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Liquid–Liquid Equilibrium in Binary System [bmim][PF₆] + 1-Butanol

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In the present paper, liquid–liquid equilibrium in binary system 1-butyl-3-methylimidazolium hexafluorophosphate + 1-butanol has been studied. Experimental liquid phase behavior was investigated using a volumetric method and a cloud-point method, the former enabling us to obtain tie lines (compositions of equilibrium phases), the latter yielding points of the binodal curve. The results have been compared with previous works and correlated by the NRTL and the Flory–Huggins equations. In addition, as data were obtained in the critical region of the binary system, they were described using the extended scaling-law equation.

Introduction

Room-temperature ionic liquids (RTILs) have received increased attention recently and have been investigated as new, more efficient solvents for both laboratory and industrial use. RTILs are organic salts with melting points lower than 100 °C and practically zero vapor pressure. More than 500 RTILs have been synthesized to date with approximately another million of other possible new compounds. They are therefore considered to be prospective “designer solvents”, variations in cations or in anions accounting for their adjustability to various applications (e.g., as entrainers in extractive distillations,¹ liquid pistons for the compression of hydrogen (www.linde.com), lubricants,² etc.). Their low vapor pressure makes them suitable recyclable alternatives to volatile organic compounds but also as solvents in processes undertaken at low to vacuum pressures (e.g., at ultrahigh vacuum conditions at 10^{−9} mbar in X-ray photoelectron spectroscopy³). To obtain reliable thermodynamic data on systems containing ionic liquids, including liquid–liquid equilibria (LLE), is therefore of great importance for the design of more efficient and possibly greener industrial processes.

In the present work, LLE in the binary system 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) + 1-butanol was investigated. The binary system [bmim][PF₆] + 1-butanol was chosen as a model system for which literature data were available^{4–6} to test the suitability of a volumetric method⁷ using an evaluation of phase volumes proposed by Řehák et al.⁸ for determining LLE in mixtures of ionic liquids. By means of the volumetric method, compositions of the equilibrium phases at several temperatures were obtained. To check the measurements, the cloud-point method was used, enabling us to acquire points of the binodal curve not only in the temperature interval in which the volumetric data were measured but also in the immediate vicinity of the critical point. The experimental results were then compared with literature data of Wu et al.,⁴ Sahandzhieva et al.,⁵ and Shiflett and Yokozeki.⁶

To correlate the measurements, three thermodynamic models were used: two classical and one non-classical equation. The correlation results were then compared. The classical G^E models were the NRTL¹⁰ and the modified Flory–Huggins^{11–13} equa-

tions. The former is a widely used and flexible model; the choice of the latter was based on findings that mixtures of ionic liquids behave similar to polymer mixtures.^{15,16} As data in the critical region were obtained as well, an extended non-classical scaling-law equation proposed by Ewing et al.¹⁷ was used to describe the results.

Experimental Section

The ionic liquid was provided by Solvent Innovation GmbH. Prior to measurements, it was dried under 10^{−4} Pa vacuum for at least 48 h. 1-Butanol (puriss. p.a.) was provided by Fluka and was dried over molecular sieves before experiments. Table 1 gives an overview of purity data stated by the manufacturers and the water contents determined using Karl Fischer titration. Refractive indices of the chemicals obtained in our laboratory are compared with literature values in Table 1. Refractive indices were measured with an uncertainty of ± 0.00002 using a Bellingham and Stanley Abbe refractometer 60/ED.

Two experimental methods were used to determine the LLE. To acquire tie lines at several temperatures, a volumetric method⁷ using an evaluation proposed by Řehák et al.⁸ was used; points of the binodal curve were measured by means of the cloud-point method.

