1302 *J. Chem. Eng. Data* **2007,** *52,* 1302−1306

Liquid−Liquid Equilibria in Binary Mixtures of 1,3-Propanediol + Ionic Liquids [bmim][PF_6], [bmim][BF_4], and [emim][BF_4]

Mark B. Shiflett*,† **and A. Yokozeki**‡

DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880, and DuPont Fluoroproducts Laboratory, Chestnut Run Plaza 711, Wilmington, Delaware 19880

Binary liquid−liquid equilibria (LLE) in mixtures of 1,3-propanediol and three ionic liquids have been measured using the volumetric and cloud-point methods. The room-temperature ionic liquids studied are 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4], and 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4]. All three binary systems show upper critical solution temperatures (UCSTs), with about 299 K for [bmim][BF_4], about 310 K for [emim][BF_4], and about 360 K for [bmim][PF_6]. The limited solubility behaviors with UCSTs are similar to the cases of various monoalcohols with ionic liquids reported in the literature. Observed LLE are well correlated by use of the nonrandom two liquid (NRTL) solution model.

Introduction

The present report is a part of our continuing studies on the phase behavior of room-temperature ionic liquids (RTILs) with various chemicals such as hydrofluorocarbons (HFCs), carbon dioxide, and ammonia. Although there are many solubility studies of monoalcohol + RTIL mixtures,[1−13] no detailed studies on 1,3-propanediol (PDO) + RTIL systems have been reported in the literature, except for a "screening experiment" for an approximate liquid−liquid critical point temperature.[11] 1,3-Propanediol is an important industrial compound in the synthesis of polyesters and other new polymers, refrigeration applications, paints, and plastics.[14−17] Particularly, due to the recent intense interest in environmental protection and sustainable development, bio-based 1,3-propanediol production by fermentation of corn is preferable and more environmentally beneficial than the petrochemical ethylene oxide pathway.[15]

The recovery of 1,3-propanediol from the fermentation broth can be carried out by ordinary distillation techniques.[18] RTILs, which are often called "green solvents" (environmentally friendly solvents), may be useful for such separation processes. Therefore, understanding the solubility behavior of 1,3-propanediol + RTIL mixtures is important in many applications. In this report, we have studied liquid−liquid equilibria (LLE) of binary mixtures of 1,3-propanediol + ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4], and 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4]. LLE experiments have been performed using the volumetric and cloud-point methods.[19−21] Solubility data and data correlation with the nonrandom two liquid (NRTL) solution model[22] are presented.

Experimental Procedures

Materials. The [bmim][PF_6] (assay ≥ 96 %, $C_8H_{15}F_6N_2P$, lot and filling code 1242554 15005226, CAS no. 174501-64-5), [bmim][BF_4] (assay ≥ 97 %, $C_8H_{15}F_4N_2B$, lot and filling code 1142017 31205158, CAS no. 174501-65-6), and [emim][BF_4] (assay ≥ 97 %, $C_6H_{11}F_4N_2B$, lot and filling code 1167450 50705116, CAS no. 143314-16-3) were purchased from Fluka (Buchs, Switzerland). The 1,3-propanediol (99.6 % purity, $C_3H_8O_2$, product and batch no. 533734-1KG-A 11528TO, CAS no. 504-63-2) was obtained from Sigma-Aldrich, Inc. (St. Louis, MO). Methyl alcohol (99.93 % purity, Sigma-Aldrich, 27,047-4, lot no. DS 00462CS, CAS no. 67-56-1) was used as a reference fluid for volumetric calibration of the experimental apparatus.

The ionic liquid samples were dried and degassed by first placing the samples in borosilicate glass tubes and pulling a coarse vacuum on the samples with a diaphragm pump (Pfeiffer, model MVP055-3, Nashua, NH) for about 3 h. Next, the samples were fully evacuated using a turbopump (Pfeiffer, model TSH-071) to a pressure of about $4 \cdot 10^{-7}$ kPa while simultaneously heating and stirring the ionic liquids at a temperature of about 348 K for 48 to 96 h. The mass fractions of water remaining in the dried samples were measured by Karl Fischer titration (AquaStar C3000, solutions AquaStar Coulomat C and A) and were 363, 272, and 207 ppm for [bmim][PF_6], [bmim][BF_4], and [emim][BF_4], respectively.

