] far away from the critical point. The degree of dissociation α_{diss} [8] of the salt for the critical mixture is estimated from the value of the Walden product [9] computed at the critical temperature, which characterize the critical mixture of (IBAW) with XM [KCl] and limit the one phase stability.

This article is organized as follows. The experimental methods used in this work are discussed in section 2. The data collection and analysis techniques we used are treated in section 3, and conclusions are given in section 4.

2. Experimental details

The isobutyric acid (IBA) was purchased from Riedel de Haen (Germany). The purity was stated to be 99.99 mol%. The main impurity is probably water. The water was obtained from deionization and triple distillation, and had a specific conductivity of about $10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. These 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 [4]. The guaranteed purity of the KCl salt (Merck, Germany) is better than 99.5%. In this mixture, this salt can be dissolved in totality. All electrolytes were prepared from weighed amounts of the pure components. The weight was obtained with a resolution of 0.1 mg.

2.1. *Electrical conductivity measurements*

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 $41\,\mathrm{cm}^{-1}$ when filled with 100 mL of the sample. The cell constant is changed by no more than 0.1%. The calibration of the cell was made by using liquids of known electrical conductivity of 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 more than 0.03°C. The temperature of the cell was varied from to $T - T_{\mathrm{PS}} = 0.05°\mathrm{C}$ in steps of 0.20°C and the overall accuracy of the temperature determination was 0.02°C. 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 to 0.01% $10^{-3}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. The cell containing the solution was immersed in 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.

2.2. *Shear viscosity determination*

The shear viscosity η [10^{-2} Poise (P)] of the electrolyte at different temperatures and concentration of (K^+, CL^-) ions, was determined by measuring the density φ expressed in ($\mathrm{g\,cm^{-3}}$) and the kinematic viscosity υ [10^{-2} Stokes (St)]. The densities were measured in a digital precision densimeter, (PAAR, Graz, Austria) which was modified in our laboratory. The density of a solution was calculated from the electronically measured frequency of a mechanical oscillator filled with the solution. Filling was accomplished by means of a medical syringe. During filling, the absence of air bubbles was ensured. The oscillator was U-shaped glass tubing (volume $0.7\,\mathrm{cm}^3$) placed in a metal block which was controlled temperature to about $\pm(10^{-3})^{\circ}$C. This apparatus needs to be carefully calibrated with two liquids of different densities; we chose water as standard, with density data from [10], and methanol, with density data from [11]. The sensitivity of such measurements is high, and to ensure a final φ accuracy of 10^{-4} a thermal regulation of the sample to within 3 mK is needed. This was obtained by circulating water from thermostat. The temperature is read by a quartz thermometer. The precision of the density measurement was about $\pm 0.1\,\mathrm{mg\,cm^{-3}}$.

The kinematic viscosities ν were measured using an Ubbelhode type viscosimeter. The length of the capillary was 20 cm and its constant $k = 0.03991 \times 10^{-2}\,\mathrm{St\,s^{-1}}$. The times at which the meniscus passed by to two marks of the viscosimeter were recorded automatically to ±0.01 s. The coefficient ν was calculated from the following equation:

$$\nu = k(\tau - \theta) \tag{1}$$

where τ is the flow time between the two marks, k is a constant for a given viscosimeter, and θ is the correction time. The viscosimeter was calibrated with fluids of known density and viscosity.

3. Data collection and analysis

We measured the electrical conductivity of three different solutions: Isobutyric acid–water IBAW, IBAW + 5×10^{-4} M [KCl], IBAW + 5×10^{-3} M [KCl], IBAW + 10^{-2} M [KCl], IBAW + 5×10^{-2} M [KCl], IBAW + 10^{-1} M [KCl], with *versus* temperature above the separation temperature T_t at each concentration X of the isobutyric acid along the coexistence curve. The conductivity data for these solutions cover a good range of temperature above 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 T_c, the separation temperature for the critical concentration X_c, $T_c = T_t$ ($X = X_c$, X_c is the critical mole fraction of isobutyric acid–water (IBAW) + KCl)):

IBAW (pure): $X_c = 38.00\%$; $T_c = 300.095\,\mathrm{K}$
IBAW + 5×10^{-4} M [KCl]: $X_c = 39.90\%$; $T_c = 300.235\,\mathrm{K}$
IBAW + 5×10^{-3} M [KCl]: $X_c = 42.63\%$; $T_c = 301.638\,\mathrm{K}$
IBAW + 10^{-2} M [KCl]: $X_c = 43.00\%$; $T_c = 301.902\,\mathrm{K}$
IBAW + 5×10^{-2} M [KCl]: $X_c = 48.00\%$; $T_c = 307.977\,\mathrm{K}$
IBAW + 10^{-1} M [KCl]: $X_c = 60.00\%$; $T_c = 316.500\,\mathrm{K}$

The critical temperature T_c and the critical composition X_c increased linearly with the increasing of 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 [5].

