Room Temperature Ionic Liquids as Replacements for Conventional Solvents - A Review

Kenneth N. Marsh[†], Alex Deev, Alex C-T. Wu, Emma Tran and A. Klamt*

Department of Chemical and Process Engineering, University of Canterbury, New Zealand
*Cosmologic, Leverkusen, D-51381, Germany

Abstract−Room temperature ionic liquids are salts that are liquids at ambient temperature. They are excellent solvents for a broad range of polar organic compounds and they show partial miscibility with aromatic hydrocarbons. Typical room temperature ionic liquids have a stable liquid range of over 300 K and have a very low vapor pressure at room temperature. Ionic liquids that are not hydrolyzed show a wide range of solubility in water. These unique properties have suggested that they might be useful as environmentally benign solvents that could replace volatile organic compounds (VOC). By varying the length and branching of the alkane chains of the cationic core and the anionic precursor, the solvent properties of ionic liquids should be able to be tailored to meet the requirements of specific applications to create an almost infinitely set of "designer solvents". A review of recent applications of ionic liquids is presented along with some results of measurements of liquid-liquid equilibria and partition coefficients with alcohols. The results are compared with predictions based on quantum mechanic calculations.

Key words: Ionic Liquids, Liquid-Liquid Equilibria, Prediction, Quantum Chemical Calculations

INTRODUCTION

The term "room-temperature ionic liquids" has been assigned to organic salts that are liquids at close to ambient conditions. Ionic liquids are normally composed of relatively large organic cations and inorganic or organic anions. Examples of cations are 1-alkyl-3-alkylimidazolium or 1-alkylpyridinium and examples of anions are hexafluorophosphate, tetrafluoroborate, aluminium(III) chloride and various organic ions based on fluorinated amides, nitrides and methides. Room temperature ionic liquids have negligible vapor pressure at room temperature and are generally stable over their wide temperature range. They show considerable variation in their stability to moisture and their solubility in water, polar and nonpolar organic liquids. Some typical examples of ionic liquids are 1-methyl-3-propylimidazolium hexafluorophosphate and 1-methyl-3-butyl-imidazolium tetrafluoroborate.

Early studies on ionic liquids focussed on their use as electrolytes in batteries. The studies by Fannin et al. [1984] and Liao et al. [1996] were primarily on the electrochemical and physical properties of non-stoichiometric mixtures of alkylpyridinium and 1-alkyl-3-alkylimidazolium ions with aluminum (III) chloride. More recent studies by Fuller et al. [1997], and Bonhôte et al. [1996] were on alkylpyridinium and 1-alkyl-3-alkylimidazolium cations with anions such as tetrafluoroborate, bis(trifyl)amide and trifluoroacetate. These conducting liquids have a wide electrochemical window making them ideal solvents for electrochemical reactions with use in new battery technologies as the ultimate goal. The ionic liquids based on aluminum chloride are generally very hygroscopic and studies have to be made in the absence of moisture. Ionic liquids based on tetrafluorborate are generally stable to moisture but have a high solubility in water while those based on hexafluorophosphate, bis(trifyl)amide and tris(trifyl)methide are generally less soluble in water.

In recent years there has been a significant increase in research into other properties of room-temperature ionic liquids since being proposed as of use as new media for chemical reactions. Additionally, they are good solvents for a wide range of metal catalysts as well as polar organic and aromatic liquids. The initial focus was on ionic liquids that were water and air stable such as those based on PF_6^- and BF_4^- anions with the 1-alkyl-3-alkylimidazolium cation. Ionic liquids have been used as the solvent for a variety of organic reactions such as hydrogenation [Müller et al., 1998], hydroformylation [Chauvin et al., 1995], and dimerization [Silva et al., 1998]. Some example reactions include the hydrogenation of 1,3-butadiene with 100% selectivity to but-1-ene using $[bmim]_3[Co(CN)_5]$ as the catalyst in $[bmim][BF_4]$ as the solvent, where [bmim] stands for the 1-butyl-3-methylimidazolium cation [Suarez et al., 1997]. Many other reactions including Heck coupling reactions (the C-C coupling of an aromatic to a compound containing a vinyl group) have been studied in a range of ionic liquids [Kaufmann et al., 1996]. Reviews by Welton [1999], Cull et al. [2000] and Wasserscheid and Keim [2000] have summarized the use of ionic liquids as solvents for synthesis with and without the presence of homogeneous transition metal catalysts.

