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Liquid−Liquid Equilibria of Room-Temperature Ionic Liquids and Butan-1-ol[†]

C.-T. Wu, Kenneth N. Marsh,* Alexander V. Deev, and John A. Boxall

Department of Chemical & Process Engineering, University of Canterbury, Private Bag 4800,
Christchurch 8004, New Zealand

Room-temperature ionic liquids are salts that are liquid at room temperature. Their use as catalysts and catalytic support has been studied extensively. However, there are very few measurements on their solubility and phase equilibria in common organic solvents. In this work, the liquid−liquid phase equilibria of mixtures of room-temperature ionic liquids, 1-alkyl-3-methylimidazolium hexafluorophosphate, $[R_n\mathrm{mim}][PF_6]$ (1) where R_n = butyl, pentyl, hexyl, heptyl, and octyl, with butan-1-ol (2) over a composition range have been measured. The binodal coexistence curves of the mixtures were found to have an upper critical solution temperature (USCT) at $x_2 \approx 0.9$. The UCST decreases with increase in the length of the alkyl chain of the ionic liquid, with the UCST of the butyl at 373 K and that of the octyl at 326 K. Both the UCST and the composition at the UCST as a function of the 1-alkyl group chain length can be reasonably well predicted from theory on the basis of unimolecular quantum chemical calculations.

Introduction

Room-temperature ionic liquids, which are salts that are liquids at ambient temperature, are normally composed of relatively large organic cations and inorganic or organic anions. Unlike molecular liquids, the ionic nature of these liquids results in a unique combination of properties such as very low vapor pressure at room temperature and a stable liquid range of over 300 K. Some ionic liquids are readily hydrolyzed while some show unusual solubility behavior in water and organic solvents. For example, the ionic liquids based on aluminum chloride are generally very hydroscopic, and studies have to be made in the absence of moisture. Those based on tetrafluoroborate are generally stable to moisture but have a relatively high solubility in water while ionic liquids based on, for example, hexafluorophosphate and bis(trifluormethylsulfyl)-imide are generally less soluble in water. Additionally, the change in chain length of the 1-alkyl group from 1 to 8 on 1-alkyl-3-methylimadazolium hexafluorophosphate can turn the liquid from being highly soluble in water to very immiscible. Thus, by judicious variation in the length and branching of the alkyl chains of the anionic core and variation in the cationic precursor, it should be possible to design a solvent for a specific application. Initially, the research of these "designer solvents" was focused on their use as electrolytes,[1−4] but later studies focused on their application as new media for chemical reactions such as solvents for homogeneous catalysis[5,6] for a variety of organic reactions.[7−10] Reviews on the use of ionic liquids as solvents for synthesis, with and without catalysis, have been given by Welton[11] and Wasserscheid.[12]

In particular, ionic liquids have appeal as alternative solvents in liquid−liquid extraction.[13,14] Their low vapor pressure allows the extracted product to be separated from the ionic liquid by low-pressure distillation with the potential for energy savings. In addition, they are potentially recoverable for reuse. Hence, the replacement of conventional organic solvents by ionic liquids in extraction processes is seen as a promising field of investigation. For the extraction of polar organic products of chemical reactions that proceed in aqueous media, ionic liquids that have low solubility in water and high solubility in the organic liquid would be preferred. An important criterion for any ionic liquid used in extraction is that it be air and water stable, thus enabling extractions without special procedures. Our work concentrates on the 1-alkyl-3-alkylimidazolium hexafluorophosphates that are liquids at room temperature, have low solubility in water, and do not hydrolyze at close to ambient conditions. The compounds studied were 1-alkyl-3-methylimidazolium hexafluorophosphates ($[R_n\mathrm{mim}][PF_6]$), where R_n stands for an alkyl group with *n* carbon atoms) having from (4 to 8) carbon atoms in the 1-alkyl chain. The chemical structure is shown in Figure 1.

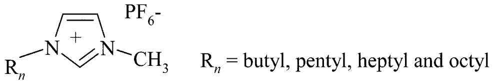

Figure 1. Chemical structure of ionic liquids used in this work.