Experimental Method. A detailed description of the experimental equipment, procedure, and principle of the method are available in our previous reports.[19,20] Therefore, only the basic experimental technique and experimental uncertainties are given here.

Low-pressure sample containers were fabricated from borosilicate glass tubing with an outside diameter of 12.69 mm, an inside diameter of 7.94 mm, and an overall length of 15.5 cm. The glass tubing was sealed with a torch on one end and open on the other. The borosilicate glass tubes were cleaned in an ultrasonic bath filled with acetone for 2 h and dried overnight in a vacuum oven at 348.15 K. The volume of each liquid layer was obtained by measuring the liquid height from the bottom of the glass tubing, as described in our previous works,[19,20] using an electronic caliper (Mitutoyo Corp., model no. CD-6″ CS, code no. 500-196) with an accuracy of ± 0.01 mm. The volume,

---

* Corresponding author. E-mail: mark.b.shiflett@usa.dupont.com.
† DuPont Central Research and Development.
‡ DuPont Fluoroproducts Laboratory.

10.1021/je700037z CCC: $37.00

Table 1. 1,3-Propanediol (1) + [bmim][PF$_6$] (2) System[a]

T/K	$100x'_1$	$100x_1$	V'/cm^3·mol^{-1}	V/cm^3·mol^{-1}	$V^{E'}$/cm^3·mol^{-1}	V^E/cm^3·mol^{-1}
286.6 ± 0.2	10.9 ± 1.7	99.4 ± 0.1	184.5 ± 2.2	71.5 ± 0.2	−7.1 ± 2.2	−1.3 ± 0.2
287.8 ± 0.2	11.4 ± 2.3	99.4 ± 0.1	184.2 ± 3.0	71.6 ± 0.1	−6.9 ± 3.0	−1.2 ± 0.1
288.2 ± 0.2	11.8 ± 1.6	99.4 ± 0.1	183.4 ± 2.1	71.8 ± 0.2	−7.2 ± 2.1	−1.1 ± 0.2
291.9 ± 0.2	13.3 ± 1.9	99.1 ± 0.1	182.6 ± 2.4	72.3 ± 0.1	−6.5 ± 2.4	−1.0 ± 0.1
298.3 ± 0.2	15.0 ± 2.4	99.0 ± 0.1	181.1 ± 3.1	72.6 ± 0.1	−6.4 ± 3.1	−1.2 ± 0.1
303.3 ± 0.2	15.5 ± 1.5	98.8 ± 0.1	180.9 ± 2.0	73.0 ± 0.2	−6.4 ± 2.0	−1.3 ± 0.2
313.5 ± 0.2	19.0 ± 1.9	98.5 ± 0.1	176.8 ± 2.4	74.1 ± 0.1	−7.0 ± 2.4	−1.0 ± 0.1
323.4 ± 0.2	24.3 ± 1.5	97.8 ± 0.1	171.2 ± 1.9	75.5 ± 0.1	−6.3 ± 1.9	−1.1 ± 0.1

[a] V', observed molar volume lower phase; V, observed molar volume upper phase; $V^{E'}$, excess molar volume lower phase; V^E, excess molar volume upper phase.

Table 2. 1,3-Propanediol (1) + [bmim][BF$_4$] (2) System[a]

T/K	$100x'_1$	$100x_1$	V'/cm^3·mol^{-1}	V/cm^3·mol^{-1}	$V^{E'}$/cm^3·mol^{-1}	V^E/cm^3·mol^{-1}
286.7 ± 0.2	36.8 ± 0.2	95.8 ± 0.8	144.0 ± 0.2	75.2 ± 0.2	−0.5 ± 0.2	−1.6 ± 0.2
287.9 ± 0.2	38.4 ± 0.4	95.2 ± 0.2	141.8 ± 0.4	75.7 ± 0.2	−1.0 ± 0.4	−1.8 ± 0.2
289.1 ± 0.2	39.7 ± 0.4	94.9 ± 0.2	140.7 ± 0.5	76.0 ± 0.3	−0.6 ± 0.5	−1.8 ± 0.3
291.9 ± 0.2	47.0 ± 0.5	93.1 ± 0.1	131.6 ± 0.5	78.9 ± 0.1	−1.6 ± 0.5	−1.2 ± 0.1

[a] V', observed molar volume lower phase; V, observed molar volume upper phase; $V^{E'}$, excess molar volume lower phase; V^E, excess molar volume upper phase.

v, vs the height, h, was calibrated experimentally using methyl alcohol, and a linear relation was obtained. The uncertainty in the volume is estimated to be ± 0.25 %.

