320 *J. Chem. Eng. Data* **2010,** *55,* 320–326

Transport Properties in 1,4-Dioxane + Water + Saturated KCl Critical Mixture by Measuring Viscosity and Electrical Conductivity

Taoufik Kouissi[†,§] **and Moncef Bouanz***[,†,‡]

Laboratoire de Physique des Liquides et d'Optique Non Linéaire, Département de Physique, Faculté des Sciences de Tunis, Campus Universitaire, 2092 El Manar, Tunisia, and Laboratoire de Physique des Liquides Critiques, Département de Physique, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisia

The ternary critical mixture of 1,4-dioxane (1) + water (2) + saturated KCl (3) has a lower critical point. The viscosity η and electrical conductivity κ of this system have been measured as function of temperature for nine critical mixtures along the coexistence curve below the temperature of phase transition. The water mole fraction in free basis x'_2 in the mixtures extends from (0.550 to 0.880) and the molality m of KCl from (0.47 to 2.039) $\text{mol}\cdot\text{kg}^{-1}$. The viscosity was found to decrease with an increase in temperature, water mole fraction, and the molality of KCl, while the electrical conductivity increases with an increase in temperature, with the water mole fraction and molality of salt. The viscosity and electrical conductivity represented anomalies near the critical temperature T_c. The critical electrical conductivity κ_c varies with water mass fraction w_2 as a second degree polynomial and with the molality m of salt as a third degree polynomial. The variation of critical composition in water and in the molality of salt varied the temperature of separation of phase, T_t. The activation energy $E_a(\kappa)$ for ionic conduction decreased with increasing x'_2 and consequently with molality, but they are not influenced in the activation energy $E_a(\eta)$ for viscous flow.

Introduction

Research on the physicochemical properties of liquid−liquid mixtures has been attempted to understand the thermodynamic behavior and transport properties. These properties provide information about intermolecular interactions and also for association, pair-formation, and clustering phenomena. We have been investigating and reporting data for the critical properties of isobutyric acid + water for many years: transport phenomena,[2] ionic structures,[3] solvation phenomena in the binary fluid,[4] the effect of ions on mixture,[5] and phase equilibrium properties occurring in the presence of added ions.[6−8] The electrical conductivity of the above mixture has been also studied.[9−14] In a previous paper,[1] we investigated conductivity κ and refractive index n along the coexistence curve of the system 1,4-dioxane (1) + water (2) + saturated KCl (3) and in the one-phase region near and far away from the critical temperature. We note that 1,4-dioxane and water are miscible in all proportions at all temperatures. We have reported that the electrical conductivity κ in the above system constitutes an order parameter as well as the refractive index n.[1] The addition of salt to a homogeneous 1,4-dioxane + water mixture causes at in certain composition, a phase separation.[15−23]

We report in this paper the viscosity η and electrical conductivity κ of the ternary system 1,4-dioxane (1) + water (2) + saturated KCl (3) along the coexistence curve below of the temperature of phase transition for nine compositions in that the water mole fraction in free basis x'_2 extends from (0.550 to 0.880) and the molality m of KCl extends from (0.7 to 2.039) $\text{mol}\cdot\text{kg}^{-1}$.

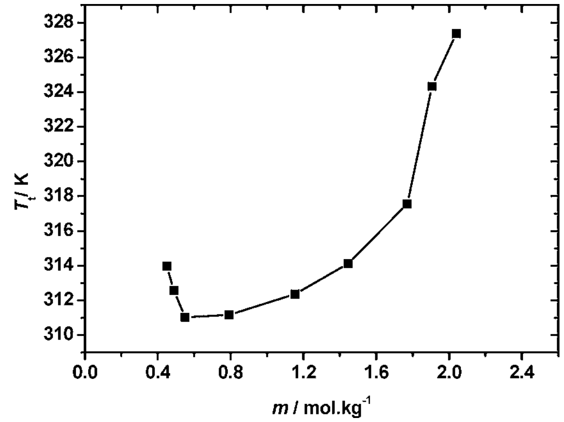

Figure 1. Variation of the temperature of phase separation with the molality m of KCl.

Experimental Procedure

Sample Preparation. The 1,4-dioxane was provided by Merck. The purity was stated to be 99.99 %. The water was obtained from deionized and three times distilled water and has a specific conductivity of about 10^{-6} $\Omega^{-1}\cdot\text{cm}^{-1}$ or less.

The guaranteed purity of the potassium chloride (Merck product) is better than 99.5 %. All mixtures were prepared by masses, with a resolution of 10^{-3} g. Some care was taken to avoid moisture and dust in the final sample, by baking the syringes and the cells overnight under vacuum and preparing the mixtures in a dust-free area.

The solution was brought to temperature equilibrium, with stirring to dissolve completely the excess salt. Additional purification had not been considered necessary. The main impurity in the salt and 1,4-dioxane was probably water. After, the sample is let to reach the equilibrium which continues with a separation of two phases.

---

* To whom all correspondences should be addressed. E-mail: moncef.bouanz@fsb.rnu.tn.
[†] Faculté des Sciences de Tunis.
[‡] Faculté des Sciences de Bizerte.
[§] E-mail: taoufik.kouissi@fst.rnu.tn.

10.1021/je900351t CCC: $40.75

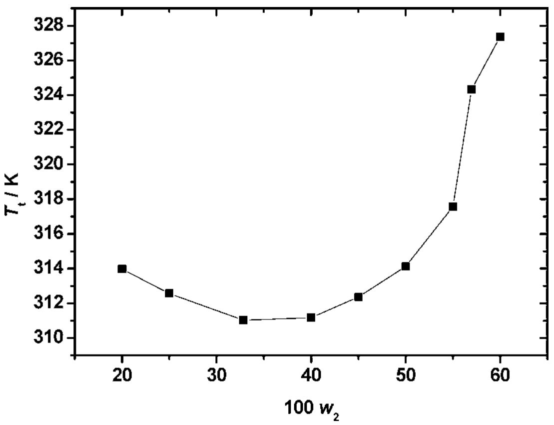

Figure 2. Variation of the temperature of phase separation with a function of water mass fraction w_2.

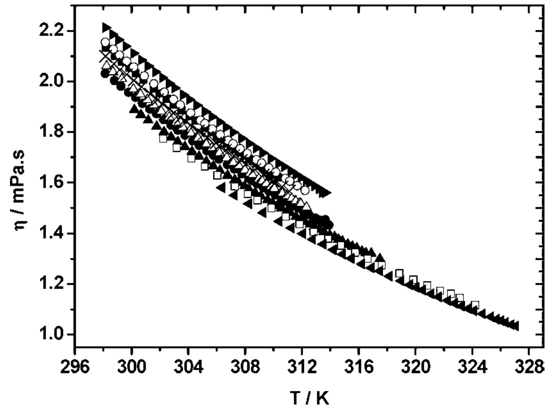

Figure 3. Temperature dependence of viscosity η for 1,4-dioxane (1) + water (2) + saturated KCl (3) with composition: ○, $w_2 = 0.20$, $m = 0.470$ mol·kg^{-1}; right-pointing triangle, $w_2 = 0.25$, $m = 0.488$ mol·kg^{-1}; ■, $w_2 = 0.328$, $m = 0.55$ mol·kg^{-1}; ×, $w_2 = 0.40$, $m = 0.792$ mol·kg^{-1}; △, $w_2 = 0.45$, $m = 1.154$ mol·kg^{-1}; ●, $w_2 = 0.50$, $m = 1.446$ mol·kg^{-1}; ▲, $w_2 = 55$, $m = 1.771$ mol·kg^{-1}; □, $w_2 = 0.57$, $m = 1.906$ mol·kg^{-1}; left-pointing triangle, $w_2 = 0.60$, $m = 2.039$ mol·kg^{-1}.