At the present time, measurements on the solubility and phase equilibria in common organic solvents are limited. To our knowledge, only a few studies on solubility have been reported. Brennecke and co-workers have shown that ionic liquids are insoluble in supercritical CO_2,[15,16] suggesting that products of reactions carried out in ionic liquids can be readily extracted with supercritical CO_2. Some vapor−liquid and liquid−liquid equilibria[17] and liquid−liquid equilibria[18,19] measurements have been reported on mixtures of imidazolium-based ionic liquids with water. Some recent studies of liquid−liquid equilibria between ionic liquids and alcohols have been reported.[20,21]

Experimental Section

Materials. The ionic liquids were prepared by reaction of 1-methylimidazole with 1-alkyl chlorides followed by

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* Corresponding author. E-mail: ken.marsh@canterbury.ac.nz.

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reaction with hexafluorophosphoric acid. 1-Methylimidazole was used as received from Aldrich (99+ mass % redistilled). As the reagent was moisture sensitive, it was transferred into the reaction vessel under continuous nitrogen flushing. Hexafluorophosphoric acid was supplied by Aldrich (60 mass % solution in water) and used as received. The butan-1-ol was obtained from APS Finechem with less than 0.6 mass % impurities. The butan-1-ol was dried using activated type 5 Å molecular sieves, and the water content was found to be less than 0.05 mass % as determined by GLC (using a packed column, thermal conductivity detector, and He gas). The reagents were kept in sealed flasks in a desiccator to minimize contact with moist air. 1-Chlorobutane, 1-chloropentane, 1-chlorohexane, 1-chloroheptane, and 1-chlorooctane were obtained from Aldrich (99 mass % grade) and used without further purification.

Preparation of Ionic Liquids. The ionic liquids were prepared in-house by a metathesis method described by Welton.[11] Equimolar quantities of alkyl chlorides (1-chlorobutane through 1-chlorooctane) were reacted with 1-methylimidazole at 353 K, with stirring in a closed vessel under an atmosphere of nitrogen for 72 h, to produce the 1-alkyl-3-methylimidazolium chlorides. The 1-alkyl-3-methylimidazolium chlorides were then mixed with hexafluorophosphoric acid in aqueous solution, and the ionic liquids separated as a denser liquid phase. Residual chloride ion was removed from the ionic liquids by washing with water at least 10 times until no chloride precipitate formed with silver nitrate. Initially, the ionic liquids were dried with magnesium sulfate and then filtered with tetrahydrofuran through neutral alumina. The residual volatile organic solvents and water were removed by vacuuming at 10 Pa and 353 K. The 1-alkyl-3-methylimidazolium hexafluorophosphates appeared as light-yellow transparent liquids. As this drying process has the possibility of introducing additional salts into the ionic liquid, our later purifications abandoned the drying stages using magnesium sulfate and alumina in favor of pumping the washed sample with a vacuum of 1 Pa at 340 K for over 48 h.

High purity is essential for thermophysical property measurements. The influence of chloride, water, and organic solvents on the physical properties has been reported by Seddon and co-workers.[20] The purity of the ionic liquids was investigated by various methods including nuclear magnetic resonance (NMR), infrared spectroscopy (IR), and mass spectra. H^1 NMR (in $CDCl_4$) spectra confirmed the chemical structure of the ionic liquids, and the results from mass spectra analysis show no substantial impurities such as chloride compounds. However, the sensitivity level of these instruments indicated that impurities with uncertainty better than mass fractions of (1 to 2)% could not be determined. Water could be determined by IR spectroscopy, using a cell with spacers of 0.14 mm, as two peaks for the OH^- absorbance in the (3500−3700) cm^{-1} wavelength range. Further drying in a vacuum at a pressure of less than 10 Pa allowed the removal of water down to levels approaching the sensitivity of the method, estimated at 0.01 mass % of water in ionic liquids. A more sensitive method, using a differential scanning calorimeter, was abandoned because small amounts of residual water reacted with the ionic liquid to form HF gave rise to a calorimeter response at about 410 K.