The sample containers were initially weighed to determine the tare mass. The samples were then prepared in a nitrogen-purged drybox to minimize water contact with the hygroscopic ionic liquids. A glass pipet was used to add the required amounts of ionic liquid and 1,3-propanediol. Two samples containing mole fractions of about (70 and 90) % 1,3-propanediol with [bmim][PF$_6$] were prepared. Similar mole fractions were also prepared using the ionic liquids ([bmim][BF$_4$] and [emim][BF$_4$]). The uncertainty in the mole fraction was estimated to be ± 0.01 % (i.e., 10^{-4}). A Swagelok stainless steel (SS316) cap and plug with Teflon ferrules was used to seal the open end of the glass tubing before removing it from the drybox. Care is required when tightening the cap so that the ferrules seal against the glass tubing, but overtightening can crack the glass. The masses remained constant within the accuracy (± 0.0001 g) of the balance (Mettler Toledo, model AG204) even after several weeks.

Initially, the samples were mixed at room temperature (293.2 K) by vigorously shaking the sample containers. In this system, the upper liquid phase (V) was 1,3-propanediol-rich and the lower liquid phase (V') was ionic liquid-rich: liquid density data were obtained for [bmim][PF$_6$] and [bmim][BF$_4$] from ref 23; data for 1,3-propanediol were obtained from ref 24; and data for [emim][BF$_4$] were obtained from the present study, d/g·cm^{-3} = 1.5134 − 7.8297·10^{-4} T/K.

To establish thermodynamic equilibrium, sufficient time and mixing were required. A custom-made mixing apparatus, which can hold 14 sample containers, was designed for rocking the tubes back and forth inside a water-filled Plexiglas tank, and the temperature was controlled with an external temperature bath (PolyScience, model 1190S, Niles, IL) which circulated water through a copper coil inside the tank. The water bath was stirred with an agitator (Arrow Engineering Co., Inc., model 1750, Hillside, NJ), and the temperature was measured with a thermocouple (Fluke Corporation, model 52II thermometer, Everett, WA). The Fluke thermometer was calibrated using a standard platinum resistance thermometer (SPRT model 5699, Hart Scientific, range 73 to 933 K) and readout (Blackstack model 1560 with SPRT module 2560). The Blackstack instrument and SPRT were also a NIST certified secondary temperature standard. The water bath temperature uncertainties were ± 0.2 K.

The water bath temperature was initially set at about 287 K. Before height measurements were taken, the sample holder was positioned upright below the water level of the tank for (6 to 12) h. The volume of each liquid layer was obtained by measuring the liquid height from the bottom of the glass tube using the electronic caliper. The most difficult problem of the experiments was to establish the equilibrium state. The mixing and measurement procedure was repeated each day, and the heights were plotted as a function of time until no further change in the heights was detected. Using this procedure required 5 days to reach equilibrium at 287 K. These experiments were repeated at various temperatures up to about 323 K.

Results

Measurement Results and Uncertainty Estimation. The final equilibrium results for the molar compositions and volumes are provided in Tables 1 to 3. The vapor phase was initially assumed to contain only 1,3-propanediol (negligible vapor pressure for ionic liquids). The uncertainty estimation for neglecting the moles of nitrogen in the vapor space during the filling process was calculated using an EOS program.[25] The vapor correction resulted in a negligible change in the liquid compositions (x_1 = 0.03 % and x'_1 = 0.0001 %) and molar volumes (ΔV = 0.05 cm^3·mol^{-1} and $\Delta V'$ = 0.001 cm^3·mol^{-1}); therefore, our assumption to neglect the nitrogen in the sample container was justified. Excess molar volumes in Tables 1, 2, and 3 were calculated from the liquid volumes and molar volumes of the pure compounds.[20,21]

