

Miscibility of Ionic Liquids with Polyhydric Alcohols

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Liquid–liquid miscibility temperatures as a function of composition have been determined experimentally for the binary systems formed by ionic liquids ([bmim][BF₄], [bmim][PF₆], [emim][Tf₂N], [bmim][Tf₂N], [hmim][Tf₂N]) and polyhydric alcohols (1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2,3-propanetriol, 1,2-butanediol). The impact of ionic liquid and di- or three-hydroxy alcohol characteristics focusing on the effect of the IL's anion nature, cation alkyl chain length, and alcohol structure (number of hydroxyl groups, position of the hydroxy groups in the molecule, and number of carbon atoms in the diols) is presented. It appears that all systems exhibit upper critical solution temperatures. For dihydroxy alcohols mentioned above, miscibility with 1-butyl-3-methylimidazolium ionic liquids follows the order [BF₄][−] > [Tf₂N][−] > [PF₆][−] and is dependent on the hydrogen-bond basicity of the anion. Analysis of these findings leads us to conclude that the miscibility of ionic liquids is likely related to the hydrogen-bond acceptor strength of the anion. Comparing the miscibility of 1,2-ethanediol with 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, it can be seen that surprisingly, $T_c([emim]^+) < T_c([bmim]^+) < T_c([hmim]^+)$. This arrangement of critical temperatures is opposite to that observed earlier for systems with monohydroxy alcohols. Analyzing the influence of the polyhydroxy alcohol structure, we also noticed that the miscibility of the polyhydroxy alcohols with [bmim][Tf₂N] or [bmim][BF₄] decreases when the polarity of the alcohol rises.

Introduction

Over the past decade, room temperature ionic liquids (RTILs) have become the focus of extensive studies dedicated to better understanding these materials as solvents, electrolytes, thermal fluids, and much more. RTILs have numerous advantages over molecular organic materials, particularly in their stability and negligible vapor pressure. Other advantages include easy functionalization. Therefore, the physicochemical and thermodynamic properties—in particular, the phase behavior of ionic liquids—are the subject of the intense studies. Knowledge of the phase equilibria is fundamental for the RTILs to be effectively used as solvents in liquid–liquid extraction, and on the other hand, it is important for better understanding the solute–solvent interaction in mixtures. These intermolecular interactions are represented by a well-balanced mixture of Coulomb and dispersion contributions, including hydrogen bonding.

There are many solubility studies on miscibility of ionic liquids with various chemicals, such as hydrocarbons and, in particular, with monoalcohols reported in the literature.^{1–7} Regrettably, detailed studies on the miscibility of RTILs with polyhydric alcohols are rather rare. To the best of our knowledge, there are “screening data” for approximate liquid–liquid critical point temperatures reported by Wagner et al.;⁸ for a range of ILs, more detailed data were reported by Shiflett and Yokozeki⁹ for mixtures of 1,3-propanediol and three imidazolium-based ionic liquids. One should also mention the accurate miscibility data for [bmim][Tf₂N] and 1,2-hexanediol reported by Heintz et al.⁴ The present work reports on a precise systematic study of the miscibility of the most popular imidazolium-based ionic liquids with selected polyhydroxy alcohols. Five different ionic liquids and five polyhydric alcohols have been tested. The systems investigated are as follows: (1)

[bmim][BF₄] 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2,3-propanetriol, 1,2-butanediol; (2) [bmim][PF₆] 1,2-propanediol, (3) [emim][Tf₂N]: 1,2-ethanediol; (4) [bmim][Tf₂N] 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol; and (5) [hmim][Tf₂N] 1,2-ethanediol. The purpose of these studies is to examine the influence of the molecular structure of both ionic liquids and polyhydroxy alcohols on the mutual solubility.

Experimental Section

The list of ionic liquids used in this study is as follows: 1-butyl-3-methylimidazolium tetrafluoroborate (99%, purchased from Aldrich), bis(trifluoromethylsulfonyl)imides of 1-ethyl-3-methylimidazolium (99%, Solvent Innovation), and 1-butyl-3-methylimidazolium and 1-hexyl-3-methylimidazolium (99%, Merck). All ILs were carefully purified to reduce the water content and volatile compounds.

The procedure of purifying all ionic liquids was the same. The samples were kept under vacuum in the presence of P₂O₅ (placed in a separate chamber not in contact with the IL) at 60 °C for 3 days, always immediately prior to their use. The mass fractions of water remaining in the dried samples were analyzed by coulometric Karl Fischer titration and showed 100, 150, 50, 150, and 700 ppm for [bmim][BF₄], [emim][Tf₂N], [bmim][Tf₂N], [hmim][Tf₂N], and [bmim][PF₆], respectively. All polyhydroxy alcohols used in experiments were also dried under reduced pressure and kept over molecular sieves, 5 Å, to dry them further. The purity, the source, and the water content (determined by Karl Fischer titration) of investigated alcohols were as follows: 1,2-ethanediol (99.5%, Merck, 40 ppm), 1,2-propanediol (99.5%, Fluka, 180 ppm), 1,3-propanediol (99.6%, Aldrich, 220 ppm), 1,2-butanediol (99%, Aldrich, 450 ppm), 1,2,3-propanetriol (99.8%, Merck, 650 ppm). The samples of ionic liquids and alcohols used in the experiments were regularly checked for water content.