Liquid−Liquid Equilibria Measurements. Liquid−liquid equilibria were studied for $[R_n\text{mim}][PF_6]$ (1) ($n = 4$ to 8) + butan-1-ol (2). The so-called visual "cloud point method" was used, and the binodal coexisting curves of the mixtures were obtained. The apparatus, shown in Figure 2, consists of a jacketed glass vessel containing a magnetic stirrer connected to a temperature controlled circulating bath (controlled to ±0.01 K). The vessel was closed to moisture and could be flushed with dry nitrogen. The measurements were started with the addition of a known mass of about 30 g of dry ionic liquid to the vessel. A known mass of about 1 g of butan-1-ol was added to the ionic liquid, the temperature was adjusted to about 1.5 K above the expected cloud point, and the mixture was stirred vigorously. The temperature was then reduced at the rate of 10^{-2} $K \cdot s^{-1}$ until the cloud point was observed. This step was repeated several times to confirm the cloud point temperature to within ±0.02 K. A second known mass of butan-1-ol was then added, and another cloud point temperature was measured. Additions of butan-1-ol were continued until $x_2 > x_{2(\text{UCST})}$, the mole fraction at the upper critical solution temperature (UCST), giving up to 20 cloud temperatures. The compounds were then interchanged, and the ionic liquid was added to butan-1-ol until $x_2 < x_{2(\text{UCST})}$. Agreement of the value of the UCST to within ±0.1 K approached from $x_2 = 1$ and $x_2 = 0$ indicated the reliability of the results and that the results were not affected by contamination with water (3), which would lower the UCST by approximately 0.7 K for $x_3 = 0.003$.

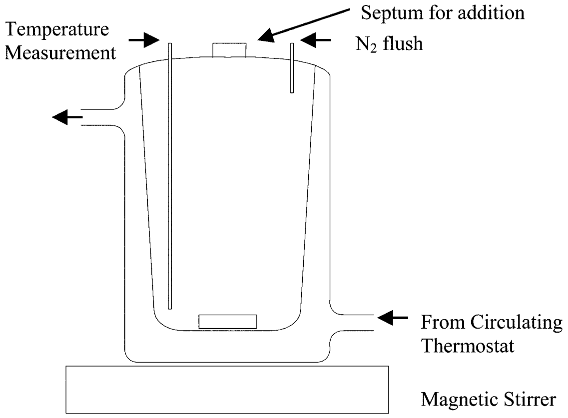

Figure 2. Apparatus used for liquid−liquid equilibria measurements.

Temperature was measured with a calibrated platinum resistance thermometer (DSIR RT200, New Zealand) with the uncertainty of ±0.01 K. Masses of liquids added were determined with an uncertainty of ±0.0003 g, and that gave an uncertainty in the mole fraction of better than 1 part in 10^4.

Results

The liquid−liquid equilibria for the mixtures $[R_n\text{mim}][PF_6]$ (1) ($n = 4$ to 8) + butan-1-ol (2) are given in Table 1 and shown as a function of x_2 in Figure 3. The curves are typical for a partially miscible two-component system with an upper critical solution temperature (UCST). Measurements were not made with ionic liquid R_n = butyl above 373 K, where x_2 was between 0.7 and 0.96, as that would require a redesign of the apparatus to enable measurements above 0.1 MPa. USCTs for the systems R_n = pentyl, hexyl, heptyl, and octyl are 366.23 K ($x_2 = 0.88$), 350.31 K ($x_2 = 0.90$), 335.47 K ($x_2 = 0.94$), and 326.38 K ($x_2 = 0.915$), respectively. The uncertainty in the UCST is estimated at ±0.1 K, and the uncertainty in the $x_{2(\text{UCST})}$ is estimated at ±0.025. For butyl the UCST was determined to be (376 ± 5) K ($x_2 = 0.88 \pm 0.05$**)** by visual interpolation. Figure 3 shows that the coexisting curve moves to a higher temper-

Table 1. Liquid−Liquid Equilibria for [R$_n$mim][PF$_6$] (1) + Butan-1-ol (2)

