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Liquid–liquid equilibria of 1-octyl-3-methylimidazolium hexafluorophosphate with 1-propanol or tert-butanol in the critical region

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ABSTRACT

Coexistences curves of liquid–liquid phase transition were reported for the binary solutions of the room temperature ionic liquid (RTIL) 1-octyl-3-methylimidazolium hexafluorophosphate ([C$_8$mim][PF$_6$]) with 1-propanol or tert-butanol. The critical amplitude B and the critical exponent β corresponding to the coexistence curve were deduced and the values of β were found to be consistent with the 3D-Ising value. Asymmetry of the diameters for the coexistence curves were examined and discussed in the frame of the complete scaling theory.

1. Introduction

The room temperature ionic liquids (RTILs) have drawn much attention in the fields of chemical industry as well as the scientific research in recent decades due to their excellent properties, such as high stability, low volatility, high conductivity, large heat capacity, noninflammability, and good dissolving capacity [1–3]. The mixtures of RTILs/organic solvents have been used as the media of chemical reactions and the advantage of liquid–liquid phase transitions of the media makes the elegant separation of products, catalyst and solvent possible by small changes of temperature or composition [4], thus it is important to acquire more knowledge of the liquid–liquid phase equilibriums of the RTILs solutions [5].

Since Pitzer discovered the liquid–liquid phase transition of an ionic liquid in an organic solvent, the field has become a prominent subject both in theoretical and experimental fields. The critical behaviors of the liquid–liquid equilibriums near the critical points driven by the coulomb interactions in RTILs solutions were expected to challenge the universality hypothesis, which postulates that the critical behaviors in fluid and fluid mixtures all belong to the Ising universality class independent of the molecular details of the system [6]. However, computer simulations [7–9] and experimental studies [10–13] on phase separation of some RTILs solutions near the critical point have clearly proved their Ising behavior. It's pointed [3] that for RTILs solutions with low permittivity organic solvents, the phase transition observed at ambient temperature may be driven by columbic interactions, while with high permittivity ones, it's considered to be driven by solvophobic mechanism.

Near the critical point, the differences of the values of the general density variable between the two coexisting phases for systems belonging to Ising universality class, may be expressed by:

$$\Delta\rho = \left|\rho_L - \rho_U\right| = B\tau^{\beta} \tag{1}$$

where ρ is the general density variable and the subscript U or L indicates each of the two coexisting phases; τ is the reduced temperature ($\tau = \left|T_c - T\right|/T_c$, T_c is the critical temperature); β is the critical exponent with the value of 0.326 calculated by renormalization group theory [14] and B is a system-dependent critical amplitude.

Fisher and co-workers [15,16] have proposed a general formulation of the complete scaling for one-component fluids to describe the asymmetric criticality of the liquid–liquid coexistence curves, which pointed that the three scaling fields should be the linear mixture of all physical fields: the chemical potential μ, the temperature T and the pressure P. Anisimov and co-workers

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Table 1
Purities, suppliers and water contents of chemicals.

Chemical name	Supplier	Purity, mass fraction	Dried and stored method	Water content
[C_8mim][PF_6]	Cheng Jie Chemical Co. Ltd.	0.99	Dried under an oil-pump vacuum at 330 K for 2 weeks and then stored in a desiccator over P_2O_5	164 ppm
1-Propanol	Alfa Aesar	0.999	stored in a desiccators over P_2O_5	112 ppm
tert-Butanol	Alfa Aesar	0.999	stored in a desiccator over P_2O_5	128 ppm

[17–19] extended the complete scaling to binary mixtures for incompressible or weakly compressible liquid mixtures. The complete scaling theory have been tested by a few experimental data of the coexistence curves for binary liquid mixtures [20,21], however more accurate coexistence-curve data for more fluids or fluid mixtures including RTILs solutions are highly required.

In this paper, we report the liquid–liquid coexistence curves of {x 1-octyl-3-methylimidazolium hexafluorophosphate (x [C_8mim][PF_6]) + (1 − x) 1-propanol} and {x [C_8mim][PF_6] + (1 − x) *tert*-butanol}. These precise experimental results were used to determine the critical exponent β and the critical amplitude B and to examine the asymmetric behavior of the diameters of the coexistence curves through the complete scaling theory [17–19].

2. Experimental

2.1. Chemicals

Table 1 lists the chemicals [C_8mim][PF_6], 1-propanol and *tert*-butanol together with their suppliers, purified methods, purities, and water contents. The mass fractions of water remaining in the samples after drying were analyzed by the coulometric Karl-Fischer titration.

2.2. Apparatus and procedure

The critical composition was determined by adjusting the proportion of the two components to achieve “equal volume” of the two phases at the phase-separation point [22]. The precision in determination of the critical mole fraction was about ±0.001. The samples with the critical concentrations were then prepared in rectangular fluorimeter cuvettes provided with Ace-thread connections and placed into a water bath. The refractive indexes in the two coexisting phases of the samples were measured using “minimum deviation angle” technique which had been described previously [23]. During the measurements of the refractive indexes, the temperature was constant within ±0.002 K. The accuracy of the measurement was ±0.003 K for the temperature difference ($T_c - T$), and ±0.0001 for the refractive index n at λ = 632.8 nm in each coexisting phase.