3.1. *Background conductivity*

The transport properties of concentrated electrolytes do not follow a simple Arrhenius behavior – $\exp(E_\sigma/k_{BT})$ where E_σ is the activation energy of electrical conductivity and k_B is Boltzmann's constant.

Seemingly, for the studied mixtures, the activation energy of electrical conductivity E_σ shows a continuous change as a function of the temperature as it is shown in figure 1.

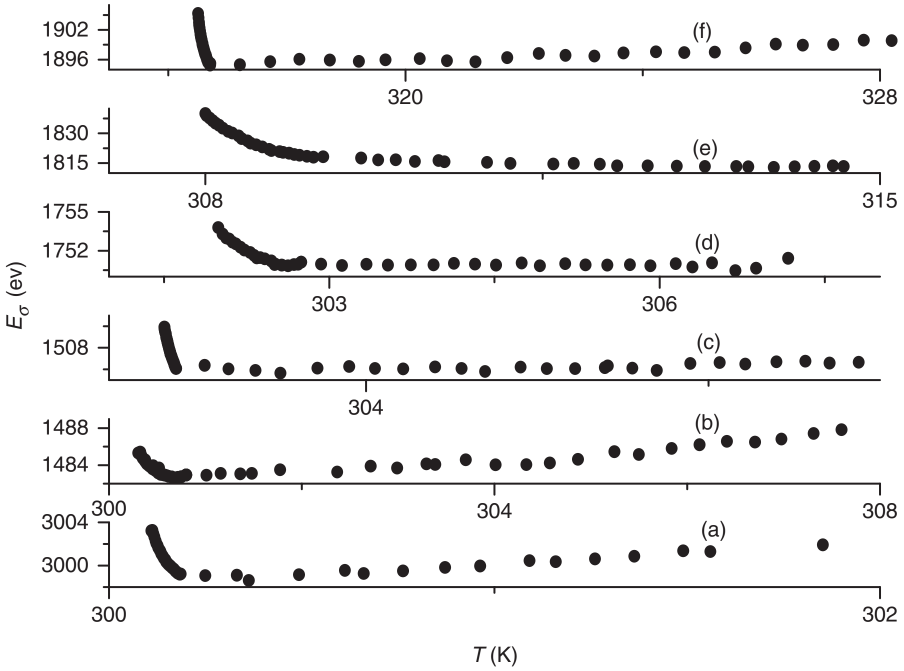

Figure 1. Temperature dependence T on Arrhenius activation energy E_σ of isobutyric acid–water (IBAW) + KCl for different values of KCl salt concentrations: (a) 0 M, (b) 5×10^{-4} M, (c) 5×10^{-3} M, (d) 10^{-2} M, (e) 5×10^{-2} M, (f) 10^{-1} M; M is mol of [KCl] per kilogram, of liquid–liquid critical mixture.

The background or regular electrical conductivity might be described by the empirical Vogel–Fulcher–Tamman (VFT) equation [12].

$$\sigma_{\text{reg}} = \sigma_{0,\text{VFT}} \exp\left(\frac{-B}{T - T_0}\right) \tag{2}$$

In equation (2), T_0 is the temperature at which the conductivity vanishes. The parameter B is related to a dependent activation energy [12].

The amplitude $\sigma_{0,\text{VFT}}$ is assumed to be constant or to have a weak temperature dependence:

$$\sigma_{0,\text{VFT}} = AT^{-1/2} \tag{3}$$

This temperature dependence is however negligible in comparison to exponential term in equation (2) [12]. Equation (2) can be linearized with respect to the temperature [13]:

$$\left[\frac{\mathrm{d}\ln \sigma_{\text{reg}}}{\mathrm{d}T}\right]^{-1/2} = B^{-1/2}(T - T_0) \tag{4}$$

Figure 2 shows the measured conductivity as a function of temperature in the linearized representation according to equation (4). One notices that the VFT law describes correctly the electrical conductivity in a temperature interval far from the critical temperature T_c.