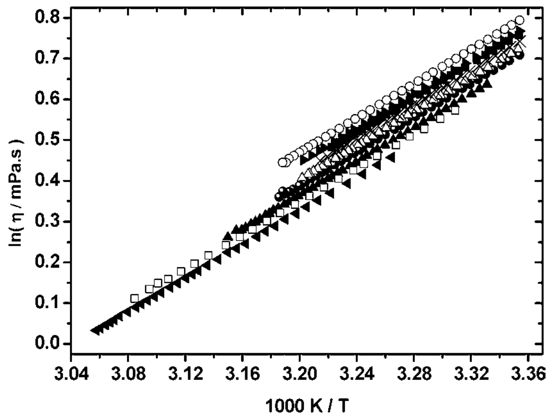

Figure 4. Arrhenius plots of viscosity η for 1,4-dioxane (1) + water (2) + saturated KCl (3) with composition: ○, $w_2 = 0.20$, $m = 0.470$ mol·kg^{-1}; right-pointing triangle, $w_2 = 0.25$, $m = 0.488$ mol·kg^{-1}; ■, $w_2 = 0.328$, $m = 0.55$ mol·kg^{-1}; ×, $w_2 = 0.40$, $m = 0.792$ mol·kg^{-1}; △, $w_2 = 0.45$, $m = 1.154$ mol·kg^{-1}; ●, $w_2 = 0.50$, $m = 1.446$ mol·kg^{-1}; ▲, $w_2 = 55$, $m = 1.771$ mol·kg^{-1}; □, $w_2 = 0.57$, $m = 1.906$ mol·kg^{-1}; left-pointing triangle, $w_2 = 0.60$, $m = 2.039$ mol·kg^{-1}.

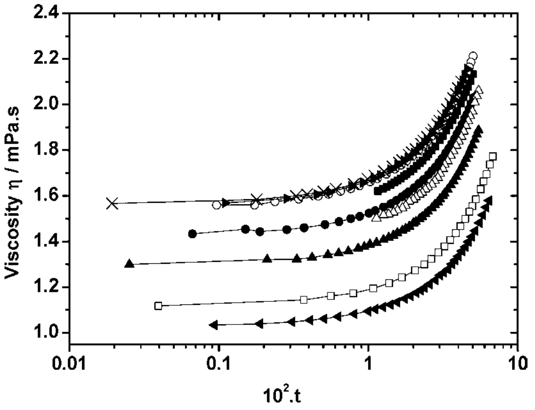

Figure 5. Reduced temperature t dependence of viscosity η for 1,4-dioxane (1) + water (2) + saturated KCl (3) with composition: ○, $w_2 = 0.20$, $m = 0.470$ mol·kg^{-1}; right-pointing triangle, $w_2 = 0.25$, $m = 0.488$ mol·kg^{-1}; ■, $w_2 = 0.328$, $m = 0.55$ mol·kg^{-1}; ×, $w_2 = 0.40$, $m = 0.792$ mol·kg^{-1}; △, $w_2 = 0.45$, $m = 1.154$ mol·kg^{-1}; ●, $w_2 = 0.50$, $m = 1.446$ mol·kg^{-1}; ▲, $w_2 = 55$, $m = 1.771$ mol·kg^{-1}; □, $w_2 = 0.57$, $m = 1.906$ mol·kg^{-1}; left-pointing triangle, $w_2 = 0.60$, $m = 2.039$ mol·kg^{-1}.

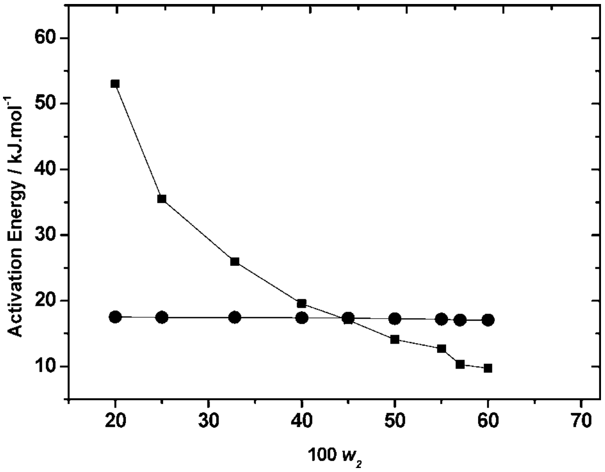

Figure 6. Representation of activation energy as function of water mass fraction w_2. The symbols are noted as follows: ■, E_a (κ); ●, E_a (η).

Transition Temperature. The temperature was measured using a quartz thermometer (HP 2804 A) giving a resolution of ± $2 \cdot 10^{-4}$ K. The densities, the kinematic viscosities, and electrical conductivities data are measured in the one-phase region at each temperature T below the temperature of phase transition T_t. To determine the transition temperature of phase transition T_t, that is, the temperature where the meniscus becomes visible, we proceeded as follows.

For all studied compositions of 1,4-dioxane (1) + water (2) + saturated KCl (3), the samples prepared are rigorously shaken and introduced into a thermostat bath at temperature T_1 until all of the quantity of salt is dissolved and the meniscus becomes visible. Then $T_1 > T_t$, the temperature of the bath was decreased to T_2, and the same operation was repeated. If the meniscus was not visible, the temperature of the bath was changed to T_3, while shaking the sample. This method allows T_t to be determined by $T^+ > T_t$ and $T^- < T_t$. When $(T^+ - T^-) \cong 2 \cdot 10^{-3}$ K, we stopped the operation and verified that, after having heated and vigorously shaken the sample outside the bath, the meniscus was again visible at T^+ and not visible at T^-.