The volumetric method consists of measuring volumes of the equilibrium phases in two mixtures of known compositions. Calculation of the equilibrium compositions is then carried out from the mass balance:⁹

$$x_1^{(1)} = \frac{n_{1,I}V_{2,II} - n_{1,II}V_{2,I}}{V_{2,II}(n_{1,I} + n_{2,I}) - V_{2,I}(n_{1,II} + n_{2,II})} \quad (1)$$

$$x_1^{(2)} = \frac{n_{1,II}V_{1,I} - n_{1,I}V_{1,II}}{V_{1,I}(n_{1,II} + n_{2,II}) - V_{1,II}(n_{1,I} + n_{2,I})} \quad (2)$$

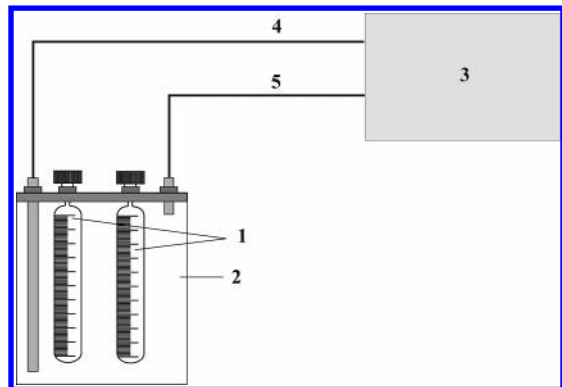
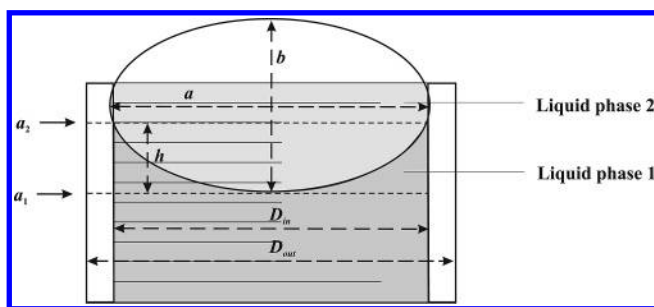
where $x_i^{(k)}$ is the mole fraction of the i th component in the k th phase; $V_{k,I}$ and $V_{k,II}$ are the volume of the k th phase in the first and second set of measurements, respectively; and $n_{i,I}$ and $n_{i,II}$ are the amount of substance of the i th component in the first set and second set of measurements, respectively.

An apparatus built in our laboratory was used for this purpose (see Figure 1). It consists of two calibrated glass ampoules (250 mm length × 13 mm diameter, volume 25 cm³) fixed in a glass

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Table 1. Purity Data, Water Contents, and Refractive Indices of Chemicals Used

compound	purity ^a mass %	water content mg·mL ⁻¹	<i>n</i> _D at 298.15 K	
			this work	lit.
[bmim][PF ₆]	99	0.05	1.40925	1.409 ²⁵ 1.411 ²⁶
1-butanol	≥99.5	0.16	1.39686	1.3993 ²⁷

^a Stated by the manufacturer.**Figure 1.** Volumetric method: 1, calibrated ampoules; 2, thermostated jacket; 3, thermostat; 4, thermostat out; 5, thermostat in.**Figure 2.** Volumetric method: evaluation of liquid-phase volumes.

jacket connected to an external thermostat. The ampoules were calibrated with known amounts of water. Known masses of both components were weighed into the ampoules, the ratios of the masses of the individual components being approximately 1:4 and 4:1 in each ampule, respectively. The temperature in the jacket was brought to the required experimental value. The apparatus was then placed horizontally on a shaker; by rocking the apparatus back and forth at the required constant temperature for at least 12 h, the contents of the ampoules was mixed thoroughly. Afterward, the apparatus was set in vertical position to allow the mixtures to separate at the experimental temperature for at least another 12 h. The time of settling was determined from experiments during which phase volumes were measured at defined time intervals; the values of the measured volumes were found to remain constant after 12 h.

As the phase interfaces were not flat, corrections for the curvature had to be made. The interfaces were photographed, and the exact volumes were determined graphically from the snapshots. In Figure 2, a schema of such evaluation is shown. In the figure, $h = a_1 - a_2$ is the height of the meniscus; a_1 and a_2 are the read-outs on the volume scale for the lower and the upper meniscus edge, respectively; D_{in} and D_{out} are the ampule's inner and outer diameter, respectively; and a and b are the horizontal semiaxes of the ellipsoid approximating the meniscus shape. The dimensions of the meniscus are calculated from the relation between the ampule outer diameter in the figure and its precisely measured outer diameter. The volume of the liquid above the a_2 read-out is then

$$V_{sur} = \pi r_{in}^2 h - \frac{\pi}{3} \left(\frac{b}{2} - h \right) \left(\frac{ah}{b} \right)^2 \quad (3)$$

where $r_{in} = D_{in}/2$. Řehák et al.⁸ give a detailed overview of the evaluation procedure.