Ionic liquids have been proposed for extracting products of reactions, and as "green" solvents [Huddleston et al., 1998]. They show unusual solubility behaviour in water and organic solvents and by the judicious variation of the anions and cations it should be possible to design a solvent for a specific application.

In particular, ionic liquids appeal as replacement solvents in liquid-liquid extractions [Brennecke and Maginn, 2001]. 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, as a result of their low vapour pressure, they are 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 products of chemical reactions that proceed

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[†]To whom correspondence should be addressed.
E-mail: k.marsh@cape.canterbury.ac.nz

in aqueous media, such as fermentation, where polar organic compounds are the products, 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 they be air and water stable, thus enabling extractions without special procedures.

As an alternative to extraction of products from aqueous solution resulting from enzyme catalysis, enzymatic catalysis directly in the ionic liquid phase offers distinct advantages. Recently Erbeldinger et al. [2000] has reported on the thermolysin-catalysed synthesis of Z-aspartame in pure 1-butyl-3-methylimidazolium hexafluorophosphate. Other applications of ionic liquids include their use as a stationary phase for gas-liquid chromatography [Armstrong et al., 1999], desulfuring of Diesel fuel [Boesmann et al., 2001]. Of particular interest is the use of task-specific ionic liquids for specific applications outlined by Bates et al. [2002]. They describe the use of 1-butyl-3-butylamineimidazolium tetrafluoroborate for the adsorption of carbon dioxide from gas streams. The drawback of this task-specific ionic liquid was its high viscosity.

To design any process involving ionic liquids on an industrial scale it is necessary to know a range of physical properties including viscosity, density, interfacial tension and heat capacity of the ionic liquids, as well as their solubility in organic solvents, partition coefficients and vapor-liquid equilibrium data, particularly at infinite dilution. It would not be possible to measure all the properties of the almost infinite set of pure ionic liquids and their mixtures with organic solvents, so it is essential to develop and verify both correlations and predictive schemes. The development of such schemes requires the judicious selection of the pure ionic liquids and their mixtures to be studied in detail. At the present time, measurements on the thermophysical properties of ionic liquids are limited. To our knowledge only a few studies on the properties of pure 1-alkyl-3-alkylimidazolium hexafluorophosphates and their mixtures have been reported. Brennecke and coworkers [Blanchard et al., 1999, 2001a, b] have shown that ionic liquids are insoluble in supercritical CO_2, suggesting that products of reactions carried out in ionic liquids can be readily extracted with supercritical CO_2.

Various studies have suggested that ionic liquids could be used as replacement solvents for volatile organic solvents because of their benign nature and their non-volatility. Solvent properties can be varied readily. For example, the change in length of the 1-alkyl chain from 1 to 9 on 1-alkyl-3-methylimadazolium hexafluorophosphate turns the liquid from being highly soluble in water to very immiscible. Replacing the hexafluorophosphate anion with tetrafluoroborate increases the solubility of the ionic liquid in water while replacement with the carbide $(CF_3SO_2)_3C^-$ anion is thought to decrease the water solubility. Thus by judicious variation of the anions and cations it should be possible to design an ionic liquid solvent for a specific solvent application. In particular, ionic liquids could be used as alternative solvents in liquid-liquid extractions. 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, as a result of their low vapour pressure, ionic liquids can be readily recovered for reuse. Hence, the replacement of conventional organic solvents by ionic liquids in extraction processes is seen as a promising field of investigation. There have been few thermophysical property measurements on mixtures of ionic

liquids with organic solvents. A brief summary of measurements follow: Anthony et al. [2002] reported vapor-liquid and liquid-liquid equilibria measurements on mixtures of imidazolium based ionic liquids with water. Wong et al. [2002] measured liquid-liquid phase equilibria of ionic liquids and water. Koel [2000], Huddleston et al. [2001] and Suarez et al. [1998] determined physical properties including density, viscosity, surface tension, melting point, thermal stability and water solubility of a wide range of pure ionic liquids based on the imidazolium cation. The stability of imidazolium based ionic liquids has been reported by Ngo et al. [2000].

We have commenced a study of the thermophysical properties of selected pure 1-alkyl-3-alkylimidazolium hexafluorophosphates as well as liquid-liquid equilibria and partitioning measurements for mixtures of ionic liquids with conventional organic solvents and water. Liquid-liquid equilibria for a series on 1-alkanols with [bmim] [PF_6]) and the effect of water impurity and the partitioning of ethanol between ionic liquid and water are presented here.