Density. The density data in the homogeneous phase was measured with a commercial digital densitometer (Anton Paar, model DMA 46, Austria) which was modified in our laboratory. The density of the mixture was calculated from the electronically measured frequency of a mechanical oscillator filled with the fluid. The filling was accomplished by means of a medical syringe to prevent preferential evaporation and to reduce possible the errors. The densitometer needs to be carefully calibrated periodically with triple-distilled water[24] and methanol[25] at

Table 1. Viscosities η and Electrical Conductivies κ of the Mixture at Different Temperatures for ($w_2 = 0.20$; $m = 0.470\ \mathrm{mol \cdot kg^{-1}}$), ($w_2 = 0.25$; $m = 0.488\ \mathrm{mol \cdot kg^{-1}}$), ($w_2 = 0.328$; $m = 0.55\ \mathrm{mol \cdot kg^{-1}}$), ($w_2 = 0.40$; $m = 0.792\ \mathrm{mol \cdot kg^{-1}}$), ($w_2 = 0.45$; $m = 1.154\ \mathrm{mol \cdot kg^{-1}}$), ($w_2 = 0.50$; $m = 1.446\ \mathrm{mol \cdot kg^{-1}}$), ($w_2 = 55$; $m = 1.771\ \mathrm{mol \cdot kg^{-1}}$), ($w_2 = 0.57$; $m = 1.906\ \mathrm{mol \cdot kg^{-1}}$), and ($w_2 = 0.60$; $m = 2.039\ \mathrm{mol \cdot kg^{-1}}$)[a]

$m = 0.470\ \mathrm{mol \cdot kg^{-1}}$; $w_2 = 0.20$; $T_t^{\mathrm{Exprtl}} = 313.973$ K

T/K	η/mPa·s	κ/mS·cm^{-1}
298.151	2.21289	0.898
298.662	2.18623	0.947
299.086	2.16450	0.996
299.585	2.13915	1.014
300.144	2.11133	1.068
300.676	2.08529	1.130
301.174	2.06139	1.188
301.674	2.03768	1.246
302.165	2.01452	1.303
302.641	1.99254	1.358
303.037	1.97457	1.403
303.64	1.94757	1.473
304.070	1.92846	1.523
304.597	1.90557	1.584
305.172	1.88109	1.651
305.653	1.86058	1.706
306.176	1.83951	1.767
306.662	1.81902	1.823
307.152	1.79905	1.880
307.758	1.77496	1.950
308.287	1.75435	2.011
308.760	1.73594	2.066
309.230	1.71803	2.121
309.814	1.69588	2.188
310.358	1.67603	2.251
310.731	1.66248	2.294
311.239	1.64416	2.353
311.581	1.63197	2.393
311.923	1.61994	2.432
312.274	1.60771	2.473
312.519	1.59935	2.501
312.898	1.58623	2.545
313.227	1.57505	2.583
313.428	1.56037	2.607
313.670	1.56019	2.635

$m = 0.792\ \mathrm{mol \cdot kg^{-1}}$; $w_2 = 0.40$; $T_t^{\mathrm{Exprtl}} = 311.17$ K

T/K	η/mPa·s	κ/mS·cm^{-1}
298.153	2.10047	17.58
298.752	2.07064	17.91
299.16	2.04582	18.13
299.653	2.02725	18.35
300.151	2.00367	18.62
300.69	1.97892	18.87
301.322	1.95018	19.19
301.82	1.92792	19.54
302.167	1.91265	19.67
302.674	1.89055	19.98
302.973	1.87566	20.13
303.444	1.85735	20.37
303.843	1.84078	20.58
304.153	1.82715	20.76
304.713	1.80485	21.06
305.07	1.79035	21.23
305.355	1.77893	21.41
305.921	1.75667	21.69
306.19	1.74593	21.85
306.636	1.72861	22.04
307.209	1.70762	22.37
307.730	1.68728	22.64
308.092	1.67366	22.87
308.683	1.65201	23.15
309.281	1.63051	23.47
309.611	1.61871	23.67
309.96	1.60646	23.80
310.15	1.5998	23.871
310.613	1.58346	24.21
311.11	1.56676	24.44

$m = 2.039\ \mathrm{mol \cdot kg^{-1}}$; $w_2 = 0.60$; $T_t^{\mathrm{Exprtl}} = 327.365$ K

T/K	η/mPa·s	κ/mS·cm^{-1}
306.35	1.57987	93.06
307.259	1.55013	94.17
308.246	1.5162	95.27
309.264	1.48201	96.52
310.392	1.44758	98.19

$m = 0.488\ \mathrm{mol \cdot kg^{-1}}$; $w_2 = 0.25$; $T_t^{\mathrm{Exprtl}} = 312.567$ K

T/K	η/mPa·s	κ/mS·cm^{-1}
298.158	2.15543	1.773
298.706	2.12772	1.836
299.162	2.10509	1.891
299.660	2.08044	1.951
300.153	2.05688	2.03
300.902	2.02199	2.059
301.565	1.99119	2.21
302.305	1.95743	2.26
302.954	1.92846	2.33
303.436	1.90736	2.391
304.167	1.87575	2.47
304.852	1.84694	2.55
305.163	1.83395	2.60
305.696	1.81209	2.65
306.255	1.78945	2.72
306.812	1.76731	2.781
307.151	1.75391	2.819
307.653	1.73450	2.88
308.154	1.71530	2.94
308.814	1.69048	3.001
309.170	1.67732	3.06
309.680	1.65861	3.11
310.164	1.64114	3.167
310.843	1.61703	3.25
311.151	1.60617	3.29
311.680	1.58785	3.34
312.223	1.56936	3.41

$m = 1.154\ \mathrm{mol \cdot kg^{-1}}$; $w_2 = 0.45$; $T_t^{\mathrm{Exprtl}} = 312.357$ K

T/K	η/mPa·s	κ/mS·cm^{-1}
298.243	2.1588	26.12
298.685	2.13775	26.35
299.31	2.1050	26.78
300.132	2.0635	27.38
300.632	2.03825	27.73
301.113	2.01351	27.92
301.576	1.98909	28.43
302.102	1.96481	28.70
302.654	1.94134	29.07
303.142	1.91802	29.43
303.608	1.89678	29.79
304.202	1.87046	30.10
304.686	1.84828	30.55
305.274	1.82737	31.02
305.674	1.80699	31.20
306.19	1.78659	31.58
306.703	1.7664	31.97
307.181	1.74677	32.25
307.56	1.73207	32.50
307.992	1.71561	32.82
308.343	1.70509	33.03
308.541	1.69371	33.13
308.97	1.67986	33.40
309.215	1.6686	33.63
309.501	1.6591	33.73
309.841	1.64972	33.95
310.065	1.64096	34.17
310.618	1.62139	34.60
310.934	1.60844	34.70
311.274	1.59894	34.90
311.565	1.59015	35.09
311.829	1.58986	35.29
311.921	1.58482	35.27
312.320	1.57178	35.52

$m = 1.771\ \mathrm{mol \cdot kg^{-1}}$; $w_2 = 0.55$; $T_t^{\mathrm{Exprtl}} = 317.565$ K

T/K	η/mPa·s	κ/mS·cm^{-1}
300.194	1.88857	56.42
300.662	1.86866	57.02
301.173	1.84675	57.43
301.770	1.82181	58.35
302.280	1.80076	58.87
302.786	1.78007	59.19
303.256	1.76174	59.58
303.759	1.74142	60.4
304.248	1.72232	60.9

$m = 0.55\ \mathrm{mol \cdot kg^{-1}}$; $w_2 = 0.328$; $T_t^{\mathrm{Exprtl}} = 311.032$ K

