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Liquid−Liquid Coexistence Curves of {*x* 1-Butyl-3-methylimidazolium Tetrafluoroborate + (1 − *x*) 1,3-Propanediol} and {*x* 1-Butyl-3-methylimidazolium Tetrafluoroborate + (1 − *x*) 1,4-Butanediol}

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The liquid−liquid coexistence curves of the binary solutions of 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4]) + 1,3-propanediol and [C_4mim][BF_4] + 1,4-butanediol were determined by measuring the temperature dependence of the refractive index in the two phases of the samples with critical compositions. The critical amplitude B and the critical exponent β have been deduced from the coexistence curves. The experimental values of β are consistent with theoretical prediction. The results have also been analyzed to determine the Wegner-correction terms and to examine the asymmetric behavior of the diameters of the coexistence curves.

Introduction

The character of critical behavior in physical systems depends on the range of interactions. Ising criticality observed in fluid phase transitions requires short-range interactions as driving potential.[1,2] When sufficiently close to the critical point, the correlation length of critical fluctuation becomes so large that microscopic details of short-range intermolecular interactions become unimportant. Therefore, near the critical point, a variety of systems, including anisotropic ferromagnets, binary alloys, simple fluids, fluid mixtures, and polymer blends, belong to the same universal class of 3D-Ising model.[3−7]

Mean-field exponents are expected when long-range interactions such as Coulombic interactions[1,2] drive the phase transition. Phase separation driven by Coulombic interactions between ions is expected in a solvent of low dielectric constant for large size ions, so room temperature ionic liquids (RTILs) are thought to be a good model to study the nature of the critical point in liquid−liquid phase transitions driven by Coulombic interactions. Most simulations[8−10] on phase separation driven by Coulombic forces evidenced that it belongs to the Ising universality class. Many experimental results on ionic systems with solvents being low dielectric constant confirmed this result.[11−15] It was attributed to the shielding effect due to Debye−Hückel charge order in the ionic system, which makes long-range Coulomb interactions become effectively short-range.

As a system is departing from the critical point, it experiences a crossover from the asymptotic Ising behavior to the mean field one. The nonasymptotic critical behavior is system dependent: molecular solutions always show monotonic crossover to mean-field behavior, while nonmonotonic crossover behavior was found in many ionic solutions.[16−18] It was attributed to the greater strength and larger range of particle interaction and the possible additional mesoscopic length scale in the ionic solutions,[16−18] which is required to be further clarified.

Measurement of the coexistence curve in the critical region is an important way to study nonasymptotic critical behavior and test the complete scaling theory proposed by Anisimov and Sengers.[19] Besides the scientific interest in investigation of the nature of critical phenomena in liquid−liquid phase transition driven by the Coulombic interaction, study of the coexistence curves of RTIL solutions is of technical interest in application as the reaction medium and in a separation process.[15,20,21]

Most coexistence curves reported in the literature were determined by visual observations of the phase separation points of the solutions with known compositions. This method is not accurate enough to determine the critical exponents. Some coexistence curves were determined by the measurements of refractive indexes of two coexisting phases, which is capable of determining the critical exponents accurately. However, to obtain the coexistence curves described by experimental composition variables such as mole fraction, volume fraction, and mass fraction, the Lorenz−Lorenz relation was required to be used in conversion of refractive index to the experimental concentration variables. This conversion could yield an uncertainty in mole fraction as much as 0.1,[15] although it may be reduced partly by the corrections for nonideal behaviors. An alternative choice for the conversions is to determine the dependence of refractive index on the mole fraction,[22] which is believed to be a more accurate conversion process.

In this paper, we report the refractive indexes of coexisting phases at various temperatures for the systems of {x [C_4mim][BF_4] + (1 − x) 1,3-propanediol} and {x [C_4mim][BF_4] + (1 − x) 1,4-butanediol}. We also report the refractive indexes at various temperatures in the single-phase region for a series of binary solutions with known compositions and deduce the dependences of the refractive index on the temperature and the concentration, which are used to convert the refractive indexes of the coexistence curves to the mole fractions and further the volume fractions for the above two systems. The results are analyzed to obtain the critical exponents

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and critical amplitudes and to examine the asymptotic and the crossover behaviors of the coexistence curves over a wide temperature range.

Experimental Section

1,3-Propanediol and 1,4-butanediol were purchased from Acros, with purity > 99.5 % and > 99 %, respectively. They were dried and stored over 0.4 nm molecular sieves. The ionic liquid [C_4mim][BF_4] was purchased from LiHua Pharmaceutical Co. Ltd., with purity ≥ 99 %. Traces of water were removed from the ionic liquid by keeping it for three days at about 330 K under an oil-pump vacuum and then storing it in desiccators. Solutions were made up by weighing with a precision of ± 0.1 mg.

The coexistence curves were determined by measurements of refractive indexes of two coexisting phases using the technique of "minimum deviations". The apparatus and the experimental procedures for measurements of refractive index and the techniques for determining the critical concentration and the critical temperature have been described previously.[22] During the measurements, the temperature was constant at ± 0.001 K. The accuracy and the precision of the temperature measurement were ± 0.01 K and ± 0.001 K, respectively. The accuracy of measurement was ± 0.003 K for the temperature difference ($T - T_c$), ± 0.0001 for the refractive index in each coexisting phase, and ± 0.001 for the critical mole fraction x_c.