EXPERIMENTAL

1. Preparation of Ionic Liquids

The C_4 to C_9 1-alkyl-3-methylimidazolium hexafluorophosphate were prepared in-house by a method described by Welton [2000]. The alkyl chloride (1-chlorobutane through 1-chlorononane) was mixed with 1-methylimidazole at 70 °C and stirred in a closed vessel with an atmosphere of nitrogen to produce 1-alkyl-3-methylimidazolium chloride. This compound was then reacted with hexafluorophosphoric acid at room temperature to produce the ionic liquid as a separate liquid phase. Residual chloride ion and solvent were removed from the ionic liquid by washing with water. Initially, the ionic liquid was dried with magnesium sulfate and filtered through activated charcoal and alumina and the volatile organic solvents and residual water were removed by vacuuming at 10 Pa and 80 °C. The 1-alkyl-3-methylimidazolium hexafluorophosphates appear as yellow or light-yellow transparent liquids. This drying process has the possibility of introducing additional salts into the ionic liquid [Sneddon et al., 2000]. In later purifications, the drying stages using magnesium sulfate and alumina were abandoned in favor of washing with water, then pumping with a vacuum of 1 Pa at 75 °C for over 48 h [Sneddon, 2001].

Property measurements were made initially on 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]). For high-quality thermophysical property measurements it is essential to have pure samples. The methods used to determine the purity of the ionic liquids have not been well documented in the literature. Methods investigated in this work included nuclear magnetic resonance (NMR), infrared spectroscopy (IR), mass spectra, high-sensitivity differential scanning calorimetry (DSC), gas-liquid chromatography (GLC) and high-pressure liquid chromatography with mass spectra detection (HPLC-MS). NMR and mass spectra analysis did not show substantial impurities. However, the sensitivity level of these instruments indicated that we should not expect to determine impurities of less than about 1 mass %. 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 (3,500-3,700) cm^{-1} wavelength range. Further drying in 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 [bmim][PF$_6$].

DSC scans using a Calorimetric Sciences Corporation 4100 multicell DSC with samples of approximately 0.6 g in the temperature range (−40 to +200) °C at a scan rate 0.5 K·h^{-1} showed no solid-liquid phase transition. An endothermic process in the temperature range of (140 to 150) °C appeared to be associated with the removal of trace amounts of bound water, as the peak only occurred during the first temperature scan. Subsequently, this peak was attributed to the reaction of water with the ionic liquid to give HF [Sneddon, 2001; Huddleston et al., 2001]. This decomposition to HF in the presence of water remains a problem with salts containing the PF$_6^-$ anion, particularly when the ionic liquid is used as a catalyst or as a solvent for a catalyst at higher temperatures. A noticeable amount of HF is produced when the ionic liquid is subject to vacuum at temperature > about 85 °C when water is present. The peak areas observed during the DSC scan were calibrated by the addition of known masses of water to the ionic liquid. It was estimated that the residual amount of water in the ionic liquid varied in the range (0.03 to 0.15) mass %, depending on the drying technique used. The method for analysis of water content was abandoned, as the HF could damage the DSC cells. The method was sensitive to water at the 0.005 mass % level.

A typical enthalpy - temperature plot for [bmim][PF$_6$] is shown in Fig. 1. The melting point of [bmim][PF$_6$] was determined by Huddleston et al. [2001] at about 10 °C. Samples containing water, when kept in a test tube at −30 °C for several days, showed a solid-liquid phase transition in the vicinity of 5 °C. This agrees with the value of 4 °C reported by Huddleston et al. [2001]. Ionic liquids with water content <0.1 mass % supercooled and showed no signs of a liquid-solid phase transition when subjected to multiple temperature scans in the range (−40 to +40) °C. Solid-liquid phase transitions were also not observed for ionic liquids with 5 to 8 carbon atoms in the 1-alkyl chain when they were dried.

Purity determination using HPLC was not successful. More than one large peak was observed using a Alltech Econosphere C$_{18}$ 5μ column with acetonitrile as the solvent. Analysis of the peaks via a mass spectrometer indicated that one peak was the pure ionic liquid with the other peaks containing a mixture of compounds that resulted from an interaction of the ionic liquid with the column packing.
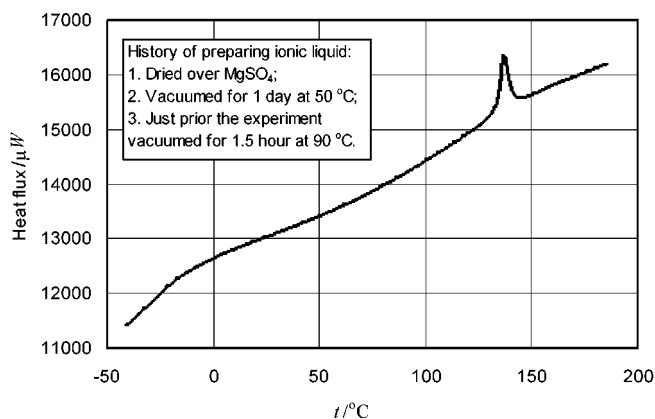

Fig. 1. DSC scan of 1 g of [bmim][PF$_6$] at the scan rate 30 K·h^{-1}. Estimated amount of water 0.03 mass %.