T/K	η/mPa·s	κ/mS·cm^{-1}
298.205	2.13371	7.95
298.827	2.10267	8.17
299.311	2.0789	8.30
299.820	2.05427	8.40
300.294	2.03169	8.60
300.830	2.00672	8.80
301.590	1.97155	9.00
301.986	1.95361	9.20
302.480	1.93166	9.40
302.968	1.91009	9.50
303.505	1.88678	9.70
304.066	1.86287	9.94
304.490	1.84506	10.04
305.155	1.81753	10.27
305.615	1.7988	10.44
306.012	1.78284	10.51
306.274	1.77241	10.61
306.701	1.75553	10.77
307.010	1.74347	10.85
307.310	1.7319	10.92
307.647	1.7190	11.08
307.975	1.70653	11.19
308.283	1.69494	11.25
308.52	1.6861	11.34
308.806	1.67582	11.45
309.04	1.66689	11.51
309.275	1.65828	11.65
309.52	1.6494	11.77
309.80	1.63932	11.87
310.043	1.63062	11.93
310.32	1.62083	11.95

$m = 1.446\ \mathrm{mol \cdot kg^{-1}}$; $w_2 = 0.50$; $T_t^{\mathrm{Exprtl}} = 314.122$ K

T/K	η/mPa·s	κ/mS·cm^{-1}
298.150	2.03157	39.88
298.802	2.00381	40.48
299.260	1.98163	40.86
299.783	1.95739	41.29
300.283	1.9375	41.81
300.760	1.91397	42.14
301.280	1.89116	42.59
301.754	1.87251	42.98
302.255	1.84945	43.52
302.772	1.82805	43.92
303.258	1.80758	44.52
303.749	1.78824	44.83
304.305	1.76562	45.36
304.772	1.74688	45.70
305.290	1.72673	45.92
305.771	1.7082	46.45
306.160	1.69342	46.87
306.757	1.67121	47.27
307.251	1.65401	47.88
307.762	1.63593	48.13
308.267	1.61795	48.76
308.480	1.60879	48.93
308.843	1.59602	48.97
309.282	1.58077	49.31
309.683	1.56549	49.85
310.137	1.5517	50.06
310.615	1.5356	50.41
310.950	1.52467	50.72
311.365	1.51029	51.46
311.720	1.50084	51.38
312.120	1.48667	51.73
312.510	1.47434	52.13
312.952	1.46066	52.41
313.226	1.45242	52.65
313.529	1.44415	52.89
313.648	1.45383	52.96
313.913	1.43363	53.22

$m = 1.906\ \mathrm{mol \cdot kg^{-1}}$; $w_2 = 0.57$; $T_t^{\mathrm{Exprtl}} = 324.325$ K

T/K	η/mPa·s	κ/mS·cm^{-1}
302.220	1.77342	75.28
303.166	1.73775	76.55

Table 1. Continued

T / K	η / mPa·s	κ / mS·cm^{-1}	T / K	η / mPa·s	κ / mS·cm^{-1}	T / K	η / mPa·s	κ / mS·cm^{-1}
$m = 0.470$ mol·kg^{-1}; $w_2 = 0.20$; $T_t^{\text{Exprtl}} = 313.973$ K			$m = 0.488$ mol·kg^{-1}; $w_2 = 0.25$; $T_t^{\text{Exprtl}} = 312.567$ K			$m = 0.55$ mol·kg^{-1}; $w_2 = 0.328$; $T_t^{\text{Exprtl}} = 311.032$ K		
311.252	1.42127	99.24	304.758	1.7037	61.33	304.213	1.6952	77.71
312.048	1.39902	99.91	305.271	1.68332	61.86	305.160	1.66344	78.96
312.758	1.37676	101.1	305.758	1.66526	62.36	306.050	1.62848	79.84
313.499	1.35785	101.9	306.231	1.64777	62.95	307.285	1.58526	81.51
314.207	1.3358	102.7	306.771	1.62829	63.51	308.179	1.55513	82.6
314.859	1.31812	103.6	307.272	1.61027	64.02	308.882	1.5310	82.88
315.467	1.30141	104.4	307.545	1.6010	64.30	309.86	1.49965	83.96
316.217	1.27876	105.6	307.972	1.58607	64.75	310.86	1.4674	85.17
316.883	1.26414	106.5	308.287	1.57293	65.07	311.835	1.43732	86.15
317.486	1.25186	106.9	308.708	1.56063	65.50	312.834	1.40732	87.26
318.166	1.23113	107.8	309.102	1.54734	65.91	313.853	1.37893	88.59
318.972	1.21277	108.8	309.586	1.53147	66.21	314.754	1.35198	89.69
319.590	1.19701	109.4	309.917	1.52023	66.75	315.766	1.32399	90.51
320.040	1.1863	109.9	310.278	1.50861	67.12	316.628	1.3007	91.46
320.502	1.1758	110.8	310.563	1.49923	67.41	317.632	1.27416	92.58
321.091	1.16145	111.5	310.958	1.48657	67.82	318.870	1.24246	93.95
321.62	1.14904	111.9	311.202	1.48026	68.07	319.860	1.21785	95.04
322.27	1.13452	112.7	311.59	1.46663	68.47	320.825	1.19473	96.11
322.76	1.12337	113.4	311.921	1.45626	68.82	321.750	1.1731	97.14
323.248	1.11269	113.9	312.200	1.44769	69.1	322.500	1.16113	97.97
323.72	1.10322	114.5	312.590	1.43708	69.61	323.123	1.14464	98.66
324.101	1.09434	114.9	312.881	1.42678	69.89	324.197	1.11765	99.85
324.721	1.08212	115.6	313.220	1.41664	70.15			
325.31	1.07055	116.4	313.548	1.4069	70.69			
325.705	1.0610	116.8	313.965	1.39458	70.92			
326.028	1.05486	117.2	314.305	1.38759	71.37			
326.351	1.04765	117.8	314.580	1.3767	71.66			
326.75	1.03924	118.7	314.850	1.36974	71.83			
327.06	1.03364	118.7	315.231	1.35737	72.43			
			315.552	1.34897	72.76			
			315.860	1.34165	72.88			
			316.231	1.33007	73.56			
			316.51	1.32238	73.75			
			316.896	1.3208	73.95			
			317.485	1.29958	74.55			

[a] w_2 and T_t^{Exprtl} are respectively the water mass fraction and temperature of phase transition.