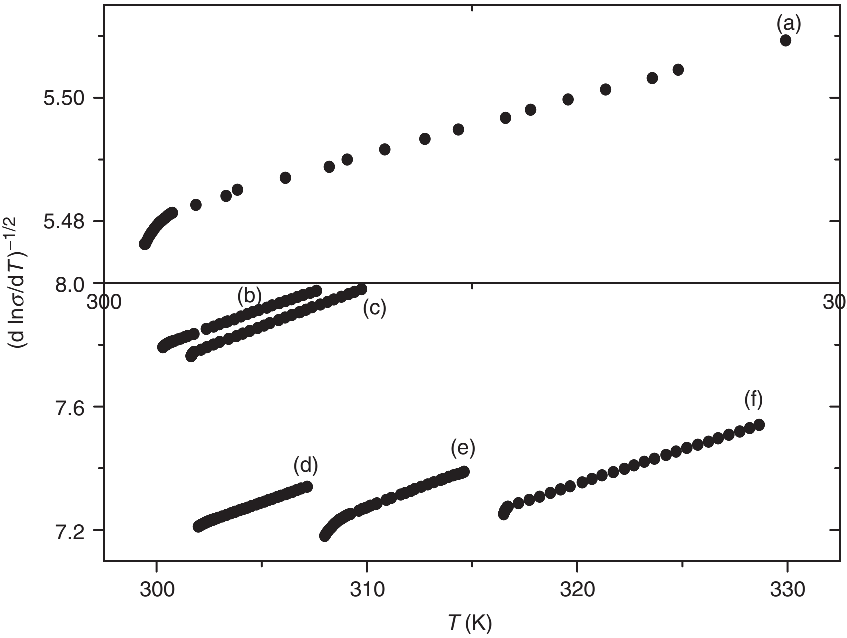

Figure 2. Specific electrical conductivity σ in a $(\mathrm{d}\ln\sigma/\mathrm{d}t)^{-1/2}$ *vs.* T representation of isobutyric acid–water (IBAW) + KCl for different values of KCl salt concentrations: (a) 0 M, (b) 5×10^{-4} M, (c) 5×10^{-3} M, (d) 10^{-2} M, (e) 5×10^{-2} M, and (f) 10^{-1} M; M is mol of [KCl] per kilogram, of liquid–liquid critical mixture.

Table 1. Fit of the regular conductivity σ_{reg} with equation (2), $\sigma_{0,\mathrm{VFT}}$, B and T_0 are the parameters of VFT law equation (2), σ_c and $\Delta\sigma_c$ are the values of specific electrical conductivity and conductivity anomaly at T_c, respectively; $\Delta\sigma_c = \sigma_c - \sigma_{\mathrm{reg}}(T_c)$.

Systems	$\sigma_{0,\mathrm{VFT}}$ (ms cm^{-1})	B (K)	T_0 (K)	σ_c (ms cm^{-1})	$\Delta\sigma_c$ (ms cm^{-1})	$\lvert\Delta\sigma_c\rvert/\sigma_c$ (%)
IBAW	0.511	2.306	292.455	0.374	−0.004	1.07
IBAW + 5×10^{-4} M [KCl]	0.765	4.838	285.050	0.549	−0.007	1.27
IBAW + 5×10^{-3} M [KCl]	1.432	11.538	278.639	0.86	−0.007	0.81
IBAW + 10^{-2} M [KCl]	2.355	18.087	273.993	1.221	−0.011	0.90
IBAW + 5×10^{-2} M [KCl]	22.160	135.556	241.125	2.779	−0.138	4.96
IBAW + 10^{-1} M [KCl]	26.151	183.306	221.607	3.697	−0.092	2.48

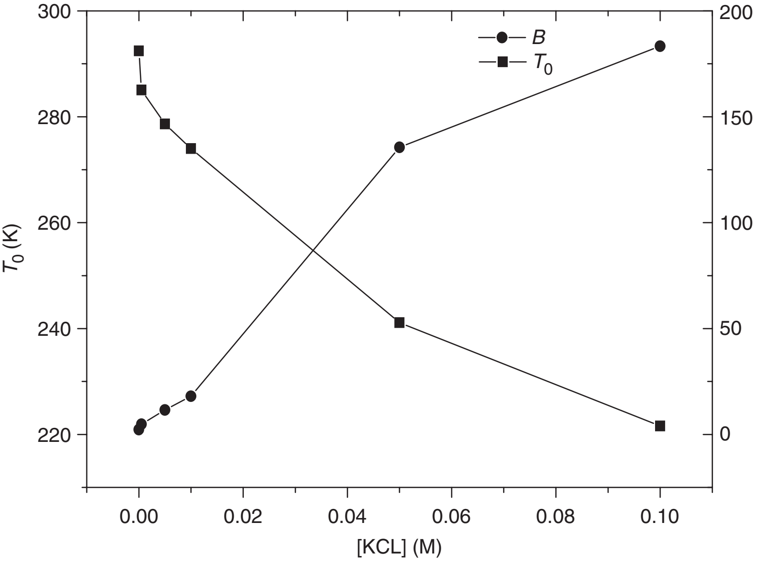

Figure 3. Parameter B and Vogel temperature T_0 as a function of the molar concentration [KCl] ions. B and T_o are obtained from a fit of the regular electrical conductivity with the VFT law, equation (2).

Close T_c the conductivity deviates substantially from the regular VFT law behavior. The values of the parameters $\sigma_{0,\mathrm{VFT}}$, B, and T_o, are given in table 1.