R$_n$ = butyl		R$_n$ = pentyl		R$_n$ = hexyl		R$_n$ = heptyl		R$_n$ = octyl	
T/K	x_2	*T*/K	x_2	*T*/K	x_2	*T*/K	x_2	*T*/K	x_2
298.21	0.262	<275.15	0.137	<277.15	0.102	<276.15	0.217	<274.70	0.049
319.78	0.345	280.09	0.209	291.34	0.345	282.17	0.362	274.90	0.361
331.78	0.402	299.53	0.297	309.68	0.441	295.09	0.446	284.53	0.423
337.39	0.433	308.34	0.337	318.66	0.502	301.43	0.493	293.99	0.496
346.93	0.488	313.51	0.361	328.64	0.568	307.83	0.544	299.10	0.536
352.31	0.525	318.00	0.391	334.05	0.615	314.18	0.598	304.40	0.580
356.23	0.553	324.53	0.433	338.00	0.657	319.88	0.648	306.52	0.599
361.69	0.597	332.34	0.482	343.19	0.715	325.37	0.703	311.73	0.648
365.53	0.631	337.02	0.514	347.26	0.776	328.18	0.737	316.94	0.701
369.09	0.669	343.40	0.558	349.64	0.843	331.76	0.788	320.45	0.748
372.91	0.716	347.88	0.593	350.18	0.881	334.10	0.838	323.03	0.788
371.83	0.977	354.28	0.650	350.31	0.905	334.79	0.887	325.01	0.827
369.28	0.981	357.90	0.690	350.30	0.925	335.08	0.909	325.66	0.851
365.75	0.985	360.13	0.717	350.08	0.937	335.32	0.918	326.11	0.884
355.58	0.991	362.20	0.747	348.57	0.957	335.47	0.936	326.29	0.903
		363.72	0.774	345.60	0.973	335.05	0.952	326.38	0.915
		365.28	0.804	336.08	0.989	333.56	0.969	326.31	0.925
		365.78	0.823	316.98	0.996	330.10	0.981	326.29	0.933
		366.15	0.859			314.89	0.995	326.25	0.939
		366.23	0.875					326.17	0.943
		366.18	0.900					321.91	0.978
		365.99	0.922					318.57	0.986
		365.11	0.944					316.31	0.990
		362.98	0.962						
		357.87	0.978						
		329.90	0.995						

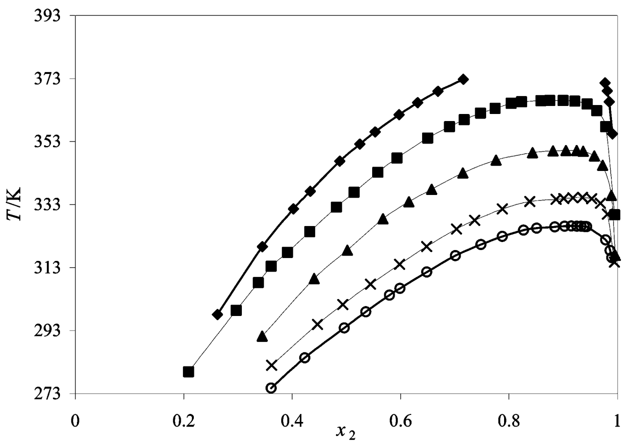

Figure 3. Phase diagrams for the systems [R$_n$mim][PF$_6$] (1) + butan-1-ol (2) at 1 bar: ◆, butyl; ■, pentyl; ▲, hexyl; ×, heptyl; ○, octyl.

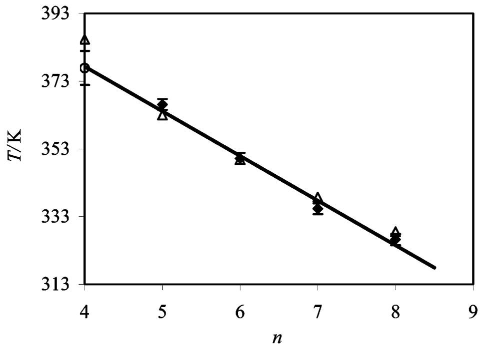

Figure 4. Relationship between the UCST and the number of carbons in R$_n$: ◆, experiment; ○, 1-butyl estimated from experimental data; △, COSMO*therm*.

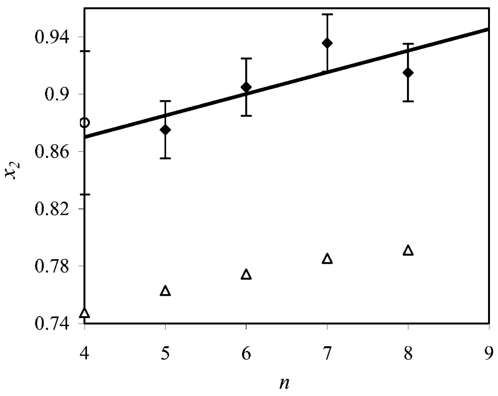

Figure 5. Relationship between x_2 of the UCST and the number of carbons in R$_n$ for [R$_n$mim][PF$_6$] (1) + butan-1-ol (2): ◆, experiment; ○, 1-butyl estimated from experiment data; △, COSMO*therm*.

ature with a decrease of the alkyl chain length of the cationic core. Hence, the higher the "organic content" of the ionic liquid, the higher is its solubility in butan-1-ol.

