Liquid-liquid Equilibrium in a Binary System 1-butyl-3-methylimidazolium Hexafluorophosphate + Water: Experiment and Data Correlation

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Abstract

Experimental liquid-liquid equilibrium in the binary system 1-butyl-3-methylimidazolium hexafluorophosphate (abbr. [bmim][PF_6]) + water was investigated and the results were compared with literature values. Quantitative comparison of the individual datasets was carried out by correlating the measurements and literature data by the modified Flory-Huggins equation and a molecular-thermodynamic lattice model proposed by Qin and Prausnitz. Gnostic regression was used to fit the models to these data.

Keywords: Liquid-liquid equilibria, ionic liquids, thermodynamic models, data correlation, gnostic regression.

1. Introduction

There is an ever increasing interest in room-temperature ionic liquids (RTILs) as prospective more efficient and greener substitutes of volatile organic compounds. Many laboratory and industrial applications already use ILs, e.g. at ultra-high vacuum conditions at 10^{-9} mbar in X-ray photoelectron spectroscopy (Smith et al., 2005), as lubricants (e.g. Jiménez et al., 2006), liquid pistons (www.linde.com) or entrainers in extractive distillation (e.g. Jork et al., 2004 and Seiler et al., 2004).

Knowledge of the liquid-liquid equilibria in binary and multicomponent systems is of essential importance in the design of fluid separation processes, and particularly extraction. Similarly important is critical assessment of the obtained data and their comparison with existent literature ones; data concerning systems with ionic liquids often show large discrepancies, and there is therefore a strong need for a reliable quantitative analysis. For this purpose, robust evaluation tools able to detect possible outliers and/or thermodynamically inconsistent data are necessary.

In this work, liquid-liquid equilibrium in the binary system 1-butyl-3-methylimidazolium hexafluoro-phosphate + water was measured by means of the volumetric and cloud-point methods. The obtained data were correlated by the modified Flory-Huggins equation (de Sousa and Rebelo, 2000) and the molecular-thermodynamic lattice model proposed by Qin and Prausnitz (2005). Both models were originally derived to describe mixtures of polymers, but their use for mixtures of ionic liquids seems justified by statements that RTILs tend to present polymer-like behaviour (see e.g. Kazarian et al., 2000 and Dupont et al., 2002). The experimental data acquired in the present work were also quantitatively compared with literature data. Both in the correlations and in the quantitative comparison of the individual datasets a gnostic regression method was used. This enabled us to compare the data reliably.

2. Experimental

In this work, 1-butyl-3-methylimidazolium hexafluorophosphate (abbr. [bmim][PF_6]) was

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provided by Solvent Innovation (www.solvent-innovation.com) and was dried for at least 48 hrs under vacuum at room temperature before the measurements. The water content determined by the Karl-Fischer titration in the dried ionic liquid was then found to be 50 ppm. Refractive index of the ionic liquid was measured in our laboratory with an accuracy of ±0.00002 using a Bellingham and Stanley Ltd. Abbe refractometer 60/ED and is reported in previous work (Bendová and Wagner 2006). Distilled water with conductivity 2.1 $\mu S \cdot m^{-1}$ prepared in our laboratory was used in the experiments.

To measure tie lines, a simple volumetric experiment was used. A volumetric apparatus was built in our laboratory and is described in detail in previous work (Bendová and Wagner, 2006). The experiment consists of measuring the volumes of the equilibrium phases and of subsequent calculation of their compositions from mass balances (Novák et al, 1987 and Řehák et al., 2005). The experimental uncertainty estimated by means of the error-propagation law was found to be ± 0.02 and ± 0.0001 in mole fraction for the ionic-liquid phase and the aqueous 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 cm^3, and weighing was carried out with an uncertainty of ± 0.00002 g. As was already discussed in previous work (Bendová and Wagner, 2006), the volumetric method presents differences in uncertainties for the individual phases that are due to differences in molar masses. This is particularly evident in this case, with the molar masses of water and the studied ionic liquid presenting a large difference (M_{H2O} = 18.02 $g \cdot mol^{-1}$, $M_{[bmim][PF6]}$ = 284.2 $g \cdot mol^{-1}$).