The values of the parameter B and the temperature T_o as a function of the salt concentration [KCl] are shown in figure 3. A nonmonotonic dependence of B and T_o *versus* [KCl] is noticed. While T_o does not change a lot, the parameter B shows a much larger variation with the concentration of (K^+, Cl^-) ions. The largest values of B are observed for the system IBAW + 5×10^{-2} M [KCL] and IBAW + 10^{-1} M [KCl]. The biggest value of T_o is observed for the mixture pure without the presence of (K^+, Cl^-) ions. The coefficient B increases with the increase of the concentration of the salt [KCl]. The decrease of T_o has been observed for the concentration 10^{-1} M [KCl].

3.2. *Critical anomaly*

The deviation of the electrical conductivity from the regular VFT behavior, equation (2) is shown in figure 4 for the six mixtures. The deviation is observed relatively far from T_c

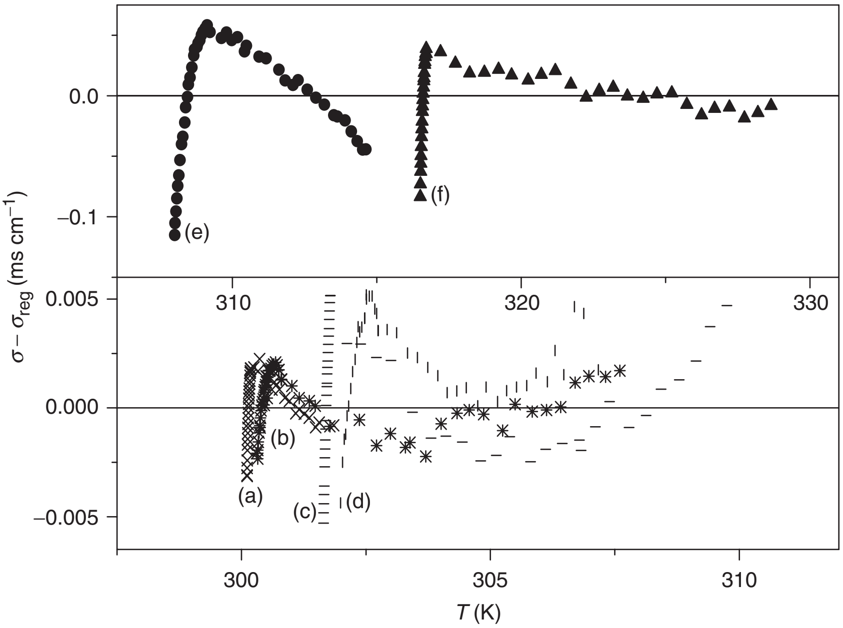

Figure 4. Specific electrical conductivity anomaly $\sigma - \sigma_{reg}$ of isobutyric acid–water (IBAW) + KCl as a function of temperature T for different values of KCl salt concentrations: (a) 0 M, (b) 5×10^{-4} M, (c) 5×10^{-3} M, (d) 10^{-2} M, (e) 5×10^{-2} M, and (f) 10^{-1} M; M is mol of [KCl] per kilogram, of liquid–liquid critical mixture.

for temperature values $(T - T_c)$ between 0.1 and 1.2 K. It is the largest close to T_c and is attributed to a critical anomaly of the electrical conductivity. The critical anomaly corresponds to a weak decrease of the electrical conductivity with respect to the critical behavior. The electrical conductivity has a finite value at T_c, $\sigma(T_c) = \sigma_c$ (table 1).

Let us define the value at T_c of the critical anomaly $\Delta\sigma_c$ at the difference between σ_c and the regular VFT conductivity, equation (2) extrapolated at T_c:

$$\Delta\sigma_c = \sigma_c(T_c) - \sigma_{reg}(T_c) \tag{5}$$

The ratio $|\Delta\sigma_c/\sigma_c|$ determined from the specific conductivity is given in table 1.

Along a path of constant critical concentration, the temperature dependence of the critical anomaly reads [12,13]:

$$\sigma_{crit} = \sigma - \sigma_{reg} \tag{6}$$

According to [14], the temperature derivative of the critical anomaly σ_{crit} should vary along a patch as the specific heat anomaly:

$$\frac{d\sigma_{crit}}{dT} = \sigma_0 t^{-\alpha} + B_{crit} \tag{7}$$

where $\alpha = 1.109$ [15] is the critical exponent of the specific heat anomaly at constant pressure, and σ_0 and B_{crit} are respectively, the critical amplitude and the