The relationship between number of carbon atoms on the R$_n$ group and the UCST, shown in Figure 4, is linear within experimental error. The relationship between $x_{2(\mathrm{UCST})}$ and the number of carbons on R$_n$ is also linear within experimental error, as shown in Figure 5.

Comparison with Theory

Traditional approaches for correlating or predicting the properties of fluid mixtures include equation of state (EOS) methods and schemes based primarily on dividing the molecules into various groups (group contribution methods) such as UNIFAC. EOS methods require an estimate of the gas−liquid critical properties of the pure fluids while group contribution schemes require the determination of residual interaction terms between the various functional groups on the ions as well as interaction terms between these functional groups and the functional groups on the organic solvent. To determine the parameters that would be suitable to predict vapor−liquid equilibria and liquid−liquid equilibria would require an extensive experimental program. At the present time the major requirement is a predictive method that could screen the many possible ionic liquids and their mixtures with organic liquids and water

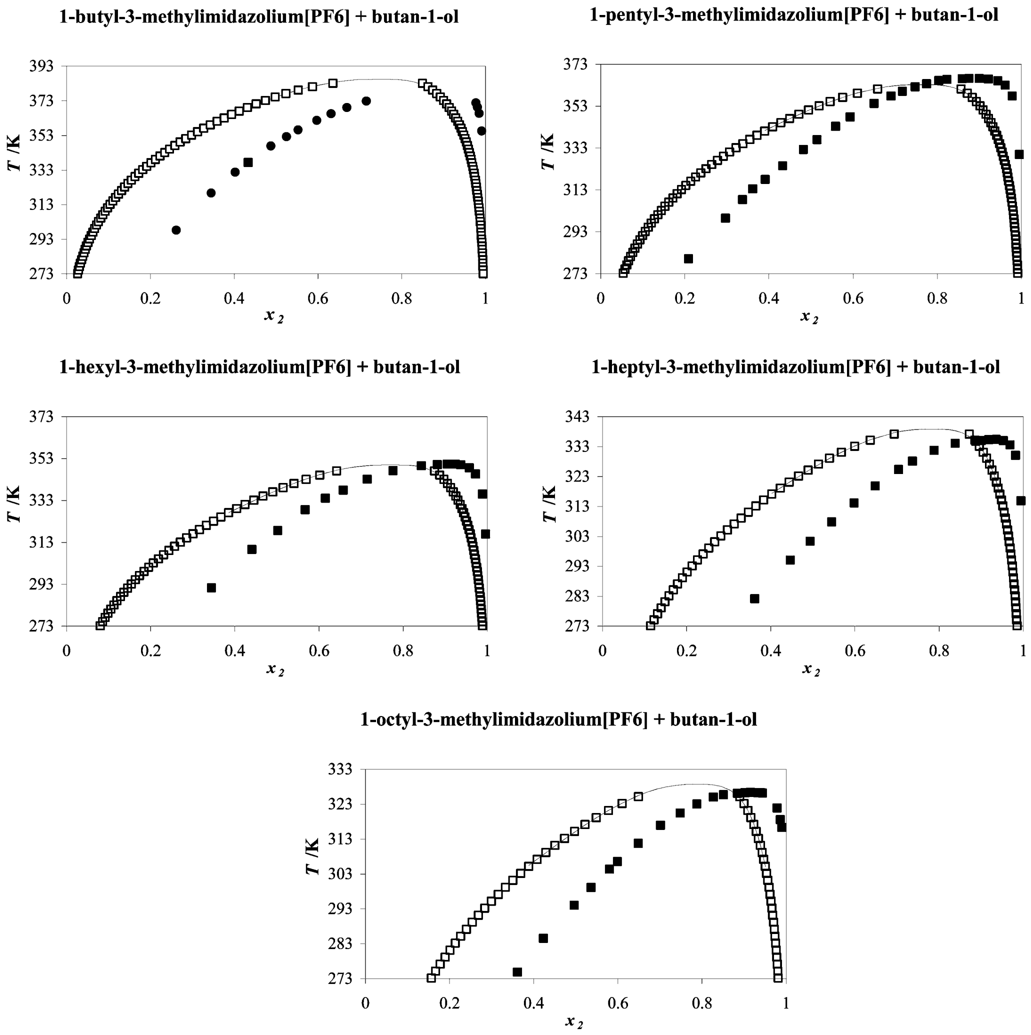

Figure 6. Comparison of experimental liquid–liquid phase diagrams for the systems $[R_n\text{mim}][PF_6]$ (1) + butan-1-ol (2) at 1 bar with values calculated from COSMO*therm*: ■, experimental; □, COSMO*therm*; —, eq 1 fit to COSMO*therm*.

for properties that would be required for particular applications, prior to making extensive measurements.

COSMO-RS[24] is a method for predicting the thermodynamic properties of mixtures on the basis of unimolecular quantum chemical calculations of the individual molecules.[23,24] The mixture properties are then calculated from an entropy term based on the surface area and volume of the molecules, and the enthalpy term is calculated from the energies of interaction between the surfaces of the molecules. The COSMO-RS calculation, as implemented in COSMO*therm*,[25] first assumes the molecule is imbedded in a conductor and gives the screening charge density σ on each part of the molecular surface. It also calculates both the surface area and volume of the molecule. The second step is to describe all interactions between molecules as contact interactions of the molecular surfaces, and these interactions can then be related to the screening charge densities σ and σ' of the interacting surface pieces. For an efficient statistical mechanical calculation, the molecular surface is split into small areas a_{eff} and contact with each of these areas is considered to be independent. This step is similar to the assumption of interacting surfaces in group contribution methods and has been shown elsewhere to give good results for interaction energies calculated from molecular mechanics.