Generally, one should take into account the influence of the vapor phase on the equilibrium. In this experimental setup, the ampoules were filled so that a minimum dead volume (less than 1 cm³) was present. The presence of this small volume of vapor in the ampoules is essential, as the bubble provides for mixing on shaking. In this particular case the dead-volume vapor phase consists mainly of air and a small amount of 1-butanol, the ionic liquid having practically zero vapor pressure; the influence of the vapor phase on the LLE may therefore be neglected.⁶

The experimental uncertainty estimated by means of the error-propagation law⁸ was found to be ± 0.003 and ± 0.0004 in mole fraction for the IL phase and the alcohol phase, respectively. The overall uncertainty in the global composition was found to be ± 0.0002 in mole fraction. Phase volumes were determined with an uncertainty of ± 0.01 cm³, and weighing was carried out with an uncertainty of ± 0.00002 g. Higher uncertainty in the IL phase is due to the large difference between the molar masses of both compounds ($M_{BuOH} = 74.12$ g·mol⁻¹, $M_{[BMIM][PF_6]} = 284.2$ g·mol⁻¹). The experimental uncertainty improves with decreasing difference in the molar masses. However, the volumetric method may be used as a simple experiment to estimate with fair to good accuracy the mutual solubilities of binary mixtures of ILs. The temperature was controlled within ± 0.01 K using a Julabo ME F25 thermostat. The stability and uncertainty of the temperature control was checked prior to the measurements using an ASL F250 MKII precision thermometer with a Pt 100 probe by measuring the temperature directly in the thermostated jacket of the apparatus. The thermometer had been previously calibrated to a Leeds & Northrup platinum resistance thermometer provided with a National Bureau of Standards certificate coupled to an ASL F17A bridge. The temperature uncertainty for the calibration thermometer was found to be better than ± 0.002 K. The uncertainty in temperature measurements was estimated to be ± 0.02 K, as confirmed by measurements over a large time span of more than 8 h. Measurements were carried out in a limited range of temperatures not significantly different from ambient, because at higher temperatures heat losses in the thermostated jacket could not be prevented.

In the cloud-point measurements, an apparatus enabling us to measure solubility temperatures in mixtures of known compositions was used (see Figure 3). A known mixture was weighed into a thermostated cell and then brought to a temperature at which it was homogeneous. Subsequently, using a programmable thermostat, the temperature was decreased in a defined manner (< 0.002 K·s⁻¹) to find the narrowest possible temperature interval in which demixing occurred, and the cloud-point temperature was determined. The same procedure was repeated by increasing the temperature to determine the temperature at which the mixture became homogeneous again (the clear-point temperature). The changes in homogeneity were determined visually. Hysteresis in the read-outs of approximately 0.5 K and 0.2 K outside and in the critical region, respectively, was observed. The resulting solubility temperature was then determined as the average of the two readings. A HE F25 Julabo thermostat was used for temperature control. At temperatures lower than 373.15 K, water was used as the thermostating liquid, whereas at temperatures above 373.15 K a Julabo Thermal H250 bath fluid was used. The temperature was measured directly in the thermostating jacket using an ASL F250 MKII precision

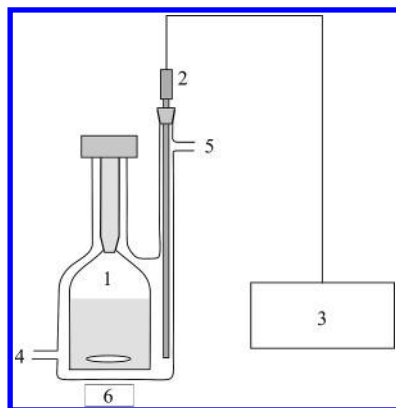


Figure 3. Cloud-point method: 1, thermostated equilibrium cell; 2, Pt 100 resistance thermometer probe; 3, ASL F250 MKII precision thermometer; 4, thermostat out; 5, thermostat in; 6, magnetic stirrer.