The densities of [C_4mim][BF_4] and 1,3-propanediol were measured with a densitometer (Anton Parr DMA-601), and the accuracy of measurement was better than ± 0.00001 $g \cdot cm^{-3}$. During the measurements of the density, the temperature was constant at ± 0.01 K.

Results and Discussion

The critical mole fractions and the critical temperatures were determined to be $x_c = (0.236 \pm 0.001)$ and $T_c = (299.4 \pm 0.1)$ K for {x [C_4mim][BF_4] + (1 − x) 1,3-propanediol} and $x_c = (0.253 \pm 0.001)$ and $T_c = (309.6 \pm 0.1)$ K for {x [C_4mim][BF_4] + (1 − x) 1,4-butanediol}, respectively.

Both the critical temperature and the critical concentration are higher for a longer chain alcohol than those for the shorter one. The longer the chain of the alcohol, the smaller the polarity is; therefore, the increase of the critical temperature is according to the decreasing polarity of the alcohols, which is in agreement with the observations by other authors[15,23−25] and the so-called restricted primitive model (RPM) that predicts a reversed proportionality of the critical temperature with ε, where ε is dielectric constant of alcohol.

The refractive indexes n were measured for each coexisting phase at various temperatures. The results are listed in columns 2 and 3 of Table 1 for {x [C_4mim][BF_4] + (1 − x) 1,3-propanediol} and in columns 2 and 3 of Table 2 for {x [C_4mim][BF_4] + (1 − x) 1,4-butanediol}. They are also shown in Figures 1a and 2a, respectively, as the plots of temperature against refractive index and are denoted as the (T, n) coexistence curves.

The refractive index n of a pure liquid or a mixture may be expressed by a linear function of temperature in a certain temperature range[22]

$$n(T,x) = n(T^0,x) + R(x)(T - T^0) \tag{1}$$

$$R(x) = xR_A + (1 - x)R_B \tag{2}$$

Table 1. Coexistence Curves of (T, n), (T, x), and (T, ϕ) for {x [C_4mim][BF_4] + (1 − x) 1,3-Propanediol}[a]

$T_c - T$/K	n_1	n_2	x_1	x_2	ϕ_1	ϕ_2
0.006	1.4284	1.4273	0.216	0.259	0.414	0.473
0.018	1.4286	1.4270	0.209	0.271	0.401	0.486
0.050	1.4289	1.4267	0.199	0.284	0.387	0.503
0.082	1.4293	1.4265	0.185	0.294	0.368	0.517
0.116	1.4294	1.4264	0.182	0.299	0.363	0.522
0.165	1.4297	1.4263	0.172	0.304	0.351	0.531
0.217	1.4299	1.4262	0.166	0.309	0.341	0.537
0.325	1.4302	1.4260	0.158	0.320	0.327	0.550
0.446	1.4304	1.4258	0.152	0.331	0.318	0.562
0.533	1.4306	1.4257	0.147	0.337	0.309	0.569
0.621	1.4307	1.4256	0.145	0.343	0.305	0.576
0.724	1.4309	1.4255	0.139	0.349	0.296	0.583
0.856	1.4311	1.4254	0.135	0.356	0.288	0.590
1.038	1.4313	1.4253	0.130	0.364	0.280	0.598
1.243	1.4316	1.4252	0.123	0.372	0.267	0.607
1.427	1.4318	1.4251	0.119	0.380	0.259	0.615
1.678	1.4321	1.4250	0.112	0.390	0.248	0.626
1.931	1.4323	1.4249	0.109	0.399	0.240	0.633
2.183	1.4325	1.4248	0.105	0.409	0.233	0.643
2.520	1.4327	1.4247	0.102	0.420	0.228	0.653
2.913	1.4330	1.4246	0.097	0.433	0.217	0.665
3.322	1.4332	1.4246	0.094	0.439	0.212	0.670
3.712	1.4335	1.4245	0.089	0.452	0.202	0.682
4.100	1.4337	1.4245	0.087	0.459	0.199	0.688
4.488	1.4340	1.4245	0.082	0.466	0.188	0.694
5.216	1.4344	1.4245	0.076	0.479	0.176	0.705
5.943	1.4348	1.4245	0.071	0.493	0.166	0.716
7.042	1.4355	1.4245	0.061	0.514	0.144	0.733
8.057	1.4359	1.4246	0.058	0.527	0.138	0.743
10.232	1.4368	1.4248	0.051	0.557	0.123	0.766
12.188	1.4375	1.4250	0.047	0.585	0.114	0.785
13.962	1.4382	1.4253	0.041	0.600	0.100	0.796
16.135	1.4389	1.4256	0.039	0.627	0.093	0.814
18.128	1.4394	1.4258	0.037	0.642	0.086	0.826

[a] Refractive indexes n were measured at wavelength $\lambda = 632.8$ nm and $T_c = 299.403$ K. Mole fraction and volume fraction are denoted by x and ϕ, and subscripts 1 and 2 relate to upper and lower phases, respectively.