Total uncertainties in the final composition and molar volume determination are provided in Tables 1 to 3. Total uncertainties ($\delta x_{TE} = \sqrt{\delta x_{RE}{}^2 + \delta x_{SE}{}^2}$) were estimated by calculating both the overall random (δx_{RE}) and systematic uncertainties (δx_{SE}). The overall random uncertainties were estimated using the following error propagation method

Table 3. 1,3-Propanediol (1) + [emim][BF$_4$] (2) System[a]

T/K	$100x'_1$	$100x_1$	V'/cm^3·mol^{-1}	V/cm^3·mol^{-1}	$V^{E'}$/cm^3·mol^{-1}	V^E/cm^3·mol^{-1}
286.6 ± 0.2	23.8 ± 0.5	97.0 ± 0.2	129.5 ± 0.4	72.5 ± 0.2	−4.7 ± 0.4	−1.9 ± 0.2
287.8 ± 0.2	24.5 ± 0.5	97.0 ± 0.2	129.2 ± 0.4	72.7 ± 0.2	−4.5 ± 0.4	−1.8 ± 0.2
288.2 ± 0.2	24.9 ± 0.4	96.8 ± 0.2	128.9 ± 0.4	72.9 ± 0.2	−4.4 ± 0.4	−1.7 ± 0.2
291.9 ± 0.2	30.9 ± 0.4	95.8 ± 0.2	123.9 ± 0.3	74.7 ± 0.2	−4.9 ± 0.3	−1.0 ± 0.2
298.3 ± 0.2	35.8 ± 0.4	94.5 ± 0.2	120.8 ± 0.3	76.0 ± 1.2	−4.4 ± 0.3	−0.9 ± 1.2
303.3 ± 0.2	43.5 ± 0.3	92.2 ± 0.1	114.6 ± 0.2	77.5 ± 0.1	−4.6 ± 0.2	−1.6 ± 0.1

[a] V', observed molar volume lower phase; V, observed molar volume upper phase; $V^{E'}$, excess molar volume lower phase; V^E, excess molar volume upper phase.

$$\delta x_{\mathrm{RE}} = \sqrt{\sum_{i=1}^{n}\left[\delta p_i\left(\frac{\partial x}{\partial p_i}\right)\right]^2} \tag{1}$$

where δx_{RE} is the mole fraction or molar volume random uncertainty of the liquid composition; $\partial x/\partial p_i$ is the partial derivative of x with respect to the ith experimental parameter p_i, which is calculated from the sensitivity analysis of each parameter; and δp_i is the estimated uncertainty of the experimental parameter p_i. The following experimental parameters were considered to have an effect on the random uncertainty: sample container calibration constants, mass of 1,3-propanediol and ionic liquid, height of lower and upper phases. The heights had the largest overall effect. The systematic uncertainties (δx_{SE}) include properly correcting for the area expansion, meniscus, and vapor-phase moles. For additional details on estimation of total uncertainties, see refs 20 and 21.

To prove the existence of an upper critical solution temperature (UCST) on the LLE curve, cloud-point measurements have also been made. Starting at a high temperature of about 343 K, where only one liquid phase existed, the temperature was slowly lowered (1 K·h^{-1}) until a second liquid phase began to appear. The observed cloud points for 1,3-propanediol (1) and [bmim][PF$_6$] (2) were x_1 = 50.1 % 1,3-propanediol at (353.2 ± 2) K, x_1 = 70.1 % 1,3-propanediol at (357.2 ± 2) K, and x_1 = 90.4 % 1,3-propanediol at (353.2 ± 2) K. The observed cloud points for 1,3-propanediol (1) and [emim][BF$_4$] (2) were x_1 = 70.1 % 1,3-propanediol at (308.2 ± 2) K and x_1 = 90.3 % 1,3-propanediol at (304.2 ± 2) K. The observed cloud point for 1,3-propanediol (1) and [bmim][BF$_4$] (2) was x_1 = 70.1 % 1,3-propanediol at (298.2 ± 2) K.