Table 2. Cloud-Point Mole Fractions for System 1-Butyl-3-methylimidazolium Hexafluorophosphate (1) + 1-Butanol (2)

x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0056	343.87	0.0850	382.65	0.1872	383.00	0.3770	369.86
0.0078	350.83	0.0956	382.94	0.1951	382.81	0.4643	361.61
0.0285	375.40	0.1133	383.17	0.2082	382.48	0.5171	354.48
0.0376	378.39	0.1271	383.19	0.2167	382.21	0.5982	341.43
0.0493	379.97	0.1457	383.18	0.2615	380.52	0.6822	326.14
0.0641	381.69	0.1535	383.21	0.3058	376.03	0.7261	317.12
0.0762	382.39	0.1661	383.08	0.3523	373.59	0.8190	296.47

Table 3. Conjugated Phases Mole Fractions for System 1-Butyl-3-methylimidazolium Hexafluorophosphate (1) + 1-Butanol (2)

T K	IL phase x_1'	alcohol phase x_1''
288.15	0.854	0.0021
298.15	0.820	0.0024
308.15	0.780	0.0024
318.15	0.738	0.0026
328.15	0.684	0.0037

thermometer with a Pt 100 probe. The calibration of the thermometer was carried out in the same manner as the calibration of the thermometer used to control temperature in the volumetric measurements.

The experimental uncertainty of the cloud-point method was estimated to be ± 0.0002 in mole fraction and ± 0.02 K. The temperature in the equilibrium cell was controlled within ± 0.01 K, weighing was carried out with an uncertainty of ± 0.00002 g.

Results and Discussion

Experimental data acquired in the present work are summarized in Tables 2 and 3 and presented in Figures 4 and 5 (mole and mass fraction, respectively). The binary system was found to present a miscibility gap and an upper critical solution temperature at 383.20 K. Good agreement was observed between the results acquired by the volumetric method and the cloud-point method, although the volumetric method yields data with higher uncertainty in the IL phase. However, the volumetric method appears to be a very simple tool because it provides tie lines without the use of chemical or physical analysis. Good agreement with cloud-point data shows that, in spite of higher experimental uncertainty, a good initial estimate of mutual solubilities may be obtained that can further be checked by more precise methods. Moreover, it helps economize on the amount of IL, the overall volume of the IL in one set of measurements being ca. 30 cm³.

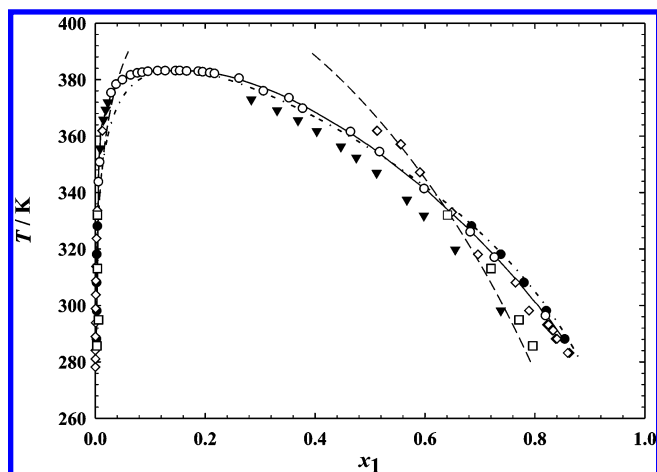


Figure 4. Liquid-liquid equilibrium in system [bmim][PF₆] (1) + 1-butanol (2) (mole fractions): ●, this work, volumetric method; ○, this work, cloud-point method; ▼, ref 4; ◇, ref 5; □, ref 6; solid line, scaling-law equation; dash-dotted line, modified Flory-Huggins equation; dashed line, NRTL equation.