where $R(x)$ is the derivative of n with respect to T for a solution with particular composition x and R_A and R_B are the values of $R(x)$ for $x = 1$ and $x = 0$, respectively. The refractive indexes of pure [C_4mim][BF_4], pure 1,3-propanediol, and pure 1,4-butanediol at various temperatures were measured and are listed in Table 3. Fitting eq 1 with the experimental results listed in Table 3 gave $R_A = -2.57 \cdot 10^{-4}$ for [C_4mim][BF_4], $R_B = -2.69 \cdot 10^{-4}$ for 1,3-propanediol, and $R_B = -2.75 \cdot 10^{-4}$ for 1,4-butanediol, respectively. A series of binary mixtures with known mole fractions x were prepared, and their refractive indexes in the single-phase region at various temperatures were measured to find the dependence of n on x and T. The results are listed in Table 4 and Table 5 and were used to fit eq 1 and eq 2 to obtain the values of $n(T^0)$ with uncertainties less than $1 \cdot 10^{-4}$, where T^0 are the middle temperatures of the coexistence curves. $T^0 = 288.15$ K for {x [C_4mim][BF_4] + (1 − x) 1,3-propanediol} and $T^0 = 298.15$ K for {x [C_4mim][BF_4] + (1 − x) 1,4-butanediol}, respectively. The values of $n(T^0)$ were fitted to the polynomial forms to obtain

$$n(T^0 = 288.15\ \mathrm{K}, x) = 1.4393 - 0.0476x + 0.0627x^2 - 0.0593x^3 + 0.0382x^4 - 0.0108x^5 \tag{3}$$

$$n(T^0 = 298.15\ \mathrm{K}, x) = 1.4436 - 0.0526x + 0.0654x^2 - 0.0885x^3 + 0.888x^4 - 0.0368x^5 \tag{4}$$

with a standard deviation of less than $2 \cdot 10^{-4}$. Equations 1 to 4 were used to convert refractive indexes to mole fractions.

The volume fraction ϕ of [C_4mim][BF_4] was then calculated from the mole fraction x through

$$1/\phi = (1 - K) + K/x \tag{5}$$

$$K = d_A M_B / d_B M_A \tag{6}$$

where d is the mass density; M is the molar mass; and the subscript A relates to $[C_4mim][BF_4]$ and B relates to 1,3-propanediol or 1,4-butanediol, respectively. The densities of $[C_4mim][BF_4]$ and 1,3-propanediol were measured in this work, and that of 1,4-butanediol was taken from the literature,[26] which are listed in Table 6. The densities at various temperatures were fitted to the linear temperature dependences which were used to calculate d_A and d_B in eq 6. The values of x and ϕ for coexisting phases at various temperatures are listed in columns 4 to 7 of Table 1 and Table 2 and are shown in Figures 1b, 1c, 2b, and 2c as the plots of temperature against mole fraction (T, x) and volume fraction (T, ϕ), respectively.

In the region sufficiently close to the critical temperature, the difference $\Delta\rho$ of a general density variable between two coexistence phases, such as mole fraction, refractive indexes, and volume fractions, exhibits universal power law dependences on the reduced temperature t

$$\Delta\rho = \rho_2 - \rho_1 = Bt^{\beta} \tag{7}$$

where $t = (T_c - T)/T_c$; T_c is the critical temperature; the subscripts 1 and 2 represent upper and lower phases; B is the critical amplitude; and β is the critical exponent. The value of critical exponent β is 0.327[27] for 3D-Ising universality class, while it is 0.5 from the classical mean-field theories.

Table 2. Coexistence Curves of (T, n), (T, x), and (T, ϕ) for {x $[C_4mim][BF_4]$ + $(1 - x)$ 1,4-Butanediol}[a]

$T_c - T$/K	n_1	n_2	x_1	x_2	ϕ_1	ϕ_2
0.009	1.4310	1.4294	0.230	0.282	0.387	0.454
0.038	1.4315	1.4289	0.215	0.299	0.367	0.474
0.060	1.4318	1.4287	0.206	0.306	0.354	0.483
0.078	1.4319	1.4285	0.203	0.313	0.350	0.491
0.117	1.4321	1.4283	0.197	0.321	0.342	0.500
0.162	1.4323	1.4281	0.192	0.328	0.335	0.508
0.231	1.4325	1.4278	0.185	0.338	0.325	0.519
0.323	1.4329	1.4276	0.177	0.348	0.313	0.530
0.403	1.4332	1.4274	0.169	0.357	0.301	0.540
0.495	1.4334	1.4273	0.164	0.361	0.293	0.545
0.590	1.4335	1.4271	0.161	0.368	0.289	0.552
0.695	1.4337	1.4270	0.157	0.375	0.283	0.559
0.818	1.4340	1.4268	0.150	0.384	0.272	0.569
0.992	1.4342	1.4266	0.146	0.394	0.266	0.579
1.217	1.4345	1.4263	0.137	0.406	0.251	0.591
1.478	1.4348	1.4262	0.134	0.416	0.247	0.601
1.866	1.4353	1.4260	0.124	0.429	0.231	0.614
2.278	1.4357	1.4258	0.117	0.442	0.219	0.626
2.848	1.4363	1.4256	0.106	0.458	0.201	0.641
3.385	1.4367	1.4254	0.099	0.473	0.189	0.655
3.992	1.4371	1.4252	0.094	0.490	0.180	0.670
4.703	1.4376	1.4251	0.087	0.504	0.168	0.683
5.382	1.4382	1.4250	0.078	0.519	0.152	0.695
6.280	1.4387	1.4249	0.071	0.536	0.139	0.710
7.140	1.4392	1.4248	0.065	0.553	0.128	0.724
8.003	1.4397	1.4248	0.060	0.565	0.119	0.733
8.987	1.4402	1.4248	0.055	0.580	0.110	0.745
10.009	1.4406	1.4248	0.052	0.596	0.104	0.757
10.947	1.4410	1.4248	0.049	0.611	0.098	0.769
12.185	1.4416	1.4249	0.044	0.625	0.089	0.779
13.524	1.4424	1.4250	0.035	0.641	0.071	0.791
15.101	1.4430	1.4251	0.031	0.662	0.063	0.806
16.671	1.4436	1.4252	0.028	0.684	0.057	0.821
19.269	1.4446	1.4253	0.022	0.722	0.045	0.846