2. Liquid-Liquid Equilibria in the System [bmim][PF$_6$]+alkan-1-ols

[bmim][PF$_6$] was chosen for a detailed study of thermophysical properties including its solubility in organic solvents. Liquid-liquid equilibria was studied for [bmim][PF$_6$]+ethanol, +1-propanol, and +1-butanol. Methanol was completely miscible with [bmim][PF$_6$] at temperatures above 10 °C. The so-called 'cloud point method' was used. A known mass of about 40 g of dry ionic liquid was placed in a temperature controlled vessel containing a stirrer. The vessel was closed to moisture and could be flushed with dry nitrogen. A known mass of about 1 g of 99.9 mass % water-free alcohol was added to the liquid in the vessel and the temperature was raised to about (2 to 5) K above the expected cloud point. The temperature was then reduced at the rate of 10^{-2} K·s^{-1} until the cloud point (seen as a cloud in the middle of liquid phase) was observed. The temperature was then cycled slowly around that temperature, enabling the cloud point to be determined to ±0.03 K. Temperature was measured with a calibrated platinum resistance thermometer with the uncertainty of ±0.01 K. Masses of liquids added were determined with an uncertainty of ±0.0003 g giving an uncertainty in the composition of better than 1 part in 10^{-4}. All three mixtures showed upper critical solution temperatures (USCT). The effect of water on the value of the UCST was determined by preparing a mixture close to the composition of the mixture exhibiting the UCST. The consulate temperature was measured and known masses of water were added and the consulate temperature redetermined.

3. Partitioning of Ethanol Between Water and [bmim][PF$_6$]

Ionic liquids have been proposed as ideal solvents for extraction processes. For products that are formed by reactions in aqueous media it is necessary to know the partition coefficient of reactants and products between the selected ionic liquid and water. We report here our initial studies of the partitioning of ethanol between water and [bmim][PF$_6$]. First, the mutual solubility of water and [bmim][PF$_6$] were determined from the area of the ^{1}H NMR peaks in the water rich and the [bmim][PF$_6$] rich phase. At 18 °C, preliminary values of the solubility of [bmim][PF$_6$] in water was 2.7 mass % and the solubility of water in the ionic liquid was 2.0 mass %.

To study the partitioning of ethanol approximately 2 g of [bmim][PF$_6$] was brought into contact with the same mass of a (water+ethanol) solution at 18 °C. The ionic liquid, being denser than water, was the lower phase. The mixture was periodically shaken to maintain the emulsion. The aqueous solution contained a known mass % ethanol. After 20 min of contacting, the water and ionic liquid phases were separated and the concentration of the components in each phase were determined from the peak areas of the ^{1}H NMR spectra using a 500 MHz spectrometer. The values were checked using glc (Shimadzu GC-R1A with a 2 m Poropak-Q column with thermal conductivity detector).

One cannot use glc to analyze for [bmim][PF$_6$] directly because of its low vapor pressure. To overcome this problem, a known mass of acetone was added to a known mass of the extracted phases. The thermal conductivity detector was calibrated using solutions of known mass fractions of water and ethanol and water and acetone. From the peak areas, the mass ratios of acetone, ethanol and water were calculated and mass balance gave the concentration of the ionic liquid. The glc method was not a satisfactory method to determine low concentrations of the ionic liquid in the water rich phase because
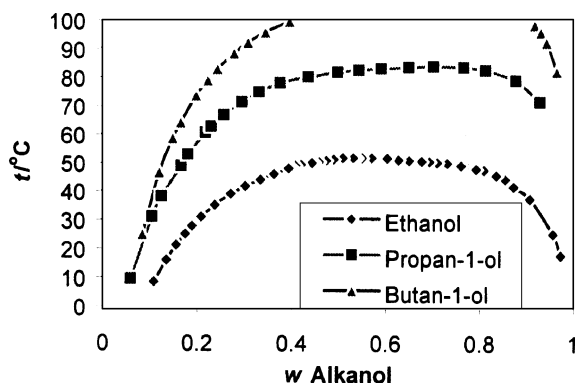
Fig. 2. LLE of the system of [bmim]PF$_6$+Alkanol.