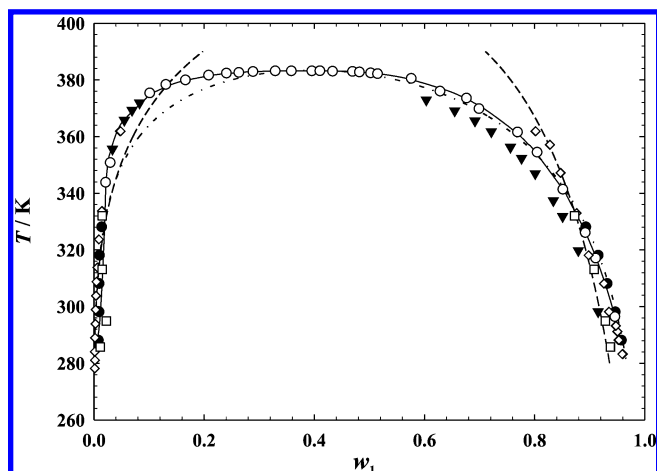


Figure 5. Liquid-liquid equilibrium in system [bmim][PF₆] (1) + 1-butanol (2) (mass fractions): ●, this work, volumetric method; ○, this work, cloud-point method; ▼, ref 4; ◇, ref 5; □, ref 6; solid line, scaling-law equation; dash-dotted line, modified Flory-Huggins equation; dashed line, NRTL equation.

Results obtained in this work are also compared with the data by Wu et al.,⁴ Sahandzhieva et al.,⁵ and Shiflett and Yokozeki⁶ in Figures 4 and 5. Good agreement between our and literature data is observed. Some deviations from the work of Wu et al. in the IL phase are evident, but analysis of residuals of simultaneous correlation of all data by the modified Flory-Huggins equation revealed their Gaussian behavior. Therefore, the differences between measurements of this work and measurements published by other authors are not significant. It is apparent from the figures that the results obtained in this work in the critical region complement the literature ones, so complete information on LLE in the system is now available.

To describe the measurements, three models were used. The flexible and widely used NRTL¹⁰ and the modified Flory-Huggins model proposed by de Sousa and Rebelo¹¹ were the classical models. The choice of the Flory-Huggins model is based on the work of Najdanovic-Visak et al.¹² and Rebelo et al.,¹³ who used it successfully in correlating LLE in mixtures of ILs, as according to these and other authors,^{15,16} ILs tend to have polymer-like behavior. This may be also assumed from the fact that on changing the field variable in the phase diagram from mass fractions to mole fractions, the equilibrium loses its

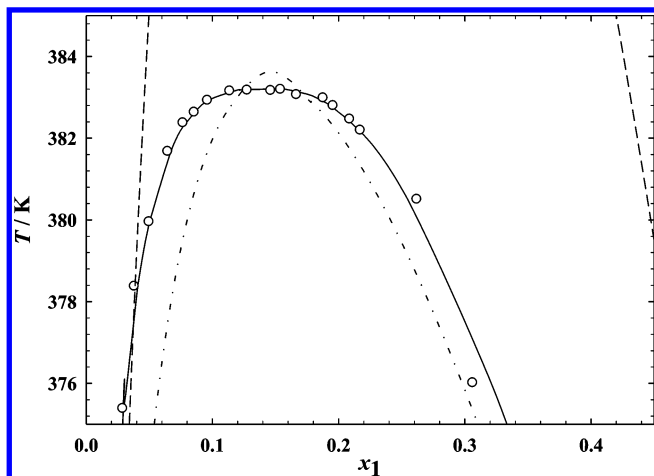


Figure 6. Liquid-liquid equilibrium in system [bmim][PF₆] (1) + 1-butanol (2) (mole fractions). Critical region: ○, this work, cloud-point method; solid line, scaling-law equation; dash-dotted line, modified Flory-Huggins equation; dashed line, NRTL equation.

Table 4. Constants of NRTL Equation in System [bmim][PF₆] (1) + 1-Butanol (2)

a_{12}	a_{21}	a_{12}	standard deviations in composition	
			IL phase σ_{x1}	alcohol phase σ_{x1}
616.37815	-648.02790	-0.70858	0.032	0.16

symmetry, an occurrence typical for polymer mixtures that is due to large differences in molar volumes (see Figures 4 and 5 for comparison). As points of the binodal curve were obtained in the critical region, the scaling-law non-classical model proposed by Ewing et al.¹⁷ was also used to correlate the data.