Model Comparisons of LLE Results. Results with the volumetric method are given in Tables 1, 2, and 3 with estimated uncertainties. LLE data including the cloud-point measurements are shown in Figures 1, 2, and 3 with the following model correlation. Observed LLE data have been modeled with the NRTL (nonrandom two liquids) solution model.[22] The binary activity coefficients of the NRTL model are given by

$$\ln\gamma_1 = x_2^{\,2}\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \tag{2}$$

$$\ln\gamma_2 = x_1^{\,2}\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] \tag{3}$$

where

$$G_{12} \equiv \exp(-\alpha\tau_{12}) \text{ and } G_{21} \equiv \exp(-\alpha\tau_{21}) \tag{4}$$

$$\tau_{12} \equiv \frac{\Delta g_1}{RT} \text{ and } \tau_{21} \equiv \frac{\Delta g_2}{RT}\text{:} \quad \text{(adjustable binary interaction parameters)} \tag{5}$$

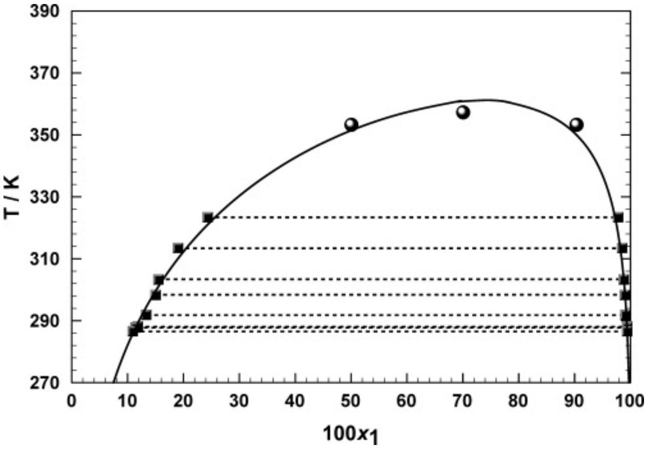

Figure 1. Temperature−composition LLE diagram of 1,3-propanediol (1) + [bmim][PF$_6$] (2): solid line, the NRTL model calculation; broken lines, experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method; ●, experimental data by the cloud-point method.

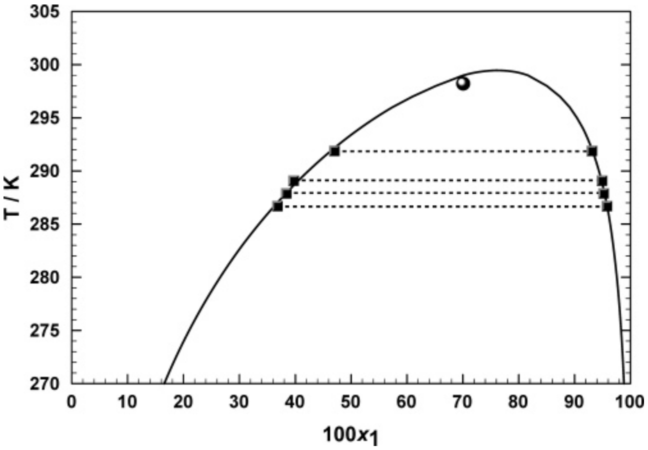

Figure 2. Temperature−composition LLE diagram of 1,3-propanediol (1) + [bmim][BF$_4$] (2): solid line, the NRTL model calculation; broken lines, experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method; ●, experimental data by the cloud-point method.

where α = 0.2 (assumed to be a constant of 0.2 in this work) and x_i = mole fraction of the ith species.

The temperature-dependent binary interaction parameter (τ_{ij}) is modeled here by a two-term empirical equation

$$\tau_{12} = \tau_{12}^{(0)} + \tau_{12}^{(1)}/T/\mathrm{K} \text{ and } \tau_{21} = \tau_{21}^{(0)} + \tau_{21}^{(1)}/T/\mathrm{K} \tag{6}$$

The binary LLE (L1 for liquid 1 and L2 for liquid 2) are mathematically described by the following equilibrium condition

$$\gamma_i^{\mathrm{L1}}x_i^{\mathrm{L1}} = \gamma_i^{\mathrm{L2}}x_i^{\mathrm{L2}} \quad (i = 1, 2) \tag{7}$$