Fig. 4. Partitioning coefficient K of ethanol (3) between water (1) and [C$_4$mim][PF$_6$] (2) at 25 °C.

of high uncertainties for low concentrations in the mass balance equation.

RESULTS

The liquid-liquid phase diagrams for ethanol, propan-1-ol and butan-1-ol are shown in Fig. 2 as a function of mass fraction of the alcohol. Mixtures of the three alcohols with [bmim][PF$_6$] exhibit upper critical solution temperatures (UCST) which increases with increase in the chain length of the 1 alkyl-substituent. The UCST for butan-1-ol was not detrermined as the apparatus could not be operated above 100 °C. The effect of water is most marked. The USCT decreases by about 10 K for the addition of 1.7 mass % water (see Fig. 3) hence it is necessary for the ionic liquids to have a water content less that 0.02 mass % to obtain an UCST with an uncertainty of <0.05 K.

The partition coefficient, defined as the ratio of the concentration of alcohol in the ionic liquid to its concentration in water, at 25 °C as a function of ethanol concentration is shown in Fig. 4. The ternary mixture becomes single phase at mass fractions of ethanol above 0.38 for an equal mass fraction water+ionic liquid mixture. The partition coefficient values obtained by the glc and NMR methods at 10 mass % ethanol in a equal mass fraction of water+ionic liquid two phase system are in qualitative agreement however the NMR method was judged to be more reliable. The reliability of the NMR
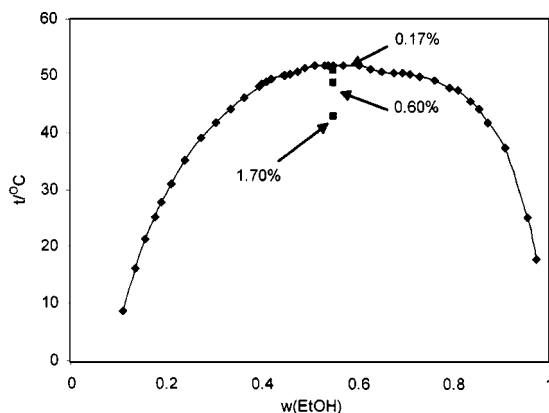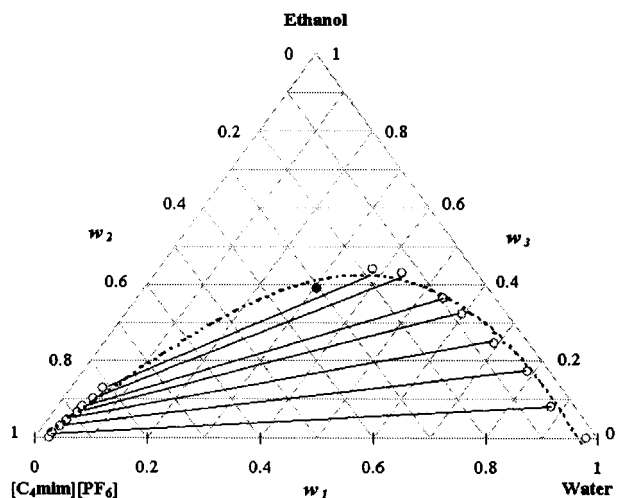

Fig. 5. Experimental liquid-liquid equilibrium data of the ternary mixture water (1)+[C$_4$mim][PF$_6$] (2)+ethanol (3) at 298.15 K; ○-○ experimental tie lines; ● experimental upper critical solution point.

measurements was confirmed by the agreement between the mass fractions determined by NMR and the actual value of each of the components determined when the mixture was one phase. The partition coefficient of ethanol between water and [bmim][PF$_6$] was 0.17 for a 10 mass % ethanol. This value is not unexpected because ethanol is miscible with water at all temperatures and only partially miscible with [bmim][PF$_6$] at temperatures below 48 °C. However, this partition coefficient does not preclude the use of [bmim][PF$_6$] as an extraction media for ethanol or higher alcohols. The three component phase diagram is shown in Fig. 5.