NRTL Equation. The excess Gibbs energy according to the NRTL model¹⁰ is expressed as

$$G^E/RT = x_1 x_2 \left(\frac{\tau_{21} g_{21}}{x_1 + x_2 g_{21}} + \frac{\tau_{12} g_{12}}{x_2 + x_1 g_{12}} \right) \quad (4)$$

where

$$\tau_{12} = \frac{a_{12}}{T} \quad \tau_{21} = \frac{a_{21}}{T} \quad (5)$$

and

$$g_{12} = \exp(-\alpha_{12} \tau_{12}) \quad g_{21} = \exp(-\alpha_{21} \tau_{21}) \quad (6)$$

where α_{12} , a_{12} , and a_{21} are adjustable parameters and $\alpha_{21} = \alpha_{12}$. Although NRTL is generally assumed to successfully correlate data with α_{12} having positive values, Marina and Tassios¹⁴ state that the model is sufficiently flexible even with a physically meaningless value of $\alpha_{12} = -1$.

Parameters of the NRTL model as found using a stochastic optimization algorithm are summarized in Table 4. The correlation of the experimental data is shown in Figures 4 to 6, Figure 6 showing details of the critical region. It is evident that the model description shows significant deviations from the experiment.

Modified Flory-Huggins Equation. The Flory-Huggins model modification as proposed by de Sousa and Rebelo¹¹ expresses the dimensionless excess Gibbs energy as

$$G^E/RT = (rx_1 + x_2)\chi(T)\varphi_1\varphi_2 \quad (7)$$

where x_i are mole fractions; $\chi(T)$ is the segment-segment interaction parameter, the temperature dependence of which is given by

$$\chi(T) = d_0 + \frac{d_1}{T} - d_2 \ln T \quad (8)$$

and φ_i are the segment fractions:

$$\varphi_1 = \frac{rx_1}{rx_1 + x_2} \quad \varphi_2 = \frac{x_2}{rx_1 + x_2} \quad (9)$$

where r is the number of segments occupied by component 1; subscripts 1 and 2 referring to the larger and smaller molecule, respectively. The interaction parameter is considered to be pressure independent in this work. The number of segments r does not differ greatly from the ratio of molar volumes of the components ($r \approx V_1/V_2$).

Phase separation is given by the attainability of a critical value of the interaction parameter:

$$\chi_c = \frac{1}{2} \left(1 + \frac{1}{\sqrt{r}} \right)^2 \quad (10)$$

The critical point is then given by

$$x_{1c} = \frac{1}{1 + r^{3/2}} \quad (11)$$

Parameters of the Flory-Huggins equation obtained by a regression along a gnostic influence function (the fitting procedure is explained in detail below) are given in Table 5. The equilibrium calculated using parameters obtained in correlation of both our data and literature values⁴⁻⁶ is represented in Figures 4 to 6. Critical data calculated from the estimated parameters are presented in Table 5. It is apparent that the Flory-Huggins equation presents a good description of the equilibrium over the entire experimental range giving only a slightly higher value of the upper critical solution temperature than observed in the experiments (see Table 5 for the comparison of the values and Figure 6 for a detail of the critical region).

The parameter-fitting procedure enabled us to compare quantitatively data obtained in this work with the literature values.⁴⁻⁶ Thus, except for correlating only data from this work, correlation of all the available data by the modified Flory-Huggins model has been carried out. The standard deviations obtained in the correlation of both our and literature data are a good criterion for the agreement between different datasets. It appears that the standard deviations obtained in correlations of our data alone do not differ significantly from those obtained in correlating all of the data (see Table 5). It follows from there that good mutual agreement has been reached between results presented in this work and the literature values.