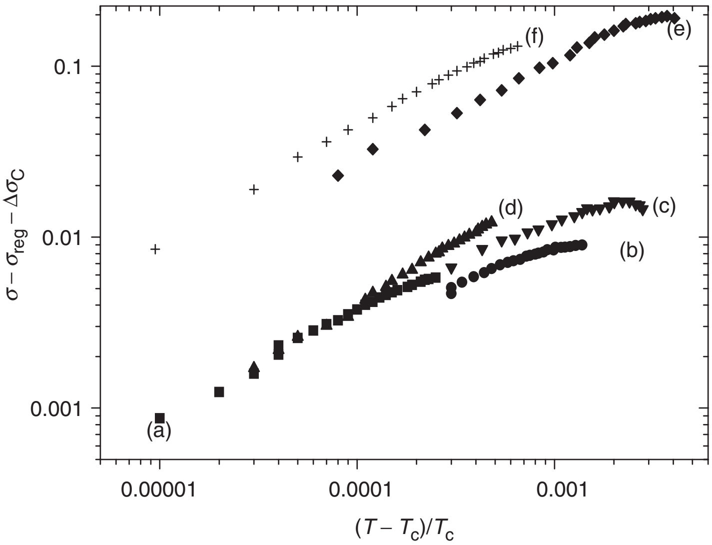

Figure 5. The critical anomaly $\sigma - \sigma_{\text{reg}} - \Delta\sigma_{\text{c}}$ of the specific electrical conductivity Isobutyric acid–water (IBAW) + KCl as a function of the reduced temperature t for different values of KCl salt concentrations: (a) 0 M, (b) 5×10^{-4} M, (c) 5×10^{-3} M, (d) 10^{-2} M, (e) 5×10^{-2} M, and (f) 10^{-1} M; M is mol of [KCl] per kilogram, of liquid–liquid critical mixture.

Table 2. Fit of the anomaly of the specific conductivity $\sigma_{\text{crit}} = \sigma - \sigma_{\text{reg}}$ with equation (8); σ_0 and B_{crit} are the critical amplitude and the critical fluctuation-induced additive constant, respectively.

Systèms	B_{crit} (ms cm^{-1})	σ_0 (ms cm^{-1})	B_{crit}/σ_0
IBAW	−118.610	0.511	−2.075
IBAW + 5×10^{-4} M [KCl]	−55.214	0.765	−1.84
IBAW + 5×10^{-3} M [KCl]	−58.384	1.432	−1.612
IBAW + 10^{-2} M [KCl]	−54.745	2.355	−1.732
IBAW + 5×10^{-2} M [KCl]	−329.948	22.160	−1.594
IBAW + 10^{-1} M [KCl]	−736.926	26.151	1.762

critical fluctuation-induced additive constant [16]. Integration of equation (7) gives:

$$\sigma_{\text{crit}} = \sigma_0\left(t^{1-\alpha} + \frac{B_{\text{crit}}}{\sigma_0}t\right) + \Delta\sigma_{\text{c}} \tag{8}$$

Figure 5 shows in log–log representation $(\sigma - \sigma_{\text{reg}} - \Delta\sigma_{\text{c}})$ as a function of the reduced temperature t for the system mixtures studied. In the temperature range $t < 10^{-3}$, a slope close to $(1 - \alpha)$ can fit the data. The value of σ_0 and B_{crit} were determined by fitting the data to equation (8). Table 2 gives the values of σ_0, B_{crit} and B_{crit}/σ_0 and the corresponding asymptotic range, where they have been computed. For the six mixtures IBAW + XM [KCl], the ratio $B_{\text{crit}}/\sigma_0 \approx -1.8 \pm 0.2$ might be regarded as "universal".

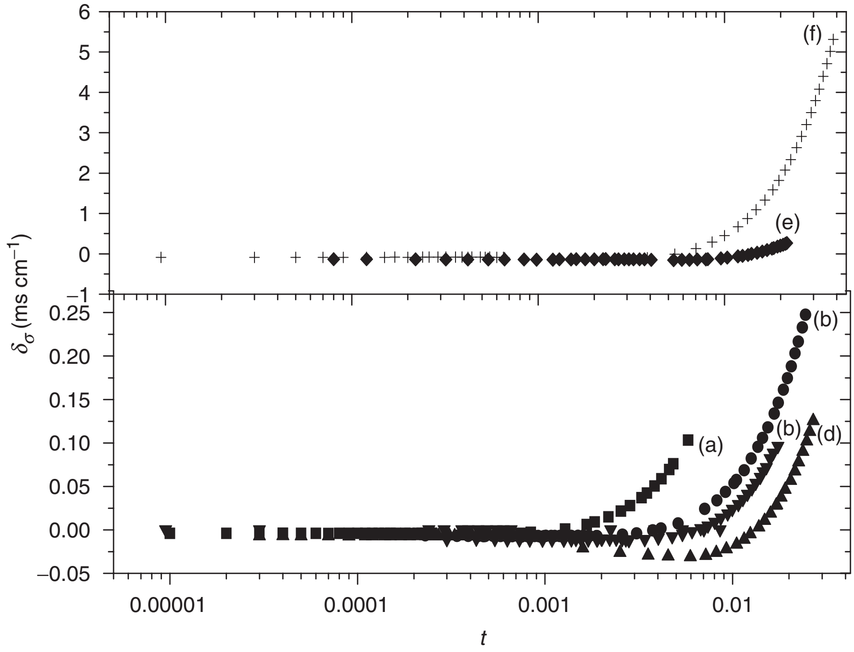

Figure 6. Deviation $\delta_\sigma = (\sigma - \sigma_{\text{reg}}) - \sigma_{\text{crit}}$ of the electrical conductivity anomaly from the asymptote behavior σ_{crit} equation (8) as a function of the reduced temperature (t).