To check the volumetric data, points of the solubility curve were measured by the cloud-point method. It consists of finding the solution temperature of a defined mixture, i.e. the temperature at which a phase change occurs in the mixture. An apparatus built in our laboratory was modified after works by Ochi et al. (1996) and Bendová et al. (2003) so that cloud-points could be determined with better accuracy and repeatability. *Figure 1* shows a schema of the experimental setup. Known amounts of both measured substances were weighed into a thermostated equilibrium cell and brought to a temperature at which the mixture became homogeneous. Then by means of a programmable thermostat, the temperature in the cell was reduced in a defined manner to find the narrowest possible temperature interval in which the phase change occurred. The cloud-point temperature was considered to be the temperature at which the first droplets of the second phase appeared. The same procedure was repeated while increasing the temperature, the clear-point temperature being the temperature at which the mixture became entirely homogeneous. Hysteresis in the read-outs of approximately 0.5 K was observed, and the resulting solubility temperature was therefore determined as the average of the two readings. The phase changes were determined optically by measuring the intensity of light scattered by the mixture. A Coherent Inc. circular beam LabLasers™ 4mW laser diode was the source of light and a photodiode connected to a National Instruments NI DAQPad – 6015 measuring card was used to detect the light signal. The temperature was measured directly in the thermostating jacket using an ASL T100-450-1D-UC Pt100 probe connected over a conversion unit to the above-mentioned measuring card. 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. Both the temperature and the photodiode signals were monitored using a data acquisition application programmed in Labview 8.01. The software was developed at the Technical University of Liberec where the temperature conversion unit previously developed in our workshops was also modified for better data acquisition.
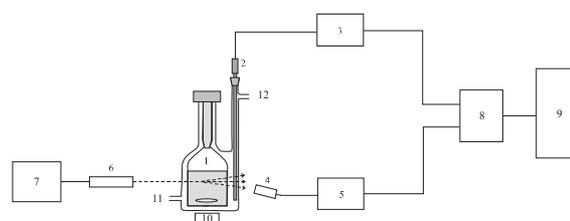

Figure 1. Cloud-point apparatus. 1 equilibrium cell; 2 Pt100 thermometer; 3 thermometer conversion unit; 4 photodiode; 5 photodiode conversion unit; 6 laser diode; 7 laser diode power supply; 8 measuring card; 9 PC; 10 magnetic stirrer; 11 thermostat in; 12 thermostat out.

The experimental uncertainty of the cloud-point method was estimated to be ± 0.0002 in mole fraction, the temperature was measured with an uncertainty of ± 0.02 K. The temperature in the equilibrium cell was controlled within ± 0.01 K using a HE F25 Julabo thermostat with water as thermostatting liquid, and weighing was carried out with an uncertainty of ± 0.00002 g.

3. Theory and calculations

Modified Flory Huggins equation

As mixtures containing ionic liquids were reported to show polymer-like behaviour (Kazarian et al., 2000 and Dupont et al., 2002), a modified Flory-Huggins equation was used in the correlations. The Flory-Huggins model modification as proposed by de Sousa and Rebelo (2000) and Rebelo et al. (2004) expresses the dimensionless excess Gibbs energy as

$$G^E/RT = (rx_1 + x_2)\,\chi(T)\,\varphi_1\varphi_2 \qquad (1)$$

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

$$\chi(T) = d_0 + d_1/T - d_2\ln(T), \qquad (2)$$

and φ_i are the segment fractions related to the mole fractions by relations

$$\varphi_1 = rx_1/(rx_1 + x_2)\,,\ \ \varphi_2 = x_2/(rx_1 + x_2) \quad (3)$$

where r is the number of segments occupied by component 1, subscripts 1 and 2 referring to the larger and smaller molecule respectively. Usually r does not differ greatly from the ratio of molar volumes of the components ($r \approx V_1/V_2$).