Then, the two unknown adjustable parameters τ_{12} and τ_{21} at a

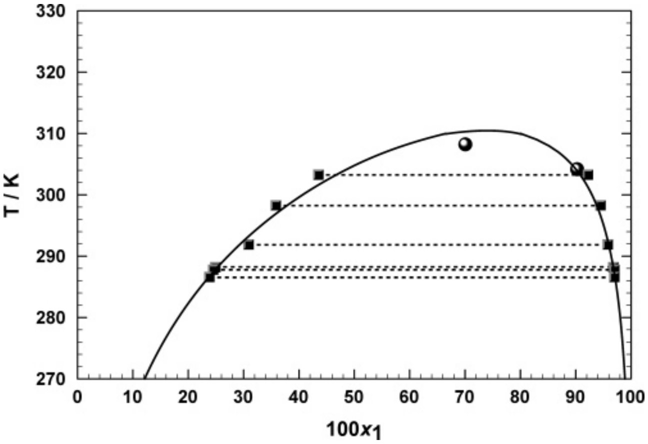

Figure 3. Temperature−composition LLE diagram of 1,3-propanediol (1) + [emim][BF$_4$] (2): solid line, the NRTL model calculation; broken lines, experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method; ●, experimental data by the cloud-point method.

Table 4. Binary Interaction Parameters in Equation 6

system (1)/(2)	$\tau_{12}^{(0)}$	$\tau_{12}^{(1)}$/K	$\tau_{21}^{(0)}$	$\tau_{21}^{(1)}$/K
PDO/[bmim][PF$_6$]	−2.8628	2130.56	−4.8828	1598.35
PDO/[bmim][BF$_4$]	−4.1484	2250.00	−10.394	2906.25
PDO/[emim][BF$_4$]	−3.0630	1908.25	−8.1996	2397.28

given T can be determined from one set of LLE experimental (volumetric method) data, using eq 7 (two nonlinearly coupled equations). We have several sets of such LLE data and can obtain τ_{12} and τ_{21} as a function of T. Thus, the empirical four parameters in eq 6 have been determined and are shown in Table 4. Lines in Figures 1, 2, and 3 are calculated with the present NRTL model using these parameters. On the basis of these calculations, the UCST for 1,3-propanediol (1) in [bmim][PF$_6$], [emim][BF$_4$], and [bmim][BF$_4$] was estimated to be (360 ± 2) K at x_1 = (74 ± 2) %, (310 ± 2) K at x_1 = (74 ± 2) %, and (299 ± 2) K at x_1 = (77 ± 2) %, respectively.

Discussion

All binary systems of the present study have shown partial immiscibilities with UCSTs, being similar to the cases of monoalcohol + ionic liquid mixtures.[1−11] The behaviors of the present UCSTs are also consistent with the reported trends in the literature: by increasing the alkyl chain length on the cation, the UCST decreases; the choice of anion has a much larger impact on the UCST of the system; and the BF$_4$ anion greatly reduces the UCST relative to the PF$_6$ anion.[3,11] The present UCSTs of 1,3-propanediol + [bmim][PF$_6$] and 1,3-propanediol + [bmim][BF$_4$] are in good agreement with those reported in the literature.[11] To see this interesting anion effect on the UCST, we have looked at the case of mixtures of two ionic liquids + 1,3-propanediol. The cloud point for a ternary mixture containing x_1 = 76 % 1,3-propanediol (1), x_2 = 12 % [bmim][PF$_6$] (2), and x_3 = 12 % [bmim][BF$_4$] (3) was (330.2 ± 2) K, which is nearly an average UCST value of both 1,3-propanediol binary mixtures.