3.3. *Crossover behavior*

Figure 6 shows the deviation $\delta_\sigma = (\sigma - \sigma_{\text{reg}}) - \sigma_{\text{crit}}$ of the conductivity anomaly from the asymptotic behavior, as a function of the reduced temperature t. In order to describe correctly the conductivity behavior in the temperature range $10^{-5} < t < 10^{-1}$, appropriate corrections to scaling were introduced. The following expression was used to fit the data [13]:

$$\sigma = \Delta\sigma_c + \sigma_{0,\text{VFT}} \exp\left(\frac{-B}{T - T_0}\right) + \sigma_0 t \left[t^{-\alpha} \left(\frac{1 + a_1 t^{\Delta}}{1 + a_2 t^{2\Delta}}\right)^y + \frac{B_{\text{crit}}}{\sigma_0} \right] \tag{9}$$

The term $[(1 + a_1 t^{\Delta})/(1 + a_2 t^{2\Delta})]^y$ generates the usual corrections to scaling, when $t \to 0$; $\Delta = 0.504$ is a universal exponent [17]. For $t \gg 1$, the critical contribution must vanish in order to obtain the regular behavior described by VFT law, equation (2). Hence, in the limit $t \to \infty$,

$$t^{-\alpha} \left(\frac{1 + a_1 t^{\Delta}}{1 + a_2 t^{2\Delta}}\right)^y + \frac{B_{\text{crit}}}{\sigma_0} = 0 \tag{10}$$

from which follow the two conditions:

$$y = -\frac{\alpha}{\Delta} \tag{11}$$

Table 3. Values of the parameters from a fit of equation (9) to the specific electrical conductivity σ.

Systems	A_1	a_2	$(a_1/a_2)^y$	$B_{\mathrm{crit}}/\sigma_0$
IBAW	420.20	2949.23	1.53	−1.91
IBAW + 5×10^{-4} M [KCl]	76.70	1357.60	1.87	−1.80
IBAW + 5×10^{-3} M [KCl]	40.10	851.01	1.84	−1.82
IBAW + 10^{-2} M [KCl]	30.77	669.75	1.84	−1.80
IBAW + 5×10^{-2} M [KCl]	22.74	489.81	1.84	−1.80
IBAW + 10^{-1} M [KCl]	88.39	2052.45	1.87	−1.93

and

$$\left(\frac{a_1}{a_2}\right)^y = -\frac{B_{\mathrm{crit}}}{\sigma_0} \tag{12}$$

The results of the fits of the electrical conductivity with equation (9) are presented in table 3. The values of the parameters $\sigma_{0,\mathrm{VFT}}$, B and T_0 of the regular VFT conductivity in equation (9) are close to those obtained from a fit with equation (2) away from T_c (table 1). The value of the universal ratio $B_{\mathrm{crit}}/\sigma_0$ of the system mixtures is almost the same as that obtained from a fit with equation (8) in the asymptotic range (table 2).

3.4. *Walden product*

The electrical conductivity σ is related to the self-diffusion coefficient D_i of the i-th ion by the Nernst–Einstein equation [18]:

$$\sigma T = Ae^2(C_1Z_1^2D_1 + C_2Z_2^2D_2 + \cdots) \tag{13}$$

where A is a numerical factor and C, Z, and e, are respectively, concentration and charges.

Assuming the validity of the stokes law shear viscosity η, the self-diffusion coefficient D_i is given by the Stokes–Einstein equation:

$$D_i = \frac{k_B T}{6\pi r_i \eta} \tag{14}$$

where K_B is Boltzmann's constant. Equation (14) assumes pure sticking conditions and is valid for large ions without specific interactions.

Combining equations (13) and (14) shows that the Walden product [9] ($\sigma\eta_{\mathrm{VFT}}$) does not depend on temperature. This is actually satisfied, when both the activation energies of the electrical conductivity and of the shear viscosity have similar values [19]. Under that condition, the Walden product depends only on the free ion concentration and any change of $\sigma\eta_{\mathrm{VFT}}$ might be attributed to a change of the free ion concentration [20]. This allows to estimate the degree of dissociation α_{diss} of the salt [9].