[a] Refractive indexes n were measured at wavelength $\lambda = 632.8$ nm and $T_c = 309.618$ K. Mole fraction and volume fraction are denoted by x and ϕ, and subscripts 1 and 2 relate to upper and lower phases, respectively.

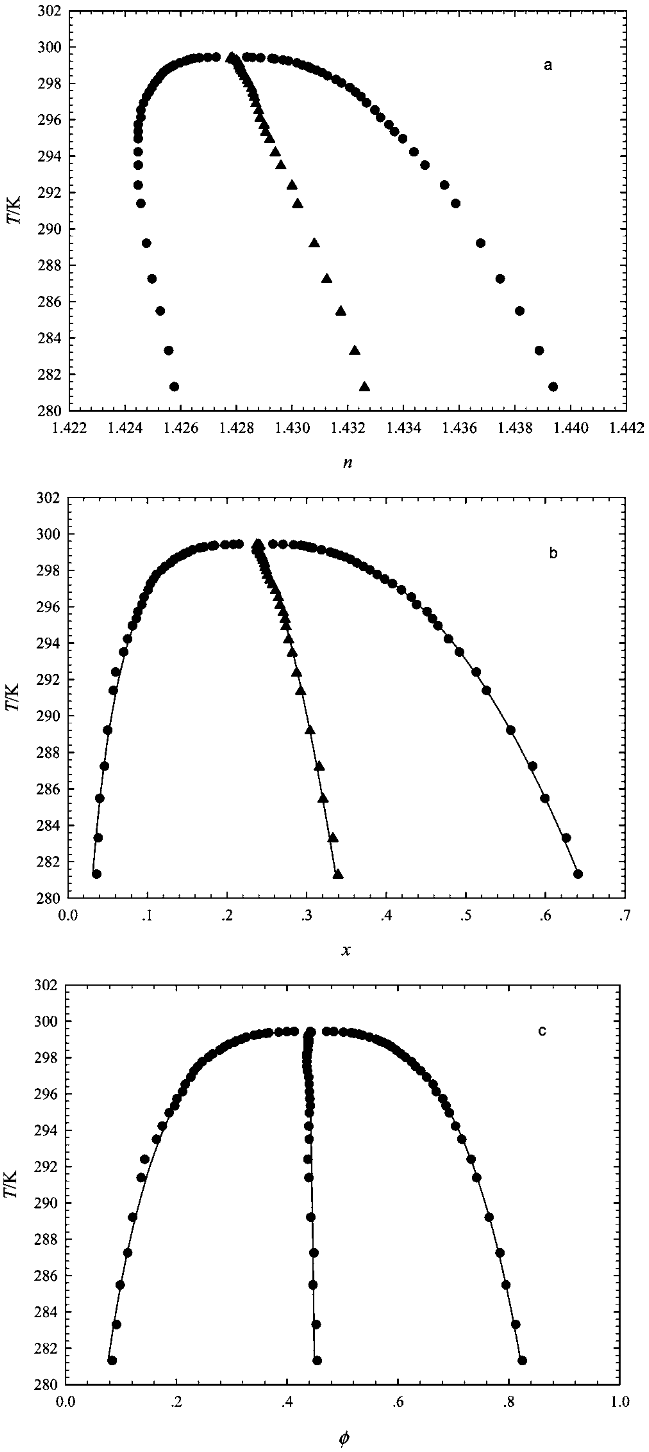

Figure 1. Coexistence curves of (T, n), (T, x), and (T, ϕ) for {x $[C_4mim][BF_4]$ + $(1 - x)$ 1,3-propanediol}. (a) Temperature T vs refractive index n; (b) temperature T vs mole fraction x; (c) temperature T vs volume fraction ϕ. ●, experimental values of concentration variables ρ of the coexisting phases; ▲, experimental values of diameter ρ_d of the coexisting phases; ---, concentration variables ρ(calc.) and diameters ρ_d(calc.) of coexisting phases calculated from eq 10 and eq 11 with coefficients listed in Table 8 and Table 9.