LLE data have been well correlated with the nonelectrolyte NRTL solution model, and this situation is similar to the case of VLE (vapor−liquid equilibrium) data of HFC + ionic liquid mixtures.[23] The present volumetric method for LLE, being different from the cloud-point method, provides the information of the excess molar volume for each separated liquid. In ordinary binary mixtures,[26] the excess molar volume is at most ± 2 cm^3·mol^{-1}, but we have found that it is very largely negative (about −10 to −25 cm^3·mol^{-1}) for ionic-liquid-rich side solutions in HFC + ionic liquid systems.[19−21] The excess molar volumes of the present two binary systems (1,3-propanediol + [bmim][PF$_6$] and 1,3-propanediol + [emim](BF$_4$]) are significantly larger than those of ordinary organic solutions but are less than those in HFC + ionic liquid systems. It is interesting to see that the excess molar volume in the 1,3-propanediol + [bmim][BF$_4$] system is small and of the order of ordinary mixtures, indicating a liquid structure different from the other 1,3-propanediol binary systems.

Conclusions

Solubilities in binary mixtures of 1,3-propanediol + RTILs ([bmim][PF$_6$], [bmim][BF$_4$], and [emim][BF$_4$]) have been studied with the volumetric and cloud-point methods. All three binary systems show partial immiscibilities with UCSTs. The UCST increases in the order [bmim][BF$_4$] (299 K) < [emim]-[BF$_4$] (310 K) < [bmim][PF$_6$] (360 K). This behavior of the UCST is similar to the cases of monoalcohol + RTIL mixtures in the literature, as for the dependence on the alkyl chain length of the cation as well as the type of anion. LLE data are well correlated with the nonelectrolyte NRTL model. The excess molar volume of the ionic-liquid-rich side solutions increases in the order [bmim][BF$_4$] < [emim][BF$_4$] < [bmim][PF$_6$].

Acknowledgment

The authors thank Mr. Joseph Nestlerode for his assistance with the liquid−liquid equilibrium experiments.

Literature Cited

(1) Sahandzhieva, K.; Tuma, D.; Breyer, S.; Pérez-Salado Kamps, Á.; Maurer, G. Liquid−liquid equilibrium in mixtures of the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate and an alkanol. *J. Chem. Eng. Data* **2006**, *51*, 1516−1525.

(2) Liu, Z.; Wu, W.; Han, B.; Dong, Z.; Zhao, G.; Wang, J.; Jiang, T.; Yang, G. Study on the phase behaviors, viscosities, and thermodynamic properties of CO$_2$/[C$_4$mim][PF$_6$]/methanol system at elevated pressures. *Chem.−Eur. J.* **2003**, *9*, 3897−3903.

(3) Crosthwaite, J. M.; Aki, S. N. K. V.; Maginn, E. J.; Brennecke, J. F. Liquid phase behavior of imidazolium-based ionic liquids with alcohols. *J. Phys. Chem. B* **2004**, *108*, 5113−5119.

(4) Heintz, A.; Lehmann, J. K.; Wertz, C.; Jacquemin, J. Thermodynamic properties of mixtures containing ionic liquids. 4. LLE of binary mixtures of [C$_2$MIM][NTf$_2$] with propan-2-ol, butan-1-ol, and pentan-1-ol and [C$_4$MIM][NTf$_2$] with cyclohexanol and 1,2-hexanediol including studies of the influence of small amounts of water. *J. Chem. Eng. Data* **2005**, *50*, 956−960.

(5) Heintz, A.; Lehmann, J. K.; Wertz, C. Thermodynamic properties of mixtures containing ionic liquids. 3. Liquid−liquid equilibria of binary mixtures of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide with propan-1-ol, butan-1-ol, and pentan-1-ol. *J. Chem. Eng. Data* **2003**, *48*, 472−474.

(6) Najdanovic-Visak, V.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; de Sousa, H. C.; Szydłowski, J. Pressure, isotope, and water co-solvent effects in liquid−liquid equilibria of (ionic liquid + alcohol) system. *J. Phys. Chem. B* **2003**, *107*, 12797−12807.

(7) Wu, C.-T.; Marsh, K. N.; Deev, A. V.; Boxall, J. A. Liquid−liquid equilibria of room-temperature ionic liquids and butan-1-ol. *J. Chem. Eng. Data* **2003**, *48*, 486−491.

(8) Najdanovic-Visak, V.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; Szydłowski, J. Phase behavior of room temperature ionic liquid solutions: an unusually large co-solvent effect in (water + ethanol). *Phys. Chem. Chem. Phys.* **2002**, *4*, 1701−1703.