Figure 7 clearly shows a viscosity anomaly near the critical point for the systems mixtures studied. The viscosity η is characterized by an exponent y according to [21]:

$$\eta = \eta_B t^y \tag{15}$$

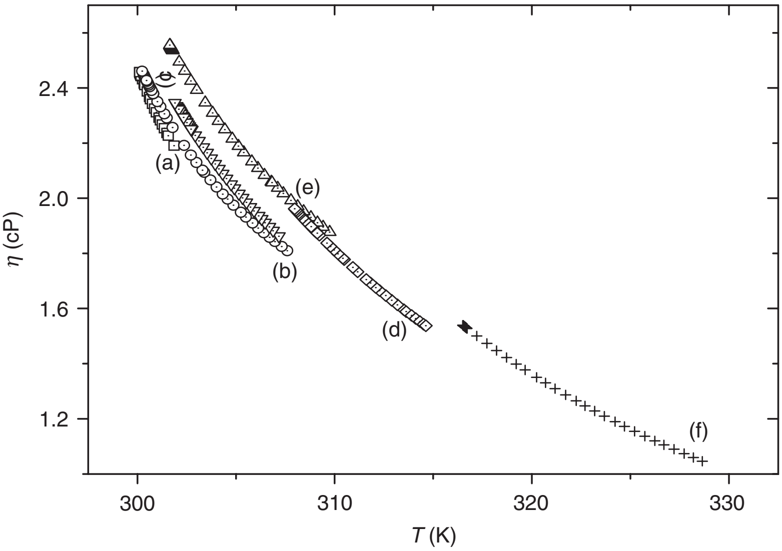

Figure 7. The measured shear viscosity near the critical point of isobutyric acid–water (IBAW) + KCl as a function of the temperature T for different values of KCl salt concentrations: (a) 0 M, (b) 5×10^{-4} M, (c) 5×10^{-3} M, (d) 10^{-2} M, (e) 5×10^{-2} M, and (f) 10^{-1} M; M is mol of [KCl] per kilogram, of liquid–liquid critical mixture.

Table 4. Parameters of VFT law equation (16), describing the background shear viscosity.

Systems	$\eta_{0,\mathrm{VFT}}$ (10^{-2} P)	B_η (K)	$T_{0,\eta}$ (K)
IBAW	1.285	5.257	291.999
IBAW + 5×10^{-4} M [KCl]	0.959	14.357	285.000
IBAW + 5×10^{-3} M [KCl]	0.764	28.525	278.000
IBAW + 10^{-2} M [KCl]	0.524	43.290	272.999
IBAW + 5×10^{-2} M [KCl]	0.219	116.541	254.805
IBAW + 10^{-1} M [KCl]	0.125	168.266	249.394

The noncritical or background viscosity is η_B, and y is the critical exponent the critical exponent. The shear viscosity was fitted to a VFT like equation:

$$\eta_\mathrm{VFT} = \eta_{0,\mathrm{VFT}} \exp\left(\frac{B_\eta}{T - T_{0,\eta}}\right) \tag{16}$$

In the investigated temperature range, the values of the parameters B_η, $\eta_{0,\mathrm{VFT}}$ and the Vogel temperature $T_{0,\eta}$ were given in table 4.

Figure 8 shows the variation of the Walden product ($\sigma\eta_\mathrm{VFT}$) as a function of temperature for six systems mixtures.

From figure 8, it can be noticed that the value of the Walden product diminishes for increasing values of [KCl] concentration indicating that the degree of dissociation of KCl in the binary mixture (IBAW) with added (K^+, Cl^-) ions is reduced. A detailed study of the Walden product for isobutyric acid in the water shows linear concentration dependence at large values of the salt concentration. The linear dependence of the

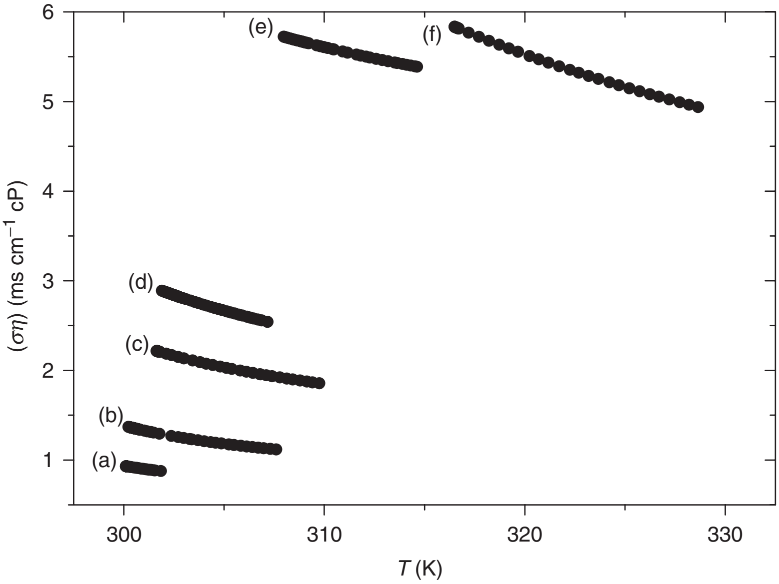

Figure 8. Walden product ($\sigma\eta_{\mathrm{VFT}}$) as a funtion of temperature T. σ is the electrical conductivity, η_{VFT} is the shear viscosity fitted with VFT law.