Extended Scaling-Law Equation. Ewing et al.¹⁷ have proposed a scaling-law equation capable of describing binary LLE data not only in the immediate vicinity of the critical point but also outside the critical region:

$$x_i = x_{ci} \pm (B_1/2)|\theta|^\beta \pm (B_2/2)|\theta|^{\beta+w} + A_1|\theta| \pm (B_3/2)|\theta|^{\beta+2w} + A_2|\theta|^{1-\alpha+w} \quad (12)$$

where $\theta = 1 - T/T_c$, $w = 0.5$ is the first Wegner correction term, α and β being critical exponents. Lorimer et al.¹⁸ have employed successfully eq 12 to correlate LLE data in binary systems methanol + hydrocarbons with powers of 1 and $1 - \alpha$

Table 5. Constants of Flory–Huggins Equation in System [bmim][PF₆] (1) + 1-Butanol (2)

	<i>r</i>	<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	χ_c^a	x_{c1}^a	<i>T</i> _c ^a	standard deviations in composition	
								IL phase	alcohol phase
								σ_{x1}	σ_{x1}
this work	3.0927	−2.8060	1549.6	5.89 10 ^{−4}	1.230	0.1553	383.58	0.01	0.02
all data	3.2555	−3.0883	1648.5	6.24 10 ^{−4}	1.208	0.1455	383.64	0.009	0.04

^a Values calculated from the obtained parameters.

Table 6. Parameters of Extended Scaling-Law Equation in System [bmim][PF₆] (1) + 1-Butanol (2)

Critical Composition and Temperature	
x_{c1}	0.1401 (± 0.002)
<i>T</i> _c	383.20 ^a
Parameters	
<i>B</i> ₁	0.4587 (± 0.02)
<i>B</i> ₂	0.5239 (± 0.10)
<i>B</i> ₃	2.3632 (± 0.09)
<i>A</i> ₁	−0.2043 (± 0.16)
<i>A</i> ₂	−2.0807 (± 0.16)
Total Standard Error of Estimate in Composition	
<i>s</i>	± 0.0065

^a Experimental value.

= 0.89 in θ being combined as a single power of unity and β = 0.325 ± 0.003. These values were also used in this work. In the calculations, the upper critical solution temperature was considered to be the average of the two maximum solubility temperatures obtained in the measurements (i.e., 383.20 K).

The extended scaling-law equation successfully represents data over a large experimental range of temperatures. Classical thermodynamic models are equally successful in describing LLE data, but they fail in the immediate vicinity of the critical region, where they give temperature dependence inconsistent with theory. The only inconvenience of the scaling equation is that it does not yield activity coefficients and, consequently, Gibbs energy that are necessary to describe additional thermodynamic properties as the excess enthalpy.

Parameters of the extended scaling-law equation obtained by the generalized least-squares method from both tie-line and cloud-point data are presented in Table 6, and the description of the equilibrium is compared to experiment in Figures 4 and 5. Figure 6 presents a detail of the critical region. It appears that the scaling-law equation yields the best description of the measurements primarily in the vicinity of the upper critical solution temperature, but also outside the critical region.

Parameter-Fitting Procedure. Parameters of the NRTL and Flory–Huggins equations were found using the following procedure. The criterion of LLE in a binary system can be written as

$$\ln x_1^{(1)} - \ln x_1^{(2)} + \ln \gamma_1^{(1)} - \ln \gamma_1^{(2)} = 0 \quad (13)$$

$$\ln x_2^{(1)} - \ln x_2^{(2)} + \ln \gamma_2^{(1)} - \ln \gamma_2^{(2)} = 0 \quad (14)$$

where $x_i^{(k)}$ and $\gamma_i^{(k)}$ are the mole fraction and the activity coefficient of the *i*th component in the *k*th phase.

At low pressures, the activity coefficients may be considered as functions of temperature and composition only. Since only a limited number of tie lines were obtained, the calculation procedure was carried out as if none of them was available. Each tie line was therefore treated in the calculations as two cloud points. Thus, one of the mole fractions in each equation was considered to be unknown. From either the temperature or

composition of a cloud point and an approximation of model parameters the other variable as well as the composition of the other phase can be calculated. One of these variables can thus be considered errorless and model parameters estimated by minimizing the differences between experimental and calculated values of the other variable. In the cloud-point measurement the mixture is prepared synthetically, and the clear-point and cloud-point temperatures are measured. Therefore, the error in the determination of composition was neglected, and the squared differences between experimental and calculated temperatures were minimized. Weighting was not used. Instead, regression along an influence curve¹⁹ using a gnostic influence function²⁰ was performed in order to detect outliers.