1. Correlation and Prediction of Thermodynamic Properties

Properties such as vapour-liquid equilibria, liquid-liquid equilibria, excess enthalpies, and excess volumes are usually correlated by equations such as the Redlich-Kister, Wilson or the NRTL (Non-Random Two Liquid) equations. The Wilson equation cannot correlate liquid-liquid equilibria. The NRTL is a more satisfactory correlation equation for mixtures containing polar compounds. These equations are of little use in developing predictive methods as they only tell us how the property varies with composition and sometimes they are applicable over a temperature range. Another popular method is based on an equation of state (EOS) approach. Many

Fig. 3. Effect of water concentration (as mass %) on the UCST in the system [C$_4$mim][PF$_6$]+ethanol.

EOS have been proposed, most using data on the gas-liquid-critical properties of the pure fluid to obtain the parameters. For ionic liquids, the prediction of the critical properties is not straightforward, and extrapolation methods are not obvious. In addition EOS methods still require knowledge of the properties, at a minimum, at one mixture composition. Hence EOS methods are essentially correlation methods with an ability to predict both the measured property and other thermodynamic and physical properties at conditions away from the measured composition and temperature.

Predictive methods are based primarily on methods that divide the molecules into various groups (group contribution methods). It is the properties such the volume and surface area of the various groups making up the molecule and the energies of interaction between the various groups on the different molecules that determine the mixing properties. Various group contribution schemes have been proposed. The mostly widely used scheme is the UNIFAC method based on the UNIQUAC equation. The method requires a knowledge of the interaction parameters between the groups. These have to determined from mixture data on components that contain the groups in question. Further, the interaction parameters determined from one property, such as VLE, cannot be readily transferred to another property such as LLE. Hence the use of the UNIFAC predictive method for mixtures containing ionic liquids would require a large amount of experimental data on a range of properties for selected mixtures in order to calculate the required interaction parameters. The area and volume parameters of the pure compounds are generally straightforward to derive.

A third method is based on unimolecular quantum chemical calculations of the individual molecules. One approach, called the COSMO approximation [Klamt and Eckert, 2002], is to make the calculations assuming the molecule is imbedded in a conductor. This calculation gives the screening charge density σ on each part of the molecular surface. In addition one 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 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 α_{eff} and contact with each of these areas are considered as independent. This approach 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. This finite area approach allows the reduction of the spatial screening charge distribution to a one-dimensional histogram, called the σ profile. A typical plot of the screening profiles for various molecules is shown in Fig. 4. The statistical thermodynamics of the mixture can then be calculated by an equation based on the UINQUAC equation to give the chemical potential of each component, from which can be derived VLE, LLE, and other properties of the mixture. The calculation can be readily extended to multicomponent mixtures. The results of those calculations for LLE for mixtures of [bmim][PF$_6$] with ethanol, butan-1-ol and propan-1-ol are shown in Fig. 6. The calculations require no knowledge of the properties of the mixture. The predicted composition dependence of the LLE is good, however the predicted curvature is not correct due to a known problem in the present calculation procedure. The predicted UCST is about (40 to
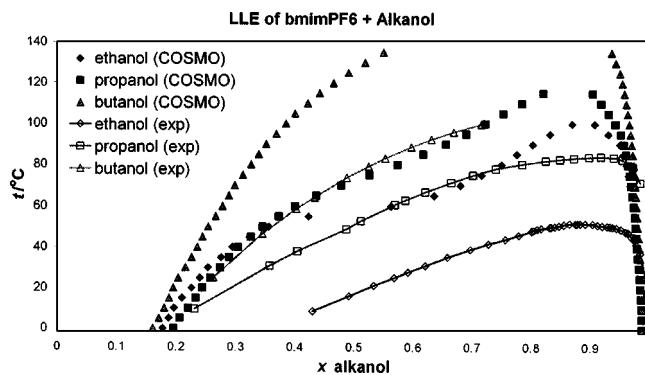

Fig. 6. Comparison of experimental liquid-liquid phase diagram with values calculated from COSMOtherm.

50) K higher that the experimental value for all mixtures. This result is very good but could be improved with the use of a single adjustable parameter applicable to all ionic liquids of this class. Even UNIFAC cannot correctly predict LLE from parameters derived from VLE data. The predicted value of the partition of ethanol between [bmim][PF$_6$] and water was 0.15, in excellent agreement with the experimental value of 0.18. This is an involved theoretical calculation as it involves a three component mixture.

CONCLUSIONS

Experimental liquid-liquid phase diagrams and partition coefficients have been measured and compared with the predictions of a calculation package based on quantum chemical calculations (COSMO*therm*). The calculated values agree surprisingly well with the experimental values.

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