(9) Swatloski, R. P.; Visser, A. E.; Reichert, W. M.; Broker, G. A.; Farina, L. M.; Holbrey, J. D.; Rogers, R. D. Solvation of 1-butyl-3-methylimidazolium hexafluorophosphate in aqueous ethanol - a green solution for dissolving 'hydrophobic' ionic liquids. *Chem. Commun.* **2001**, 2070−2071.

(10) Makowska, A.; Siporska, A.; Szydłowski, J. Isotope effects on miscibility of 1-butyl-3-methylimidazilium tetrafluoroborate with butanols. *J. Phys. Chem. B* **2006**, *110*, 17195−17199.

(11) Wagner, M.; Stanga, O.; Schröer, W. Corresponding states analysis of the critical points in binary solutions of room temperature ionic liquids. *Phys. Chem. Chem. Phys*. **2003**, *5*, 3943−3950.

(12) Domańska, U.; Bogel-Łukasik, E.; Bogel-Łukasik, R. 1-Octane/water partition coefficients of 1-alkyl-3-methylimidazolium chloride. *Chem.−Eur*. *J*. **2003**, *9*, 3033−3041.

(13) Domańska, U.; Bogel-Łukasik, E.; Bogel-Łukasik, R. Solubility of 1-dodecyl-3-methylimidazolium chloride in alcohols (C_2 − C_{12}). *J. Phys. Chem. B* **2003**, *107*, 1858−1863.

(14) Liu, Y.; Ranucci, E.; Lindblad, M. S.; Albertsson, A.-C. New Biodegradable polymers from renewable sources − segmented copolyesters of poly(1,3-propanediol succinate) and poly(ethylene glycol). *J. Bioact. Compat. Polym.* **2002**, *17*, 209−219.

(15) *Summary*, Proceedings of The World Congress on Industrial Biotechnology and Bioprocessing, Orlando, FL, April 21−23; http://nabc.cals.cornell.edu/pubs/WCIBB2004_proc.pdf, 2004; p 15.

(16) Parkinson, G. A process for producing a corn-based monomer achieves a technical milestone. *Chem. Eng.* **2002**, November 1.

(17) Park, Y.; Kim, J.-S.; Lee, H. Physical properties of the lithium bromide + 1, 3-propanediol + water system. *Int. J. Refrig*. **1997**, *20*, 319−325.

(18) Sanz, M. T.; Blanco, B.; Beltrán, S.; Cabezas, J. L.; Coca, J. Vapor liquid equilibria of binary and ternary systems with water, 1,3-propanediol, and glycerol. *J. Chem. Eng. Data* **2001**, *46*, 635−639.

(19) Shiflett, M. B.; Yokozeki, A. Vapor−liquid−liquid equilibria of pentafluoroethane and ionic liquid [bmim][PF_6] mixtures studied with the volumetric method. *J. Phys. Chem. B* **2006**, *110*, 14436−14443.

(20) Shiflett, M. B.; Yokozeki, A. Vapor−liquid−liquid equilibria of hydrofluorocarbons + 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Chem. Eng. Data* **2006**, *51*, 1931−1939.

(21) Yokozeki, A.; Shiflett, M. B. Global phase behaviors of trifluoromethane in room-temperature ionic liquid [bmim][PF_6]. *AIChE J.* **2006**, *52*, 3953−3957.

(22) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001; p 8.12.

(23) Shiflett, M. B.; Yokozeki, A. Solubility and diffusivity of hydrofluorocarbons in room-temperature ionic liquids. *AIChE J.* **2006**, *52*, 1205−1219.

(24) Design Institute for Physical Property Data (DIPPR), Brigham Young University, Provo, Utah 84602.

(25) Lemmon, E. W.; McLinden, M. O.; Huber, M. L. *NIST reference fluid thermodynamic and transport properties - REFPROP*, version 7.0, users' guide; U. S. Department of Commerce, Technology Administration, National Institute of Standards and Technology, Standard Reference Data Program: Gaithersburg, MD, 2002.

(26) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*, 3rd ed.; Butterworth: London, 1982.

Received for review January 26, 2007. Accepted April 3, 2007. The authors thank DuPont Central Research and Development for supporting the present work.

JE700037Z