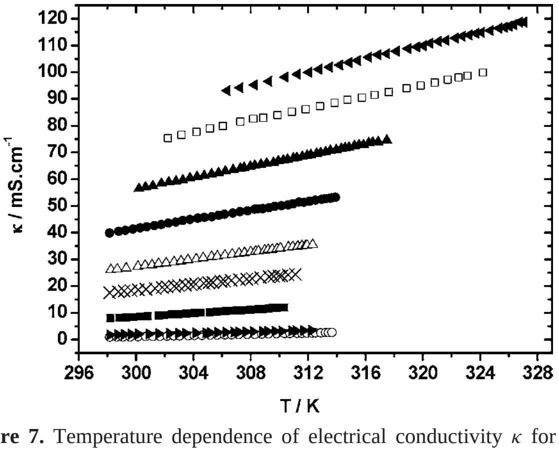

Figure 7. Temperature dependence of electrical conductivity κ for 1,4-dioxane (1) + water (2) + saturated KCl (3) with composition: ○, $w_2 = 0.20$, $m = 0.470$ mol·kg^{-1}; right-pointing triangle, $w_2 = 0.25$, $m = 0.488$ mol·kg^{-1}; ■, $w_2 = 0.328$, $m = 0.55$ mol·kg^{-1}; ×, $w_2 = 0.40$, $m = 0.792$ mol·kg^{-1}; △, $w_2 = 0.45$, $m = 1.154$ mol·kg^{-1}; ●, $w_2 = 0.50$, $m = 1.446$ mol·kg^{-1}; ▼, $w_2 = 55$, $m = 1.771$ mol·kg^{-1}; □, $w_2 = 0.57$, $m = 1.906$ mol·kg^{-1}; left-pointing triangle, $w_2 = 0.60$, $m = 2.039$ mol·kg^{-1}.

Table 2. Fit Results of the Electrical Conductivity κ According to Equation 2

m / mol·kg^{-1}	w_2	x'_2	A	B
0.470	0.20	0.550	-33.184 ± 0.141	0.1141 ± 0.0004
0.488	0.25	0.620	-32.788 ± 0.168	0.1159 ± 0.0005
0.55	0.328	0.705	-91.918 ± 0.541	0.335 ± 0.002
0.792	0.40	0.765	-140.533 ± 0.370	0.530 ± 0.001
1.154	0.45	0.800	-176.254 ± 0.893	0.678 ± 0.003
1.446	0.50	0.830	-211.400 ± 1.242	0.843 ± 0.004
1.771	0.55	0.857	-258.502 ± 0.857	1.049 ± 0.002
1.906	0.57	0.866	-257.925 ± 1.479	1.103 ± 0.004
2.039	0.60	0.880	-285.474 ± 1.468	1.235 ± 0.004

298.15 K. The uncertainties of the measured values of density were ± 10^{-4} g·cm^{-3}, and a thermal regulation of the sample, to within $3 \cdot 10^{-3}$ K, was needed. This was obtained by circulating water from a thermostat.

Viscosity. The viscosities η were obtained from the product ($\rho\nu$). The kinematic viscosities ν were measured using an Ubbelohde type viscometer. The length of the capillary was 0.20 m, and its constant $k = 3.991$ m^2·s^{-2}. The times at which the meniscus passes by two marks of the viscometer were recorded to ± 0.01 s with an electrical stop chronometer. The flow times are sufficient to minimize the kinetic energy corrections. At least five readings of the flow time with variation not exceeding ± 0.002 s were taken for each mixture. The viscosities ν were calculated from the average flow time t, by means of the relation $\nu = k(\tau - \theta)$ where τ is the correction time. The viscometer was calibrated with acetone and hexane of known density and viscosity[26,27] (high performance liquid chromatography grade). The viscometer was immersed in a thermally stabilized water bath with thermal regulation of the order of $2 \cdot 10^{-3}$ K over hours.

Electrical Conductivity. The electrical conductivity was measured with a digital conductivity meter PHYWE, Demo (13701.93), using a specially designed cell (electrode LTG 1/23) suitable for low conductivity measurement (with a cell constant

Table 3. Fitted Values of the Parameters of Equations 1 and 3

$\frac{m}{\mathrm{mol\cdot kg^{-1}}}$	w_2	x'_2	$\ln(\kappa_0/\mathrm{mS\cdot cm^{-1}})$	$\frac{E_a(\kappa)}{\mathrm{kJ\cdot mol^{-1}}}$	$\ln(\eta_0/\mathrm{mPa\cdot s})$	$\frac{E_a(\eta)}{\mathrm{kJ\cdot mol^{-1}}}$
0.470	0.20	0.550	21.343 ± 0.394	52.995 ± 1.005	−6.282 ± 0.009	17.541 ± 0.023
0.488	0.25	0.620	14.922 ± 0.229	35.487 ± 0.581	−6.277 ± 0.001	17.464 ± 0.004
0.55	0.328	0.705	12.547 ± 0.091	25.945 ± 0.231	−6.284 ± 0.001	17.459 ± 0.001
0.792	0.40	0.765	10.759 ± 0.050	19.548 ± 0.128	−6.280 ± 0.007	17.405 ± 0.018
1.154	0.45	0.800	10.147 ± 0.055	17.057 ± 0.140	−6.284 ± 0.005	17.374 ± 0.012
1.446	0.50	0.830	9.381 ± 0.043	14.097 ± 0.109	−6.259 ± 0.017	17.276 ± 0.045
1.771	0.55	0.857	9.136 ± 0.022	12.721 ± 0.058	−6.252 ± 0.010	17.190 ± 0.027
1.906	0.57	0.866	8.427 ± 0.028	10.298 ± 0.073	−6.223 ± 0.011	17.077 ± 0.028
2.039	0.60	0.880	8.356 ± 0.019	9.730 ± 0.050	−6.241 ± 0.007	17.061 ± 0.018

Table 4. Fit Results of the Electrical Conductivity κ According to Equations 4 to 6

$\frac{m}{\mathrm{mol\cdot kg^{-1}}}$	w_2	x'_2	$\frac{\kappa_c}{\mathrm{mS\cdot cm^{-1}}}$	A_1	A_{cr}	χ^2
0.470	0.20	0.550	2.685 ± 0.007	−24.082 ± 3.366	−8.633 ± 2.468	0.00013
0.488	0.25	0.620	3.446 ± 0.010	−37.378 ± 4.731	3.460 ± 0.836	0.00015
0.55	0.328	0.705	12.244 ± 0.033	−89.080 ± 17.113	12.380 ± −10.897	0.00132
0.792	0.40	0.765	24.469 ± 0.018	−165.312 ± 9.504	6.827 ± 0.222	0.00067
1.154	0.45	0.800	35.546 ± 0.029	−302.148 ± 15.552	65.156 ± 11.224	0.00254
1.446	0.50	0.830	53.289 ± 0.061	−366.400 ± 27.884	74.426 ± 20.427	0.0103
1.771	0.55	0.857	74.729 ± 0.056	−353.359 ± 22.334	16.565 ± 14.905	0.00827
1.906	0.57	0.866	99.893 ± 0.1166	−402.062 ± 38.021	33.506 ± 28.847	0.02344
2.039	0.60	0.880	118.961 ± 0.102	−447.658 ± 37.536	32.368 ± 28.155	0.02664

0.875 cm^{-1}). Before any measurement the conductivity cell was calibrated with a certified 10^{-3} mol·L^{-1} KCl solution. The uncertainty of the conductivity measurements was estimated to be ± 0.2 %. After calibration, the cell containing the solution was immersed in a thermally stabilized bath with good thermal regulation. The long-time stability of the cell was better than $3\cdot10^{-3}$ K. When the temperature of the sample was stabilized, the measurements were made as soon as possible (a few seconds) to reduce any effects that would modify the measured values (as self-heating of the samples, ionization in the electrodes, etc.), and we proceed to change the temperature for the next measurement.