3. Results and discussion

The critical mole fractions of [C_8mim][PF_6] which was defined as the second component and has larger molecular volume than the alcohols, and the critical temperatures were determined to be $x_c = (0.084 \pm 0.001)$, $T_c = (308.0 \pm 0.1)$ K for {x [C_8mim][PF_6] + (1 − x) 1-propanol} and $x_c = (0.068 \pm 0.001)$, $T_c = (320.6 \pm 0.1)$ K for {x [C_8mim][PF_6] + (1 − x) *tert*-butanol}, respectively.

The refractive indexes n measured for each coexisting phase at various temperatures are listed in columns 2 and 3 for {x [C_8mim][PF_6] + (1 − x) 1-propanol} in Table 2 and for {x [C_8mim][PF_6] + (1 − x) *tert*-butanol} in Table 3 and shown in Figs. 1a and 2a as the plots of the temperature against the refractive index, denoted as the (T, n) coexistence curve. In order to obtain the mole fractions x in each of the coexistence curve, a set of calibration measurements were carried where we measured the refractive index n as a function of temperature in one-phase region for a series of binary mixtures of {x [C_8mim][PF_6] + (1 − x) 1-propanol} and {x [C_8mim][PF_6] + (1 − x) *tert*-butanol} with various known mole fractions, which are listed in Tables 4 and 5. Because the critical anomaly in the refractive index is weak [23], the refractive index n

Table 2
Coexistence curves of (T, n), (T, x), (T, ϕ) for {x [C_8mim][PF_6] + (1 − x) 1-propanol}. Refractive indexes were measured at wavelength λ = 632.8 nm, pressure p = 85 kPa and T_c = 307.978 K. Mole fraction and volume fraction are denoted by x and ϕ. Subscripts U and L relate to upper and lower phases, respectively.[a]

T	n_U	n_L	x_U	x_L	ϕ_U	ϕ_L
307.973	1.3879	1.3900	0.074	0.094	0.226	0.274
307.970	1.3877	1.3902	0.072	0.096	0.221	0.279
307.961	1.3874	1.3906	0.069	0.100	0.213	0.288
307.956	1.3872	1.3907	0.068	0.101	0.210	0.291
307.954	1.3871	1.3908	0.067	0.102	0.208	0.293
307.949	1.3870	1.3909	0.066	0.103	0.205	0.295
307.940	1.3868	1.3911	0.064	0.105	0.200	0.300
307.932	1.3867	1.3913	0.063	0.107	0.197	0.304
307.921	1.3865	1.3914	0.062	0.108	0.194	0.306
307.906	1.3863	1.3916	0.060	0.110	0.189	0.311
307.891	1.3862	1.3918	0.059	0.112	0.186	0.315
307.868	1.3861	1.3920	0.058	0.114	0.183	0.319
307.852	1.3859	1.3922	0.056	0.116	0.178	0.324
307.823	1.3857	1.3924	0.055	0.118	0.175	0.328
307.798	1.3855	1.3926	0.053	0.120	0.169	0.332
307.764	1.3854	1.3928	0.052	0.122	0.167	0.336
307.729	1.3852	1.3931	0.050	0.126	0.161	0.345
307.692	1.3851	1.3932	0.049	0.127	0.158	0.347
307.638	1.3849	1.3935	0.048	0.130	0.155	0.353
307.573	1.3847	1.3938	0.046	0.133	0.150	0.359
307.491	1.3845	1.3942	0.044	0.138	0.144	0.369
307.399	1.3843	1.3945	0.042	0.141	0.138	0.374
307.297	1.3841	1.3948	0.040	0.144	0.132	0.380
307.178	1.3839	1.3952	0.038	0.149	0.126	0.390
307.052	1.3837	1.3956	0.036	0.153	0.120	0.397
306.911	1.3836	1.3960	0.035	0.158	0.117	0.406
306.758	1.3834	1.3963	0.033	0.161	0.111	0.412
306.592	1.3832	1.3967	0.031	0.165	0.104	0.419
306.417	1.3831	1.3971	0.030	0.170	0.101	0.429
306.225	1.3830	1.3974	0.029	0.173	0.098	0.436
306.027	1.3829	1.3977	0.028	0.176	0.095	0.441
305.818	1.3828	1.3981	0.026	0.181	0.089	0.450
305.597	1.3827	1.3985	0.025	0.186	0.086	0.456
305.354	1.3826	1.3989	0.024	0.190	0.082	0.464
305.084	1.3826	1.3993	0.023	0.195	0.079	0.472
304.787	1.3825	1.3997	0.021	0.199	0.073	0.479
304.472	1.3825	1.4001	0.020	0.204	0.069	0.486
304.125	1.3824	1.4005	0.019	0.208	0.066	0.493
303.726	1.3825	1.4010	0.018	0.214	0.063	0.502
303.269	1.3825	1.4016	0.017	0.222	0.059	0.512
302.752	1.3826	1.4021	0.016	0.227	0.056	0.520
302.247	1.3827	1.4026	0.016	0.232	0.056	0.528
301.672	1.3827	1.4032	0.014	0.240	0.049	0.537
300.885	1.3828	1.4040	0.012	0.249	0.042	0.551
300.161	1.3830	1.4047	0.012	0.258	0.042	0.562
299.160	1.3832	1.4055	0.010	0.266	0.036	0.574
298.094	1.3835	1.4064	0.010	0.277	0.036	0.586

[a] Standard uncertainties u are $u(p)$ = 10 kPa, $u(T)$ = 0.02 K, $u(T - T_c)$ = 0.002 K, $u(n)$ = 0.0001, $u(x)$ = 0.002, $u(\phi)$ = 0.002.