[24] This finite area approach allows the reduction of the spatial screening charge distribution to a one-dimensional histogram, called the σ profile. The statistical thermodynamics of the mixture can then be calculated by an equation somewhat similar to the UNIQUAC equation to give the chemical potential of each component. From the chemical potentials, vapor–liquid equilibria, liquid–liquid equilibria, and other properties of the mixture can be derived.[25] The calculations depend on a small number of adjustable parameters, some of which are predetermined from the known properties of the atoms. The others are determined from selected properties of mixtures, with none of the mixtures related to the mixtures under study here.[26] The parameters are not specific to functional groups or molecule type. As the parameters are used as a basis for the calculations only, the resulting parametrization is completely general and can be used to predict the properties of pure fluids and mixtures of many classes of compounds including metals, salts, and polar and nonpolar compounds.

The details of the COSMO calculations are outlined by Diedenhofen et al.[26] Within COSMO*therm*[25] a pseudobinary approach was used to calculate the liquid–liquid equilibrium (LLE) of a mixture composed of an ionic liquid + second component with the cation and anion of the ionic liquid input as separate compounds with the same mole fraction. The chemical potentials are calculated for the ternary system with the potential of the ionic liquid as the sum of the chemical potentials of the cation and anion. At a particular temperature, a numerical gradient approach is used to find the two compositions having equal chemical potentials of the three components (in the pseudobinary system) in the two phases. If an LLE point is found, the search steps to a new temperature using the last LLE composition. If no LLE is found (due to no LLE or the maximum number of steps being exceeded), the program terminates. This latter problem occurs as the UCST is approached.

Determination of the UCST from COSMOtherm Results. The COSMO*therm* LLE numerical gradient program was unable to complete calculations within about 4 K of the UCST, so a further method was required to complete the LLE curve to find the UCST. The critical points were obtained by fitting the COSMO*therm* data with the following equation.[27]

$$T/\mathrm{K} = T_c/\mathrm{K} + k|y - y_c|^m \tag{1}$$

where

$$y = \frac{\alpha x_2}{1 + x_2(\alpha - 1)} \tag{2}$$

$$y_c = \frac{\alpha x_{2c}}{1 + x_{2c}(\alpha - 1)} \tag{3}$$

Equation 1 expresses the exponential dependence of temperature T on the two-phase composition x_2 near the critical point. m, k, α, x_{2c} (critical composition), and T_c (critical temperature) are the coefficients to be fitted to the COSMO*therm* results. Excel's Solver was used to minimize the sum of the squared difference between the model and the result calculated by COSMO*therm*.