The differences $(\rho_2 - \rho_1)$ of general density variables n, x, and ϕ of coexisting phases obtained in this work were fitted to eq 7 to obtain β and B. The results are given in Table 7. The values of β and B are in very good agreement with the theoretical prediction of 0.327 as the temperatures are close to the critical points ($|T_c - T| < 1$ K). However, when $|T_c - T| < 20$ K, the values of critical exponents of n and ϕ are smaller

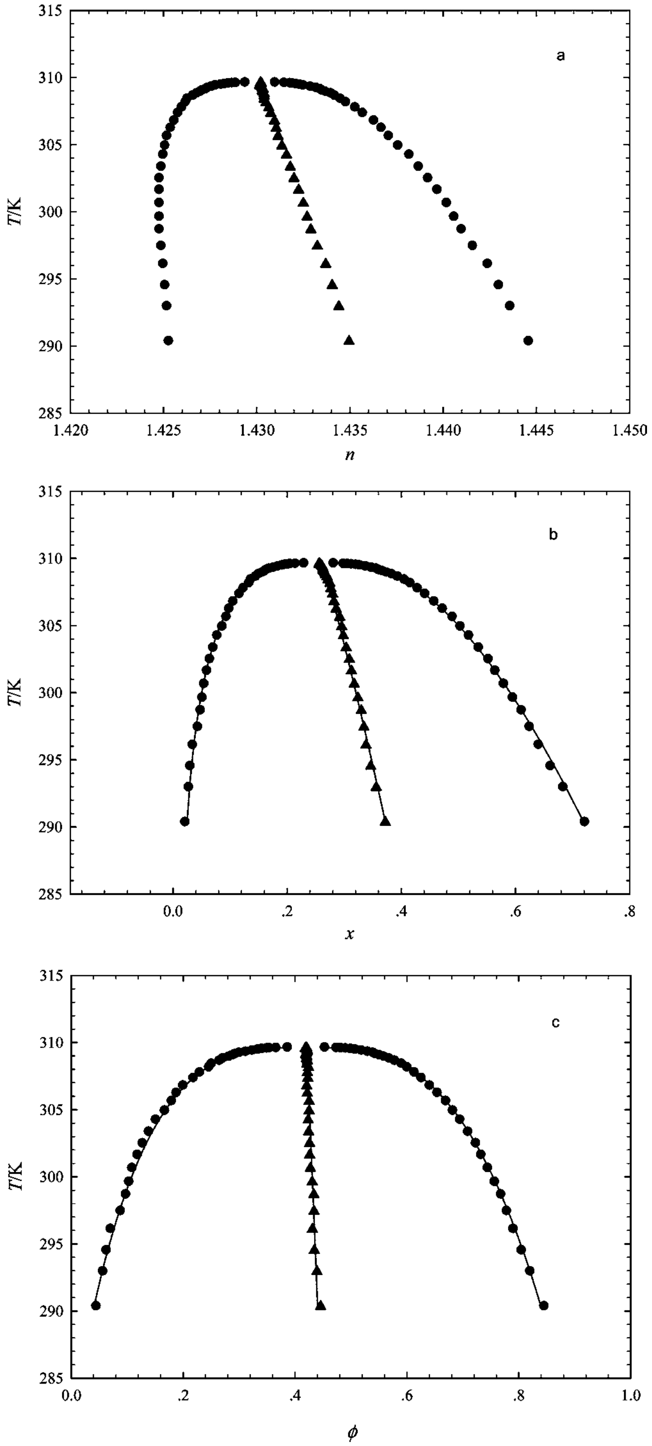

Figure 2. Coexistence curves of (T, n), (T, x), and (T, ϕ) for $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-butanediol$\}$. (a) temperature T vs refractive index n; (b) temperature T vs mole fraction x; (c) temperature T vs volume fraction ϕ. ●, experimental values of concentration variables ρ of the coexisting phases; ▲, experimental values of diameter ρ_d of the coexisting phases; ---, concentration variables ρ(calc.) and diameters ρ_d(calc.) of coexisting phases calculated from eq 10 and eq 11 with coefficients listed in Table 8 and Table 9.

than the 3D-Ising value, while the value of x is larger than the 3D-Ising value as shown in Table 7. An explanation will be given in the later part of the discussion.

The Wagner correction terms[28] were suggested to be added into eq 7 when it was applied to a wide temperature range. Thus, eq 7 becomes

$$\rho_2 - \rho_1 = Bt^{\beta} + B_1 t^{\beta+\Delta} + ... \tag{8}$$

with the critical exponents β and Δ to be fixed at the theoretical values ($\beta = 0.327$, $\Delta = 0.50$),[27] and eq 8 was used to fit the experimental results to obtain the parameters B and B_1. The results are also summarized in Table 8. The value of the critical amplitude for $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-butanediol$\}$ is larger than that for $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,3-propanediol$\}$, indicating the latter has a smaller two-phase coexisting region, which may be interpreted that the short-chain alcohol with higher polarity is more favored to interact with RTIL molecules and therefore mix with RTIL better than the long-chain alcohol. The negative values of the first Wagner correction term were obtained for the order parameters of refractive indexes and the volume fractions. Instead of taking it as the evidence of nonmonotonic crossover from the Ising value to the mean field value, we prefer to attribute it to the significantly negative contribution of the regular term to the effective exponent β_{eff}.