The NRTL model is nonlinear in parameters and an initial approximation is difficult to obtain. Stochastic optimization algorithm, generalized controlled random search with alternating heuristics, developed by Tvrdík et al.^{21–23} was used to find the global minimum. It was found that the NRTL model is not able to describe the system studied. Regression with application of the gnostic influence function was not therefore performed.

The modified Flory–Huggins model can be linearized provided the tie lines are available and the value of *r* is kept fixed. The coexistence curve consisting of all 38 cloud points was therefore first approximated by a sixth degree polynomial and pseudoexperimental tie lines were calculated in temperature range from 288 to 384 K with a step of 1 K. These data were first correlated by the modified Flory–Huggins model using the ordinary least-squares linear regression for several values of *r*, keeping *d*₂ = 0. The best result was then used as an initial approximation for the nonlinear gnostic regression. Since the initial approximation is good and the minimum is easy to obtain, the optimization algorithm by Nelder and Mead²⁴ was used. Outliers were detected and removed and the gnostic regression was repeated. The calculated curve agrees well with experimental data mainly in the critical region where measurements are more precise.

Literature data were fitted using the same procedure. A few outliers were found in the data by Wu et al., and no outlier was detected in data by Sahandzhieva et al. and Shiflett and Yokozeki. None of these data cover the critical region; therefore, the fitting algorithm does not have enough information for fitting the binodal curve and the critical temperature is overestimated. Overestimation of the critical temperature is more pronounced in the case of data by Wu et al. because their measured values do not extend below mole fraction of 0.01. Parameters are thus estimated mainly from the part of the binodal curve of the alcohol phase in the subcritical temperature, and a small number of experimental points in the IL phase do not provide sufficient information for determining the correct shape of the binodal curve. Finally all data were fitted together. Mole fractions in the alcohol phase of two first points from the volumetric method were detected as outliers; other data are in good agreement within the limits of the standard deviation.

The mole fractions in the organic and alcoholic phases differ by the order of magnitude. In order to present agreement

between the experimental data and the calculated binodal curve, the standard deviation of mole fraction of the ionic liquid was evaluated for each phase separately. The standard deviations are given in Table 4 for the NRTL model and in Table 5 for the Flory–Huggins equation.

The modified Flory–Huggins model is easier to use because a good initial approximation can be determined. The approximation obtained by the above-described method is close to a single global minimum. The objective function has other local minima but reaching them can be avoided. On the other hand the initial approximation for the NRTL model is difficult to obtain. Usage of a global optimization algorithm is thus inevitable. Due to this fact thorough calculation is considerably slower.

Conclusion

LLE was measured in the binary system [bmim][PF₆] + 1-butanol using a volumetric method and a cloud-point method. The former enabled us to acquire tie lines at several temperatures; the latter provided for the points of the binodal curve. Good agreement was observed between results obtained by the two methods. The volumetric method occurs to be a simple and economic tool to obtain tie lines without the use of an analytical method; data may be obtained with fair accuracy in binary systems with large differences in molar masses, the accuracy of the method improving as the difference in molar masses decreases. Literature data by Wu et al.,⁴ Sahandzhieva et al.,⁵ and Shiflett and Yokozeki⁶ found for the studied system were compared to those in this work. Good agreement was observed between our data and those by Sahandzhieva et al. The results by Wu et al. appear to be in good agreement in the alcohol phase; some discrepancies being observed in the IL phase turned out to be of lesser importance upon data correlation by the Flory–Huggins equation.

The experimental data were correlated by the NRTL,¹⁰ modified Flory–Huggins,^{11,12} and scaling-law¹⁷ equations, respectively. The scaling-law equation provides the best description of the data both in and outside the critical region. The modified Flory–Huggins equation yields a good description of the data, giving only a slightly higher value of the upper critical solution temperature than that obtained in the experiments. NRTL, on the other hand, fails in describing the equilibrium in the system.

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