Results and Discussion

Transition Temperature. Figures 1 and 2 display respectively the experimental variation of the temperature of phase separation as a function of the molality of potassium chloride and the water mass fraction w_2. We note that T_t have a minimum for the two cases equal to 311.032 K. The uncertainty of T_t is estimated to be ± $2\cdot10^{-3}$ K.

Viscosity. The viscosity results as a function of the temperature of 1,4-dioxane (1) + water (2) + saturated KCl (3) are reported in Table 1 and plotted in Figure 3. We note that the viscosity of the mixture decreases with increasing water mole fraction, molality of KCl, and temperature. It can explain why the increasing quantities of water or 1,4-dioxane weaken the force of interaction between the ions and increase their movement.

The viscosity η values can be correlated as a function of temperature, according to the following equation:

$$\eta = \eta_0 \exp\left(\frac{E_a(\eta)}{kT}\right) \qquad (1)$$

where η_0 is a constant and $E_a(\eta)$ is the activation energy for viscous flow. The Arrhenius representation is shown in Figure 4, and their fit results are depicted in Table 3. Figure 5 shows that the viscosities represented an anomaly near the critical temperature. This behavior is similar that reported in the literature.[28,29] It is found that the activation energy $E_a(\eta)$ values for the mixture were in the range of (17.541 ± 0.023 to 17.061 ± 0.018) kJ·mol^{-1}. Figure 6 and results in Table 3 show that the activation energy for viscous flow is not influenced by water mole fraction and with molality of KCl.

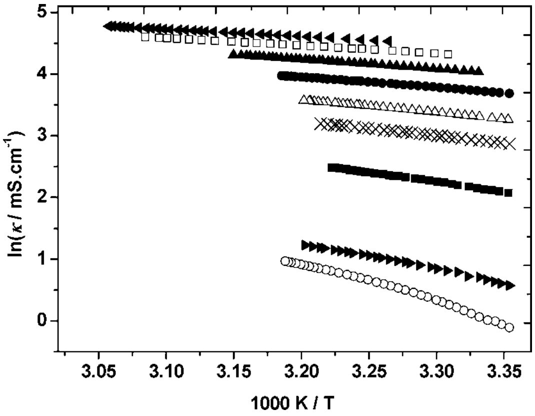

Figure 8. Arrhenius plots of electrical conductivity κ for 1,4-dioxane (1) + water (2) + saturated KCl (3) with composition: ○, $w_2 = 0.20$, $m = 0.470$ mol·kg^{-1}; right-pointing triangle, $w_2 = 0.25$, $m = 0.488$ mol·kg^{-1}; ■, $w_2 = 0.328$, $m = 0.55$ mol·kg^{-1}; ×, $w_2 = 0.40$, $m = 0.792$ mol·kg^{-1}; △, $w_2 = 0.45$, $m = 1.154$ mol·kg^{-1}; ●, $w_2 = 0.50$, $m = 1.446$ mol·kg^{-1}; ▲, $w_2 = 55$, $m = 1.771$ mol·kg^{-1}; □, $w_2 = 0.57$, $m = 1.906$ mol·kg^{-1}; left-pointing triangle, $w_2 = 0.60$, $m = 2.039$ mol·kg^{-1}.

Electrical Conductivity. The electrical conductivity results as a function of temperature of 1,4-dioxane (1) + water (2) + saturated KCl (3) are reported in Table 1 and plotted in Figure 7. We note that the electrical conductivity of mixture increases with increasing water mole fraction, molality of KCl, and temperature.

The electrical κ values can be correlated as a function of temperature, according to the following equation:

$$\kappa/\mathrm{mS{\cdot}cm^{-1}} = A + B(T/\mathrm{K}) \qquad (2)$$

The A and B coefficients for eq 2 are given in Table 2. Analyzing these coefficients, we obtained that A decreases linearly with the increase in water mole fraction and decreases with the increase in the concentration of salt, while B increases linearly with an increase in water mole fraction and increases with an increase in the concentration of salt. The conductivity

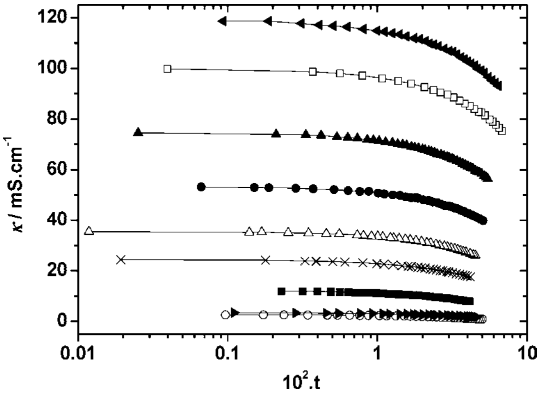

Figure 9. Reduced temperature *t* dependence of electrical conductivity *κ* for 1,4-dioxane (1) + water (2) + saturated KCl (3) with composition: ○, $w_2 = 0.20$, $m = 0.470\ \mathrm{mol\cdot kg^{-1}}$; right-pointing triangle, $w_2 = 0.25$, $m = 0.488\ \mathrm{mol\cdot kg^{-1}}$; ■, $w_2 = 0.328$, $m = 0.55\ \mathrm{mol\cdot kg^{-1}}$; ×, $w_2 = 0.40$, $m = 0.792\ \mathrm{mol\cdot kg^{-1}}$; △, $w_2 = 0.45$, $m = 1.154\ \mathrm{mol\cdot kg^{-1}}$; ●, $w_2 = 0.50$, $m = 1.446\ \mathrm{mol\cdot kg^{-1}}$; ▲, $w_2 = 55$, $m = 1.771\ \mathrm{mol\cdot kg^{-1}}$; □, $w_2 = 0.57$, $m = 1.906\ \mathrm{mol\cdot kg^{-1}}$; left-pointing triangle, $w_2 = 0.60$, $m = 2.039\ \mathrm{mol\cdot kg^{-1}}$.