Molecular-thermodynamic lattice model

Qin and Prausnitz (2005) have recently proposed a molecular-thermodynamic lattice model for binary mixtures based on the original Flory-Huggins theory (Flory, 1942, Huggins, 1942), the quasi-chemical theory of Guggenheim (1935, 1952, 1966) and Wertheim's perturbation theory (1984, 1986). The Gibbs energy of mixing is expressed as:

$$\frac{G^M}{RT} = \frac{\varphi_1}{r_1}\ln\varphi_1 + \frac{\varphi_2}{r_2}\ln\varphi_2 + \frac{z}{2}\left(\frac{\varphi_1 q_1}{r_1}\ln\frac{\theta_1}{\varphi_1} + \frac{\varphi_2 q_2}{r_2}\ln\frac{\theta_2}{\varphi_2}\right)$$
$$+ \frac{z\varphi_1\varphi_2}{2(1-\varphi_1\varphi_2)}\left[\frac{\varepsilon}{kT} - \ln(1 + \varphi_1\varphi_2 C)\right]$$
$$- \frac{b_1\varphi_1}{r_1}\ln\frac{1-\varphi_2 C}{1+\varphi_1\varphi_2 C} - \frac{b_2\varphi_2}{r_2}\ln\frac{1-\varphi_1 C}{1+\varphi_1\varphi_2 C}$$
$$(4)$$

with

$$C = \exp(\varepsilon/kT) - 1. \qquad (5)$$

and where ε is the interchange energy, z is the coordination number, φ_i is the volume (or segment) fraction, r_i is the number of segments of molecule, b_i is the number of chemical bonds in the molecule:

$$b_i = r_i - 1, \qquad (6)$$

q_i is the structural parameter (zq_i is the surface of molecule):

$$zq_i = zr_i - 2b_i, \qquad (7)$$

and θ_i is the surface fraction defined as

$$\theta_i = \frac{q_i N_i}{q_1 N_1 + q_2 N_2} \qquad (8)$$

N_i being the number of lattice sites occupied by molecules. Temperature dependence of the interchange energy is expressed as:

$$\varepsilon/k = A\exp(-BT) \qquad (9)$$

where

$$B = 2\alpha_T \qquad (10)$$

Here α_T is the coefficient of thermal expansion.

4. Results and Discussion

Experimental data obtained in this work are summarised in TABLES 1 and 2 and shown in *Figure 2*.

Figure 2 shows also the comparison of our data with literature ones and with the thermodynamic description of all the datasets by the modified Flory-Huggins equation as well as by the molecular-thermodynamic lattice model proposed by Qin and Prausnitz (2005).

TABLE I. CONJUGATED PHASES MOLE FRACTIONS FOR SYSTEM 1-BUTYL-3-METHYLIMIDAZOLIUM HEXA-FLUOROPHOSPHATE (1) + WATER (2).

	IL phase	aqueous phase
T/K	x_1'	x_1''
293.15	0.80	0.0013
303.15	0.77	0.0017
313.15	0.70	0.0019
323.15	0.64	0.0023

No data could be obtained in the critical region, because aqueous [bmim][PF$_6$] decomposes at higher temperatures (Swatloski et al., 2003). Considering the experimental uncertainties found for both methods, the data obtained by the two experiments appear to be in good agreement. Agreement of our data with the literature values was evaluated quantitatively in the correlations described below.

Parameters of the modified Flory-Huggins equation and the molecular-thermodynamic lattice model were optimized using a regression along a gnostic influence function described in detail in previous work (Bendová and Wagner, 2006). Residuals were subsequently analyzed in order to check for outliers.