Table 3. Refractive Indexes n at Wavelength $\lambda = 632.8$ nm for $[C_4mim][BF_4]$, 1,3-Propanediol, and 1,4-Butanediol at Various Temperatures

T/K	n	T/K	n	T/K	n
		$[C_4mim][BF_4]$			
286.907	1.4228	295.032	1.4207	309.020	1.4171
288.889	1.4223	297.042	1.4202	314.345	1.4157
290.923	1.4218	299.020	1.4197	318.922	1.4146
293.040	1.4212	304.123	1.4184		
		1,3-Propanediol			
287.460	1.4396	293.101	1.4381	299.087	1.4365
288.885	1.4392	295.162	1.4375	301.207	1.4359
290.941	1.4387	297.022	1.4370		
		1,4-Butanediol			
294.225	1.4447	303.233	1.4422	313.686	1.4393
297.667	1.4437	306.212	1.4414		
300.862	1.4428	309.127	1.4406		

Table 4. Refractive Indexes n at Wavelength $\lambda = 632.8$ nm for $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,3-Propanediol$\}$ at Various Compositions and Temperatures

T/K	n	T/K	n	T/K	n
		$x = 0.0947$			
297.159	1.4328	300.002	1.4321	303.058	1.4313
298.494	1.4325	301.525	1.4317	305.125	1.4308
		$x = 0.194$			
299.596	1.4289	302.170	1.4282	305.507	1.4272
301.079	1.4285	304.128	1.4276	307.323	1.4267
		$x = 0.299$			
299.537	1.4263	303.548	1.4252	307.428	1.4241
301.401	1.4258	305.296	1.4247	309.076	1.4236
		$x = 0.384$			
299.507	1.4245	303.530	1.4234	307.445	1.4223
301.217	1.4240	305.284	1.4229	308.963	1.4219
		$x = 0.513$			
296.024	1.4235	300.000	1.4224	304.012	1.4212
298.139	1.4229	302.018	1.4218	304.933	1.4209
		$x = 0.602$			
290.780	1.4239	295.080	1.4227	298.984	1.4217
293.294	1.4232	296.977	1.4222	301.098	1.4211
		$x = 0.698$			
286.796	1.4240	291.204	1.4229	294.937	1.4219
289.365	1.4234	293.301	1.4223	297.936	1.4211
		$x = 0.796$			
286.808	1.4233	290.857	1.4223	295.857	1.4211
288.867	1.4228	292.889	1.4218	297.963	1.4206
		$x = 0.901$			
287.242	1.4228	290.999	1.4219	294.987	1.4209
288.877	1.4224	292.949	1.4214	297.004	1.4204
299.997	1.4196				

Table 5. Refractive Indexes n at Wavelength $\lambda = 632.8$ nm for $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-Butanediol$\}$ at Various Compositions and Temperatures

T/K	n	T/K	n	T/K	n
		$x = 0.094$			
306.251	1.4367	308.240	1.4361	310.169	1.4355
307.203	1.4364	309.231	1.4358	312.271	1.4349
314.325	1.4343				
		$x = 0.190$			
309.545	1.4322	312.778	1.4312	316.135	1.4302
311.248	1.4317	314.291	1.4308	317.296	1.4299
		$x = 0.286$			
309.877	1.4289	312.995	1.4279	315.792	1.4271
311.224	1.4285	314.394	1.4275	317.348	1.4266
		$x = 0.381$			
309.264	1.4264	312.315	1.4255	315.655	1.4246
310.639	1.4260	313.793	1.4251	317.383	1.4241
		$x = 0.484$			
306.699	1.4247	309.725	1.4238	312.876	1.4229
308.217	1.4243	311.331	1.4234	314.312	1.4225
		$x = 0.579$			
304.220	1.4237	308.275	1.4225	312.195	1.4214
306.241	1.4231	310.223	1.4220	314.294	1.4208
		$x = 0.686$			
303.255	303.255	307.292	307.292	311.217	311.217
305.261	305.261	309.202	309.202	313.283	313.283
		$x = 0.786$			
301.241	1.4216	304.235	1.4208	309.241	1.4195
303.162	1.4211	307.212	1.4200	311.854	1.4188
		$x = 0.894$			
296.244	1.4221	300.129	1.4211	304.141	1.4200
298.195	1.4216	302.155	1.4206	306.686	1.4194

Table 6. Densities of $[C_4mim][BF_4]$, 1,3-Propanediol, and 1,4-Butanediol at Various Temperatures

T/K	$d/(g \cdot cm^{-3})$	T/K	$d/(g \cdot cm^{-3})$	T/K	$d/(g \cdot cm^{-3})$
		$[C_4mim][BF_4]$			
293.15	1.21005	303.15	1.20259	313.15	1.19524
298.15	1.20632	308.15	1.19897		
		1,3-Propanediol			
293.15	1.05348	303.15	1.04726	313.15	1.04094
298.15	1.05028	308.15	1.04411		
		1,4-Butanediol[26]			
293.15	1.01637	303.15	1.00996	313.15	1.00355
298.15	1.01304	308.15	1.00675	318.15	1.00072

Table 8. Values of Critical Amplitudes B and B_1 of Equation 8 for Coexistence Curves of (T, n), (T, x), and (T, ϕ) for $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,3-Propanediol$\}$ and $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-Butanediol$\}$

order parameter	B	B_1
	$\{x\ [C_4mim][BF_4] + (1 - x)$ 1,3-Propanediol$\}$	
n	0.0404 ± 0.0002	-0.024 ± 0.001
	0.0368 ± 0.0004	
x	1.508 ± 0.005	0.08 ± 0.02
	1.52 ± 0.01	
ϕ	2.124 ± 0.008	-1.06 ± 0.05
	1.96 ± 0.01	
	$\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-Butanediol$\}$	
n	0.0506 ± 0.0001	-0.0114 ± 0.0008
	0.0487 ± 0.0001	
x	1.581 ± 0.007	0.57 ± 0.04
	1.679 ± 0.007	
ϕ	2.016 ± 0.004	-0.39 ± 0.03
	2.016 ± 0.005	