Table 5. The degree of dissociation α_{diss} of KCl in the binary mixture (IBAW) with added (K^+, Cl^-) ions as a function of concentration of KCl. T_c and X_c are the critical temperature and the critical mole fraction, respectively.

Systems	T_c (K)	X_c (%)	α_{diss}
(IBAW) + 5×10^{-4} M [KCl]	300.23	38	0.68
(IBAW) + 5×10^{-3} M [KCl]	301.64	40	0.40
(IBAW) + 10^{-2} M [KCl]	301.90	42	0.31
(IBAW) + 5×10^{-2} M [KCl]	307.97	48	0.16
(IBAW) + 10^{-1} M [KCl]	316.500	60	0.15

Walden product with the salt concentration permits an estimation of the degree of dissociation α_{diss} according to following relation [8]:

$$\alpha_{\mathrm{diss}} = \frac{(\sigma\eta_{\mathrm{VFT}})}{(\sigma\eta_{\mathrm{VFT}})^*} \tag{17}$$

where $(\sigma\eta_{\mathrm{VFT}}) = (\sigma\eta_{\mathrm{VFT}})_{\mathrm{IBAW}} = 0.926$ (ms cm^{-1} cP) is the limiting Walden product with the fully dissociated salt, see figure 8. The values of α_{diss} of the investigated mixtures evaluated at T_c, are given in table 5: α_{diss} varies from 0.15 to 0.68.

4. Conclusions

In summary, a critical anomaly of the electrical conductivity in the concentrated critical solutions of isobutyric acid–water with XM [KCl] has been detected. The electrical conductivity remains finite at the critical consolute point. 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 by the exponent $(1-\alpha)$ predicted by the theory short-range fluctuations. The degree of dissociation α_{diss} of KCl in the binary mixture (IBAW) with added (K^+, Cl^-) ions is determined for the value of Walden product computed at the critical point: α_{diss} varies from 0.15 to 0.68. The domain of the validity of α_{diss} is in conformity with the theoretical prediction. The Coulombic interaction is the origin of the deviation.

Acknowledgments

A great acknowledgment is made to Professor Mongi Ferchichi, Chairman of KAM biotechnology board, Bristish Columbia, Canada for the partial support of this research.

References

[1] M. Bouanz. *Phys. Rev. A*, **46**, 4888 (1992).
[2] M. Bouanz, A. Gharbi. *J. Phys. Cond. Mater.*, **6**, 4429 (1994).
[3] M. Bouanz. *Quim. Anal.*, **15**, 530 (1996).
[4] M. Bouanz, D. Beysens. *J. Chem. Phys. Lett.*, **231**, 105 (1994).
[5] A. Toumi, M. Bouanz. *Eur. Phys. J.*, **E2**, 211 (2000).
[6] E. Cherif, M. Bouanz. *Int. J. Mol. Sci.*, **4**, 326 (2003).
[7] E. Cherif, M. Bouanz. *Phys. Chem. Liq.*, **44**, 419 (2006).
[8] L.C. Kenausic, E.C. Evers, C.A. Kraus. *Proc. Natl. Acad. Sci. USA*, **48**, 121 (1962); *Proc. Natl. Acad. Sci. USA*, **49**, 141 (1963).
[9] S.I. Smadley. *The Interpretation of the Ionic Conductuvity in Liquids*, Plenum, NewYork (1980).
[10] F. Riehle, B. Wende. *Physikalish-Technische Bundesanstalt*, 2nd Edn, licence Nr. 13/1985, p. 6, Chempro GmbH, D6450 Hanau.
[11] R.F. Brunel, K. Van Bibber. *International Critical Tables*, Vol. 3, p. 27, McGraw-Hill, New York (1928).
[12] G. Adam, J.H. Gibbs. *J. Chem. Phys.*, **43**, 139 (1965).
[13] F. Stickel, E.W. Fischer, R. Richert. *J. Chem. Phys.*, **102**, 6251 (1995).
[14] M.E. Fisher, J.S. Langer. *Phys. Rev. Lett.*, **20**, 665 (1968).
[15] B.V. Prafulla, T. Narayanan, A. Kumar. *Phys. Rev. A*, **46**, 7456 (1992).
[16] C. Bagnuls, C. Bervillier. *Phys. Rev. B*, **32**, 7209 (1985).
[17] R. Guida, J. Zinn-Justin. *J. Phys. A, Math. Gen.*, **31**, 8103 (1998).
[18] J.P. Hansen, I.R. McDonald. *Theory of Simple Liquids*, p. 399, Academic Press, New York (1991).
[19] N. Ouerfelli, M. Bouanz. *J. Sol. Chem.*, **35**, 121 (2006).
[20] W.E. Price, H. Weingartner. *J. Phys. Chem.*, **95**, 8933 (1991).
[21] J. Sengers. *J. Int. J. Thermophys.*, **6**, 203 (1985).