TABLE II. SOLUBILITY-CURVE MOLE FRACTIONS FOR SYSTEM 1-BUTYL-3-METHYLIMIDAZOLIUM HEXA-FLUOROPHOSPHATE (1) + WATER (2).

x_1	T/K
0.0016	306.69
0.0023	321.74
0.0026	328.67
0.0039	344.90
0.4637	342.77
0.6148	316.84
0.6355	313.42
0.6793	304.55
0.7207	296.40

Mathematical processing of the data was improved in this work; whereas in our previous paper, tie lines were treated as two cloud-points, i.e. independently of each other, in this work they were processed as interrelated values. The objective function reads as follows:

$$S = \sum_{j=1}^{J} w_j \left(\frac{T_j^{\exp} - T_j^{\text{calc}}}{\sigma_T} \right)^2 \tag{11}$$

$$+ \sum_{k=1}^{K} w_{\text{aq}k} \left[\left(\frac{x_{\text{aq}k}^{\exp} - x_{\text{aq}k}^{\text{calc}}}{\sigma_{x,aq}} \right)^2 + w_{\text{IL},k} \left(\frac{x_{\text{IL},k}^{\exp} - x_{\text{IL},k}^{\text{calc}}}{\sigma_{x,\text{IL}}} \right)^2 \right]$$

where j refers to cloud point measurements, and k refers to points on the tie lines. It is assumed that the cloud point composition is errorless and T_j^{calc} is evaluated as the temperature at which the measured phase is in equilibrium with another phase. The composition of the second phase must be calculated but it is not used in the objective function. In systems which do not exhibit loops there is always a unique solution unless the composition falls into the one-phase region. In the tie-line measurement it is assumed that the temperature is errorless. Compositions $x_{\text{IL},k}^{\text{calc}}$ and $x_{\text{aq},k}^{\text{calc}}$ are then calculated from the conditions of phase equilibrium at the given temperature T_k. The variances used reflect the precisions of measurement but may be slightly modified in order to improve calculation efficiency. The values used in this work are: $\sigma_T = 0.02$, $\sigma_{x,\text{aq}} = 0.0001$, $\sigma_{x,\text{IL}} = 0.02$. Variables w_j, $w_{\text{aq},k}$, $w_{\text{IL},k}$ denote the robustifying weights determined iteratively by application of the gnostic influence function. Their initial values are equal to one. The first iteration is therefore identical to the maximum likelihood estimation. Model parameters within the first iteration are obtained by a global optimization method

developed by Tvrdík et al. (see the work by Bendová and Wagner, 2006 and the references therein). Within the next iterations a faster simplex method of Nelder and Mead (1964) is used.
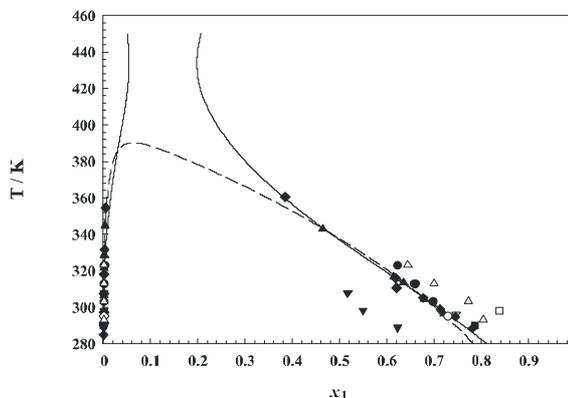

Figure 2. Liquid-liquid equilibrium in system [bmim][PF₆] (1) + water (2). △, volumetric method; ▲, cloud-point method; ●, Wong et al., 2002; ○, Anthony et al., 2001; ▽, Wu, 2003; ▼, Fadeev and Meagher, 2001; ■, Chun et al., 2001; □, Swatloski et al., 2002; ◇, Najdanovic-Visak et al., 2003; ◆, McFarlane et al., 2005.

TABLE III gives the optimized parameters for the modified Flory-Huggins equation along with the standard deviations.

TABLE IV gives parameters for the molecular-thermodynamic lattice model as well as the standard deviations. As water is a simple molecule, its number of segments r_2 was set to one, hence the parameter $b_2 = 0$. Two optimizations were carried out; first the parameter z was fixed ($z = 10$) accordingly with the paper by Qin and Prausnitz. Subsequently, z was considered as an adjustable parameter and optimized as well.

TABLE III. CONSTANTS OF FLORY-HUGGINS EQUATION IN SYSTEM [BMIM][PF₆] (1) + WATER (2).