Table 9. Coefficients ρ_c and D of Equation 9 and Standard Deviations s in ρ_d for Diameters of Coexistence Curves of (T, x) and (T, ϕ) for $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,3-Propanediol$\}$ and $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-Butanediol$\}$[a]

	(T, x)	(T, ϕ)
	$\{x\ [C_4mim][BF_4] + (1 - x)$ 1,3-Propanediol$\}$	
ρ_c(expt.)	0.235 ± 0.001	0.440 ± 0.005
	$Z = 0.654$	
ρ_c	0.233 ± 0.001	0.438 ± 0.004
D	0.65 ± 0.01	0.07 ± 0.01
s	$4.6 \cdot 10^{-4}$	$6.2 \cdot 10^{-4}$
	$Z = 0.89$	
ρ_c	0.239 ± 0.001	0.439 ± 0.003
D	1.29 ± 0.02	0.16 ± 0.02
s	$5.0 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$
	$\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-Butanediol$\}$	
ρ_c(expt.)	0.253 ± 0.003	0.418 ± 0.004
	$Z = 0.654$	
ρ_c	0.253 ± 0.001	0.419 ± 0.001
D	0.675 ± 0.009	0.119 ± 0.007
s	$2.8 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$
	$Z = 0.89$	
ρ_c	0.260 ± 0.001	0.420 ± 0.001
D	1.33 ± 0.01	0.24 ± 0.01
s	$4.6 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$

[a] ρ_c(expt.) is the critical value of the order parameter determined by the techniques described in the text.

The effective critical exponent β_{eff} of the order parameter is defined as $\beta_{eff} = -d \log(\Delta\rho)/d \log t$; the values of β_{eff} were obtained from the spline fitting of the experimental data of $\log(\Delta\rho)$ at various $\log t$ and the numeric derivative according to the definition. Figures 3 and 4 show the variations of β_{eff} with reduced temperature t for $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,3-propanediol$\}$ and $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-butanediol$\}$, respectively. We deleted the experimental points of $t < 0.001$ in spline fittings because of their larger experimental uncertainties. From Figures 3 and 4, we can see that values of β_{eff} for mole fraction x increase with t even in the region of $t < 0.01$, while the values of β_{eff} for refractive index n and volume fraction ϕ decrease significantly as $t > 0.01$. These phenomena are quite common for ionic solutions.[15,29,30] Wagner[15] attributed these phenomena to the different crossover of β_{eff} for different order parameters from the Ising value to the mean field value and

Table 7. Values of Critical Amplitudes B and Critical Exponents β of Equation 7 for Coexistence Curves of (T, n), (T, x), and (T, ϕ) for $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,3-Propanediol$\}$ and $\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-Butanediol$\}$

order parameter	$T_c - T < 1$ K		$T_c - T < 20$ K	
	B	β	B	β
		$\{x\ [C_4mim][BF_4] + (1 - x)$ 1,3-Propanediol$\}$		
n	0.038 ± 0.001	0.326 ± 0.003	0.032 ± 0.001	0.296 ± 0.002
x	1.47 ± 0.04	0.325 ± 0.004	1.54 ± 0.02	0.330 ± 0.001
ϕ	2.01 ± 0.06	0.327 ± 0.005	1.76 ± 0.02	0.300 ± 0.003
		$\{x\ [C_4mim][BF_4] + (1 - x)$ 1,4-Butanediol$\}$		
n	0.0495 ± 0.001	0.327 ± 0.003	0.0463 ± 0.003	0.313 ± 0.001
x	1.61 ± 0.04	0.326 ± 0.003	1.80 ± 0.02	0.345 ± 0.002
ϕ	2.03 ± 0.05	0.325 ± 0.004	1.94 ± 0.01	0.317 ± 0.001

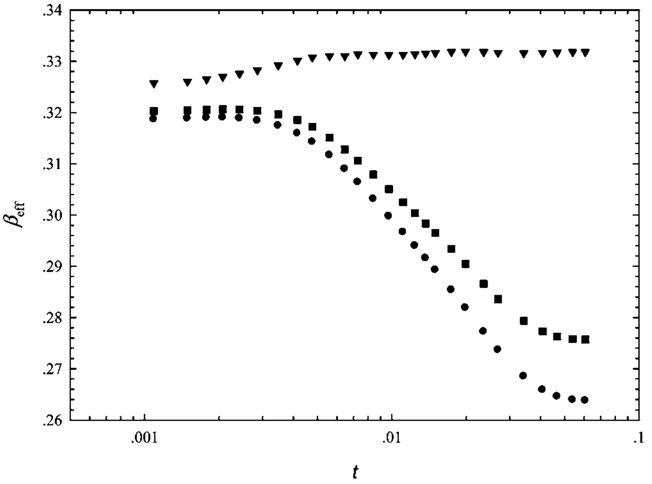

Figure 3. Relations of the effective exponent β_{eff} of the order parameter vs the reduced temperature t of {x [C$_4$mim][BF$_4$] + (1 − x) 1,3-propanediol}. ●, β_{eff} of the order parameter n; ▼, β_{eff} of the order parameter x; ■, β_{eff} of the order parameter ϕ.