The difficulty in using the above model to best fit the data was in choosing appropriate starting points for the parameters. A fair estimate can be made for the critical points; however, an estimate of the other parameters is needed for Solver to suitably converge. m has a value of 2 in classical theory but a value >2 with experimentally observed nonclassical behavior in the vicinity of a critical point.[27] The fit gave the value 2.7 ± 0.2. The parameter α scales the composition variable between mole fraction and volume fraction. All data were fit with $\alpha = 0.3 \pm 0.03$. Only values calculated with COSMO*therm* within 20 K of the UCST were used in the fit.

The results of the COSMO*therm* calculations for liquid−liquid equilibria for the mixtures of [R$_n$mim][PF$_6$] with butan-1-ol are shown in Figure 6. The predicted composition dependence of the LLE is reasonable with $x_{2(\mathrm{UCST})}$ being about 0.12 lower than the experimental values. The prediction of the UCST is remarkably good, being within 3 K for the pentyl through the octyl compounds. Even UNIFAC cannot predict liquid−liquid equilibria to this accuracy from parameters derived from VLE data. These calculations were made for a true three-component mixture where the cation and anion of equal concentrations are treated as separate species. A calculation needs to be performed on a binary mixture where the cation and anion are treated as an ion pair. This is not a simple calculation, as the optimal energy configuration of the ion pair needs to be determined.

1-Butyl-3-methylimidazolium Conformers. There are three significantly different energy states (with the energy in the order A < B < C) for the various conformers that can be formed as a result of torsional rotations on the butyl chain of 1-butyl-3-methylimidazolium. One should calculate the mixture properties with the expected equilibrium conformer concentration for that mixture. These are the results presented in Figure 6. However, it is of interest to know the effect of the composition of the various conformers on the predicted LLE. Using the expected equilibrium concentrations of the three conformers as reference, the lowest energy conformer, A, shifts the LLE so that a higher UCST and a lower $x_{2(\mathrm{UCST})}$ are predicted. With the higher energy conformers B or C or the mixture of conformers (B + C), the LLE is shifted such that a lower UCST and a higher $x_{2(\mathrm{UCST})}$ are predicted. The maximum difference in the UCST for the various conformers or conformer mixtures is about ±5 K from the equilibrium conformer mixture value, as described above, which is not significant. These results are summarized in Figure 7.

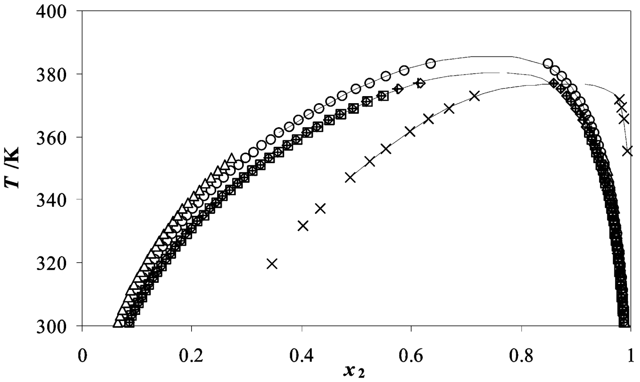

Figure 7. Comparison of liquid−liquid phase diagrams for the 1-butyl compound [bmim][PF$_6$] (1) + butan-1-ol (2) at 1 bar with those of alternative conformers of [bmim]: ×, experimental; ○, equilibrium mixture of conformers A + B + C; □, conformers B + C; △, conformer A; ◇, conformer B; +, conformer C.

Conclusions

Experimental liquid−liquid equilibrium curves for butan-1-ol in ionic liquids [R$_n$mim][PF$_6$] (n = 4 to 8) have been measured. The systems show UCST behavior, and the mutual solubility increases with an increase in the length of the alkyl chain of the cationic core. Quantum chemical calculations based on the σ profiles of the cation, the anion, and the alcohol give a good prediction of the observed LLE equilibria.

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