				Standard deviations in composition	
				IL phase	aqueous phase
r	d_0	d_1	d_2	σ_{x1}	$\sigma x1$
4.038	-80.76	5025.0	-11.58	0.002	0.06

All the datasets, including the literature values were correlated simultaneously, which enabled us to compare the data quantitatively. It is evident from the obtained standard deviations that none of the models describes the aqueous phase with sufficient accuracy; owing to very low values aqueous-phase data were given lower weights, therefore the obtained deviations present larger divergences.

TABLE IV. CONSTANTS OF THE MOLECULAR-THERMODYNAMIC LATTICE MODEL IN SYSTEM [BMIM][PF$_6$] (1) + WATER (2).

r1	A	B	z	Standard deviations in composition	
				IL phase	aqueous phase
				σ_{x1}	σ_{x1}
4.47	246.89	0.00191	10	0.0009	0.06
5.54	437.96	0.00062	4.27	0.0006	0.06

The overall data are in good agreement in the mathematical sense of the word. The inadequacy of the models to describe the aqueous-phase data is the reason why the weighted residuals in this phase spread from zero to large values, both positive and negative. The relatively smaller values of the weighted residuals in the ionic liquid phase are hidden inside the wide cluster of residuals of the aqueous-phase data and consequently the analysis of residuals considers all data to be in good mutual agreement. Although graphical presentation (see *Figure 2*) reveals differences between data measured by various authors, there is no apparent outlier. However, while both models describe the ionic liquid phase with good accuracy, the model by Qin and Prausnitz yields the best results if the parameter z is considered as adjustable.

Whereas the model by Qin and Prausnitz yields a usual binodal curve with an upper critical solution temperature (UCST), the modified Flory-Huggins model is unable of UCST prediction. As already mentioned above, data in the critical region could not be obtained, because of the decomposition of the ionic liquid. Thus chemical equilibrium comes into consideration and should be taken into account in correlations given that corresponding data are available.

5. Conclusions

In the present paper, a study of liquid-liquid equilibrium in the binary system [bmim][PF$_6$] + water is presented. Although several papers were already published addressing the same topic, the discrepancies between some of the datasets obviously required checking and critical assessment. Experimental data were obtained in this work by the volumetric and the cloud-point methods and the results were then compared with literature values by correlating them with the modified Flory-Huggins equation and by the molecular-thermodynamic lattice model proposed by Qin and Prausnitz. To optimize the model parameters a robust gnostic regression

method was used that is also able to detect possible outliers. It was found that both methods described the available data with comparable accuracy, with worse results being obtained for the aqueous-phase. The obtained standard deviations show that the individual datasets are in good agreement, with no outlier detected.

Nomenclature

A, B	parameters of the molecular-thermodynamic lattice model (see Eqs. (9) and (10))
b	number of chemical bonds of the molecule defined by Eq. (6)
C	molecular-thermodynamic lattice model parameter defined by Eq. (5)
d_0, d_1, d_2	parameters of the modified Flory-Huggins equation (see Eq. (2))
G	Gibbs energy [J·mol^{-1}]
K	Boltzmann constant [1.380662·10^{-23} J·K^{-1}]
N	number of lattice sites occupied by molecule
r	number of segments of molecule (see Eqs. (1) and (4))
R	universal gas constant [8.31441 J·K^{-1}·mol^{-1}]
q	structural parameter
T	temperature [K]
UCST	upper critical solution temperature
w	robustifying weight
x	mole fraction
z	molecular-thermodynamic lattice model parameter

Greek symbols

α_T	coefficient of thermal expansion [K^{-1}]
ε	interchange energy [J]
θ	surface fraction defined by Eq. (8)
σ	standard deviation
φ	segment fraction defined by Eq (3).
$\chi(T)$	interaction parameter defined by Eq. (2)

Superscripts

calc	calculated value
exp	experimental value

E	excess property
M	mixing property

Subscripts

aq	aqueous phase
i	component i
j	cloud-point measurement
k	tie-line measurement
IL	ionic liquid phase

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