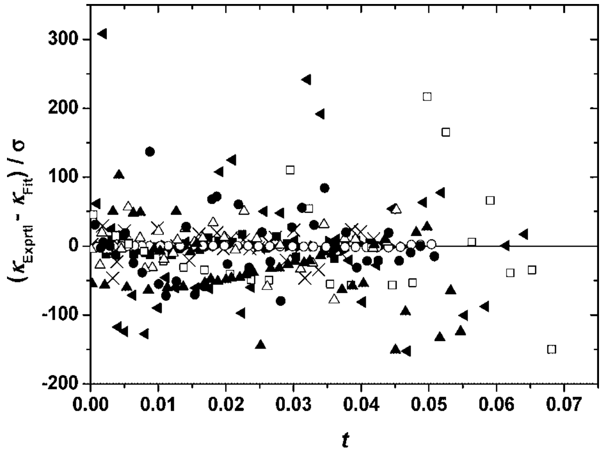

Figure 10. Deviation plot in conductivity for 1,4-dioxane (1) + water (2) + saturated KCl (3) as function of reduced temperature *t* with composition: ○, $w_2 = 0.20$, $m = 0.470\ \mathrm{mol\cdot kg^{-1}}$; right-pointing triangle, $w_2 = 0.25$, $m = 0.488\ \mathrm{mol\cdot kg^{-1}}$; ■, $w_2 = 0.328$, $m = 0.55\ \mathrm{mol\cdot kg^{-1}}$; ×, $w_2 = 0.40$, $m = 0.792\ \mathrm{mol\cdot kg^{-1}}$; △, $w_2 = 0.45$, $m = 1.154\ \mathrm{mol\cdot kg^{-1}}$; ●, $w_2 = 0.50$, $m = 1.446\ \mathrm{mol\cdot kg^{-1}}$; ▲, $w_2 = 55$, $m = 1.771\ \mathrm{mol\cdot kg^{-1}}$; □, $w_2 = 0.57$, $m = 1.906\ \mathrm{mol\cdot kg^{-1}}$; left-pointing triangle, $w_2 = 0.60$, $m = 2.039\ \mathrm{mol\cdot kg^{-1}}$.

is related to the ion mobility and the number of charge carriers. An increase in temperature results in an increase in the mobility. At a fixed composition in water and salt, the ions move faster at higher temperatured because of the relatively lower viscosity of the mixture.[28]

The variation of conductivity according to the temperature can be also fitted by Arrhenius equation:

$$\kappa = \kappa_0 \exp\left(-\frac{E_a(\kappa)}{kT}\right) \qquad (3)$$

where κ_0 is a constant and $E_a(\kappa)$ is the activation energy for ionic conduction. The Arrhenius representation is shown in Figure 8, and their fit results are depicted in Table 3. It is found that the activation energy $E_a(\kappa)$ values for the mixture were in the range of (9.730 ± 0.050 to 52.995 ± 1.005) $\mathrm{kJ\cdot mol^{-1}}$. Figure 6 shows that the activation energy for ionic conduction decreases with an increase in water mole fraction and consequently with the molality of KCl. We note that solvent−solvent interaction is strongly modified at critical composition caused by cluster formation. Also, K^+ and Cl^- ions are solvated preferentially by water, which slows down the transport phenomena.

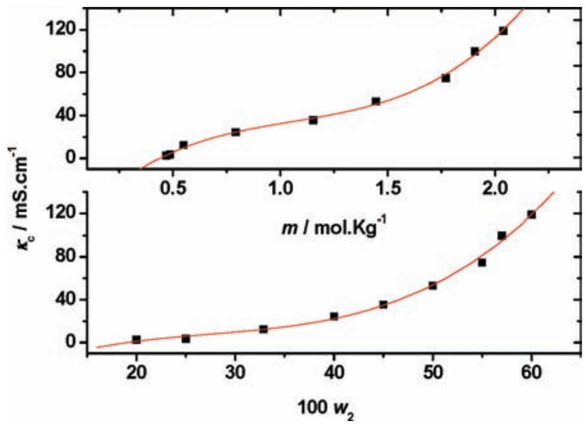

Figure 11. Critical electrical conductivity κ_c for 1,4-dioxane (1) + water (2) + saturated KCl (3) as a function of water mass fraction w_2 and molality *m* of salt.

Figure 9 shows the reduced temperature $t = |T/T_c - 1|$ dependence of the electrical conductivity, where T_c is the critical temperature of 1,4-dioxane (1) + water (2) + saturated KCl (3). The electrical conductivity anomaly was observed near the critical temperature; this behavior is similar to that reported in the literature.[29−31] There are two possible mechanisms for the anomaly, an anomalous proton-transfer rate predicted by the exponent $(1 - \alpha)$ and an anomalous extent of dissociation.[30]

Near the critical point of the liquid−liquid mixture, the electrical conductivity is given by:[29]

$$\kappa = \kappa_c + \kappa_{reg}(t) + \kappa_{crit}(t) \qquad (4)$$

where κ_c is the critical electrical conductivity. κ_{reg} is the smooth analytic function that takes into account the background or noncritical change of κ with the temperature and can be expressed as:[29]

$$\kappa_{reg}(t) = A_1 t + A_2 t^2 + ... \qquad (5)$$

The critical contribution is given by:

$$\kappa_{crit}(t) = A_{cr} t^{1-\alpha}(1 + a t^{\Delta} + b t^{2\Delta} + ...) \qquad (6)$$

where A_{cr} is the leading critical amplitude, while *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 capacity and the thermal expansivity near T_c. Table 4 gives the parameters of eqs 4 to 6. After fitting the experimental data using $\alpha = 0.11$, no correction-to-scaling terms were significant in eq 6. The deviation normalized by the estimated standard deviation is plotted in Figure 10 and is defined as $(\kappa_{Exp} - \kappa_{Fit})/\sigma$, where the standard deviation, σ, can be expressed as following:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{i=N}\left(\frac{\kappa_{i,exp} - \kappa_{i,Fit}}{\kappa_{i,exp}}\right)^2}{N - k}} \qquad (7)$$

where *N* and *k* are the numbers of data points and free parameters, respectively.

Figure 11 shows the critical conductivity κ_c varies with water mass fraction w_2 such as: $\kappa_c/\mathrm{mS\cdot cm^{-1}} = (67.197 \pm 19.971) + (-4.991 \pm 1.073)w_2 + (0.096 \pm 0.013)w_2^2$ and consequently with molality *m* of KCl such as: $\kappa_c/\mathrm{mS\cdot cm^{-1}} = (-68.001 \pm$

16.132) + (223.141 ± 49.835)(m/m_0) + (−179.050 ± 44.025) $(m/m_0)^2$ + (56.302 ± 11.737)$(m/m_0)^3$, where $m_0 = 1\ \mathrm{mol \cdot kg^{-1}}$.

Conclusion

From the above results, it can be seen that the viscosities of the mixture 1,4-dioxane (1) + water (2) + saturated KCl (3) decrease with increasing temperature, in water mole fraction and consequently in the concentration of salt, while the electrical conductivities increase.

The temperature dependence of electrical conductivity κ can be correlated by an empirical linear equation and fitted with a good precision. The temperature dependence of viscosity η and the electrical conductivity κ can be fitted to the Arrhenius equation. The activation energy $E_a(\kappa)$ for ionic conduction decreases with the increase in water mole fraction and consequently in molality of KCl, but they are not influenced in the activation energy $E_a(\eta)$ for viscous flow.

We have shown that the electrical conductivity and the viscosity presented an anomaly near the critical point. The critical electrical conductivity κ_c varies with water mass fraction w_2 as a second-degree polynomial and consequently with molality m of salt as a third-degree polynomial.

The temperature of phase transition T_t was found to vary with water mass fraction w_2 and consequently with the molality m of KCl.