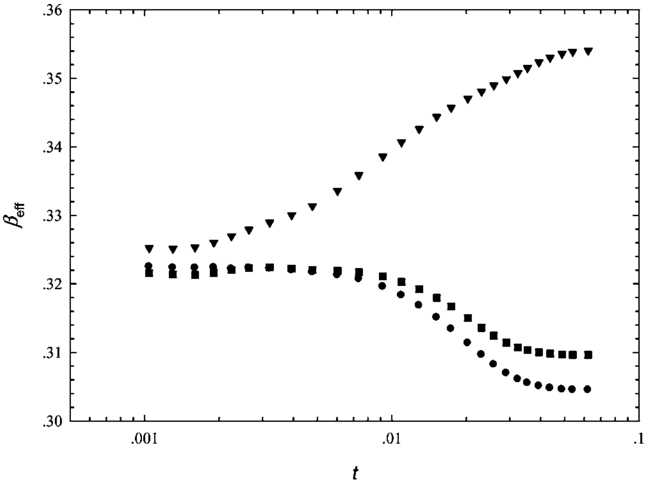

Figure 4. Relations of the effective exponent β_{eff} of the order parameter vs the reduced temperature t of {x [C$_4$mim][BF$_4$] + (1 − x) 1,4-butanediol}. ●, β_{eff} of the order parameter n; ▼, β_{eff} of the order parameter x; ■, β_{eff} of the order parameter ϕ.

took them as evidence of nonmonotonic crossover for ϕ. Sengers[17] pointed out that the regular term, which is proportional to reduced temperature t, must be accounted for at $t > 0.01$ in the analysis of the coexistence curves. Our previous study[30] of the coexistence curves on the binary mixtures of 2,6-dimethypyridine + H_2O in the critical region gave the same behavior as the present results and showed that the regular term was significant. We believe that in the binary solutions of {x [C$_4$mim][BF$_4$] + (1 − x) 1,3-propanediol} and {x [C$_4$mim][BF$_4$] + (1 − x) 1,4-butanediol} the remarkable contribution of regular terms for order parameters of n and ϕ results in significant reductions of the value of the average critical exponent listed in Table 7 in a larger temperature region and masked the monotonic crossover of β_{eff} from the Ising value to the mean field value, while the contribution of the regular term for x was insignificant.

The diameters ρ_d of coexistence curves for two choices of the order parameters of mole fraction and volume fraction were fitted with the following relation

$$\rho_d = (\rho_2 + \rho_1)/2 = \rho_c + Dt^Z \tag{9}$$

where ρ_c is the value of ρ_d at the critical point; D is the system-dependent parameter; and Z is an apparent exponent.

For a binary mixture, there is no a priori reason for choosing one order parameter over another, but order parameters may be examined by testing the symmetry of the coexisting curve and by comparing the goodness of fitting eq 9 with Z being $(1 - \alpha) = 0.89$ and $2\beta = 0.654$, respectively, where α characterizes the divergence of the heat capacity at constant volume for a pure fluid. The results are compared in Table 9. The quantity of $\Delta S = S_{1-\alpha} - S_{2\beta}$, where $S_{1-\alpha}$ and $S_{2\beta}$ are the standard deviations in fitting experimental values of ρ_d to eq 9 with $Z = 1 - \alpha$ and 2β, respectively, may be used to show the goodness of fit of the order parameters.[31] The smaller the value of ΔS is, the better the order parameter is. The values of ΔS suggest that ϕ is better than x, which is consistent with what the symmetry of the coexistence curves showed: the (T, ϕ) curves are more symmetric than the (T, x) curves for these two binary mixtures. However, the significance of the terms of $1 - \alpha$ and 2β for the order parameter ϕ is comparable, which indicates that even for a good order parameter the contribution of the 2β term could not be neglected comparing with the term of $1 - \alpha$, which is consistent with the consequence of complete scaling.[19]

The experimental values of x_c and ϕ_c presented in Table 9 were determined by the technique of "equal volumes of two coexistence phases" and calculated by using eq 5 and eq 6. The uncertainties of optimal parameters reported in Table 9 are the standard errors of fits including no systematic uncertainties resulting from converting n to x and x to ϕ, which were estimated to be about ± 0.004. Thus, the values of x_c and ϕ_c obtained from extrapolation of eq 9 are consistent with those from the observations. It is evident that no significant critical anomaly is present in the refractive indexes and that they were properly converted to mole fractions and volume fractions in our work.

Combining eq 8 and eq 9 yields

$$\rho_1 = \rho_c + Dt^Z - (1/2)Bt^{\beta} - (1/2)B_1t^{\beta+\Delta} \tag{10}$$

$$\rho_2 = \rho_c + Dt^Z + (1/2)Bt^{\beta} + (1/2)B_1t^{\beta+\Delta} \tag{11}$$

with Z, β, and Δ being fixed at 0.654, 0.327, and 0.5, T_c being fixed at 299.403 K for {x [C$_4$mim][BF$_4$] + (1 − x) 1,3-propanediol} or 309.618 K for {x [C$_4$mim][BF$_4$] + (1 − x) 1,4-butanediol}, respectively, and the values D, ρ_c, B, and B_1 being taken from Table 8 and Table 9. The values of ρ_1, ρ_2, and ρ_d were calculated by using eq 9, eq 10, and eq 11. The results are shown as lines in Figures 1 and 2. The values obtained from calculation are in good agreement with the experimental results.

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