Literature Cited

(1) Kouissi, T.; Bouanz, M.; Ouerfelli, N. KCl-Induced Phase Separation of 1,4-dioxane + Water Mixtures Studied by Electrical Conductivity and Refractive Index. *J. Chem. Eng. Data* **2009**, *54*, 566–573.

(2) Bouanz, M. Critical behavior of the self-diffusion coefficient in a binary fluid. *Phys. Rev. A* **1992**, *46*, 4888–4893.

(3) Bouanz, M.; Gharbi, A. Ionic structure in a binary fluid. *J. Phys.: Condens. Matter* **1994**, *6*, 4429–4435.

(4) Bouanz, M. The solvation phenomenon in a binary fluid. *Quim. Anal. (Barcelona, Spain)* **1996**, *15*, 530–533.

(5) Bouanz, M.; Beysens, D. Effect of ion impurities on a binary mixture of isobutyric acid and water. *J. Chem. Phys. Lett.* **1994**, *231*, 105–110.

(6) Toumi, A.; Bouanz, M. Critical behavior of the binary-fluid isobutyric acid-water with added ion (K^+, Cl^-). *Eur. Phys. J. E* **2000**, 211–216.

(7) Toumi, A.; Bouanz, M.; Gharbi, A. Coexistence curves of the binary mixture isobutyric acid-water with added ions (K^+, Cl^-). *Chem. Phys. Lett.* **2002**, *362*, 567–573.

(8) Toumi, A.; Bouanz, M.; Gharbi, A. Comportement de la relation de Lorentz -Lorentz dans un mélange binaire critique. *Phys. Chem. News* **2003**, *13*, 126–131.

(9) Kolb, H. A.; Woermann, D. Conductivity fluctuations in butyric acid /water and isobutyric acid /water mixtures. *J. Chem. Phys.* **1984**, *80*, 3781–3784.

(10) Cherif, E.; Bouanz, M. Electrical conductivity along phase diagram of the critical mixture isobutyric acid-water with added (K^+, Cl^-) ions. *Int. J. Mol. Sci.* **2003**, *4*, 326–334.

(11) Cherif, E.; Bouanz, M. Resistivity-viscosity relationship in liquid-liquid critical mixtures with added ions. *Fluid Phase Equilib.* **2007**, *251*, 71–77.

(12) Cherif, E.; Bouanz, M. Coexistence curves of electrical conductivity in critical solution: isobutyric acid-water with added ions. *Phys. Chem. Liq.* **2007**, *44*, 649–661.

(13) Hadded, N.; Bouanz, M. Electrical conductivity of the binary mixture isobutyric acid-water with added (Zn^{2+}, SO_4^{2-}) ions. *Fluid Phase Equilib.* **2008**, *266*, 47–53.

(14) Hadded, N.; Bouanz, M. Excess permittivity and excess conductivity of binary fluid mixture isobutyric acid-water along the coexistence curve. *Phys. Chem. Liq.* **2009**, *47* (2), 160–171.

(15) Takamuku, T.; Yamaguchi, A.; Matsuo, D.; Tabata, M.; Yamaguchi, T.; Otomo, T.; Adachi, T. NaCl-Induced Phase Separation of 1,4-Dioxane-Water Mixtures Studied by Large-Angle X-ray Scattering and Small-Angle Neutron Scattering Techniques. *J. Phys. Chem. B* **2001**, *105*, 10101–10110.

(16) Bogardus, H. F.; Lynch, C. C. The Ternary systems Barium Chloride-Dioxane-Water and Calcium Chloride-Dioxane-water. *J. Phys. Chem.* **1943**, *47*, 650–654.

(17) Campbell, A. N.; Kartzmak, E. M.; Maryk, W. B. The systems Sodium Chlorate-Water-Dioxane and Lithium Chlorate-Water-Dioxane at 25°C. *Can. J. Chem.* **1966**, *44*, 935–937.

(18) Campbell, A. N.; Lam, S. Y. Phase Diagrams of Sodium Chloride and of Potassium Chloride in Water-Dioxane. *Can. J. Chem.* **1972**, *50*, 3388–3390.

(19) Bešter, R. M.; Doler, D. Phase equilibria in the (Water + 1,4-Dioxane + Magnesium Chloride) system. *Acta. Chim. Slov.* **1990**, *46* (4), 463–470.

(20) Gutkowski, K.; Anisimov, M. A.; Sengers, J. V. Crossover criticality in ionic solutions. *J. Chem. Phys.* **2001**, *114* (7), 3133–3148.

(21) Bianchi, H. L.; Japas, M. L. Phase equilibria of a near-critical ionic system. Critical exponent of the order parameter. *J. Chem. Phys.* **2001**, *115* (22), 10472–10478.

(22) Gutkowski, K. I.; Bianchi, H. L.; Japas, M. L. Critical behavior of a ternary ionic system: A controversy. *J. Chem. Phys.* **2003**, *118* (6), 2808–2814.

(23) Gutkowski, K. I.; Bianchi, H. L.; Japas, M. L. Nonasymptotic Critical Behavior of a Ternary Ionic System. *J. Phys. Chem. B* **2007**, *111*, 2554–2564.

(24) *Physikalisch-Technische Bundesanstalt*, 2nd ed.; license Nr. 13/1985; Chempro GmbH, D6450: Hanau, Germany, 1985; p 6.

(25) Brunel, V. *International Critical Tables*; McGraw-Hill: New York, 1928; Vol. 3, p 27.

(26) Levitte, B. P. *Findlay's Practical Physical Chemistry*, 9th ed.; Longman: New York, 1973.

(27) Weast, R. C.; Astle, M. J. In *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1980.

(28) Yanfang, G.; Siliu, C.; Tengfang, W.; Dahong, Y.; Changjun, P.; Honglai, L.; Ying, H. Density, viscosity and electrical conductivity of 1-butyl-3-methylimidazolium hexafluorophosphate + monoethanolamine and N, N-dimethylethanolamine. *J. Mol. Liq.* **2008**, *143*, 100–108. (a) Hernández, P. M.; Ortega, F.; Ramón, G. R. Crossover critical phenomena in an aqueous electrolyte solution: light scattering, density and viscosity of the 3-methylpyridine + water + NaBr system. *J. Chem. Phys.* **2003**, *119* (8), 4428–4436.

(29) Oleinikova, A.; Bonetti, M. Electrical conductivity of highly concentrated electrolytes near the critical consolute point: A study of tetra-*n*-butylammonium picrate in alcohols of moderate dielectric constant. *J. Chem. Phys.* **2001**, *101* (21), 9871–9882.

(30) Anderson, E. M.; Greer, S. C. Chemical reactions near critical points: The dissociation of weak acids. *Phys. Rev. A* **1984**, *30*, 3129–3135.

(31) Shaw, C. H.; Goldburg, W. I. Electrical conductivity of binary mixtures near the critical point. *J. Chem. Phys.* **1976**, *65* (11), 4906.

Received for review April 13, 2009. Accepted September 24, 2009.

JE900351T