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TABLE 1: Critical Parameters from Scaling Equation

IL /solvent system	T_c/K	x_c	β	A_1	A_2	std dev
[bmim][BF ₄]/1,2,3-propanetriol	347.80 ± 0.03	0.256 ± 0.005	0.40 ± 0.02	0.96 ± 0.08	10.8 ± 1.5	0.0196
[bmim][BF ₄]/1,2-propanediol	280.62 ± 0.02	0.218 ± 0.003	0.40 ± 0.02	0.95 ± 0.08	14.3 ± 1.2	0.0086
[bmim][BF ₄]/1,3-propanediol	299.50 ± 0.01	0.263 ± 0.005	0.44 ± 0.03	1.2 ± 0.1	10.4 ± 1.4	0.0135
[bmim][BF ₄]/1,2-ethanediol	276.81 ± 0.01	0.237 ± 0.003	0.48 ± 0.02	1.23 ± 0.09	11.4 ± 0.6	0.0103
[bmim][BF ₄]/1,2- butanediol	298.17 ± 0.03	0.217 ± 0.003	0.44 ± 0.02	1.24 ± 0.1	23 ± 2	0.0088
[bmim][Tf ₂ N]/1,2-propanediol	337.86 ± 0.04	0.236 ± 0.005	0.40 ± 0.03	1.0 ± 0.1	9 ± 4	0.0135
[bmim][Tf ₂ N]/1,3-propanediol	350.15 ± 0.05	0.226 ± 0.004	0.45 ± 0.03	1.0 ± 0.1	7 ± 1	0.0117
[bmim][Tf ₂ N]/1,2-ethanediol	336.35 ± 0.07	0.201 ± 0.005	0.42 ± 0.03	0.89 ± 0.09	9.9 ± 0.7	0.0152
[emim][Tf ₂ N]/1,2-ethanediol	322.76 ± 0.03	0.259 ± 0.003	0.44 ± 0.01	0.98 ± 0.04	9.8 ± 0.6	0.0097
[hmim][Tf ₂ N]/1,2-ethanediol	350.21 ± 0.03	0.186 ± 0.002	0.46 ± 0.01	0.94 ± 0.05	10.9 ± 0.9	0.0076
[bmim][PF ₆]/1,2-propanediol	342.17 ± 0.06	0.244 ± 0.01	0.27 ± 0.08	0.7 ± 0.2	59 ± 11	0.0196

The samples for miscibility measurements were prepared gravimetrically. The technique and apparatus used for determination of the phase transitions were described earlier.¹⁰ The samples were placed in a thermostatted cell equipped with a fiber optic cable. The temperature was measured using a RTD probe (100 Ω of Omega Engineering calibrated against IPTS-68) with precision of ± 5 mK. The phase transition (cloud point) was detected by the loss of the transmitted light intensity from a 5 mW Polytec HeNe laser shining through the set of the fiber optic cables and the cell and detected by a photodiode. The temperature was changed very slowly at a rate of <0.1 K/min. The overall uncertainty in the measured transition temperatures is estimated to be 0.05 K. The details of the procedure for the determination of the transition temperatures are given elsewhere.¹¹

Results and Discussion

The liquid–liquid phase equilibria for the following binary systems were determined: ([bmim][BF₄]) 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,2,3-propanetriol; ([bmim][PF₆]) 1,2-propanediol; ([emim][Tf₂N]) 1,2-propanediol; ([bmim][Tf₂N]) 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol; ([hmim][Tf₂N]) 1,2-ethanediol. T – x diagrams of all above-mentioned systems are presented in Figures 1–3 and 5–9. The experimental results in the form of T – x data for each binary system are also given in Tables S1–S11 of the Supporting Information.

For all the investigated systems, phase transition temperatures and compositions were fitted to nonlinear fits on the basis of the scaling equation, including the first Wegner correction:^{12–14}

$$|x - x_c| = A_1 t^\beta (1 + A_2 t^{0.5})$$

In the above equation, $t = 1 - T/T_c$; x and T are the mole fraction of the ionic liquid and the temperature, x_c and T_c the corresponding critical values; and A_1 , A_2 , and β are the critical amplitudes and critical exponent, respectively.

The results of the analysis are listed in Table 1. At first sight, some obvious conclusions can be drawn directly from the analysis of the Figures (1–9) and Table 1: similar characteristics were observed for all of the liquid–liquid equilibrium systems studied. The presented data show that the miscibility curves represent the phase diagrams with the upper critical solution temperature (UCST). It can also be seen that the (T, x) projection of these binary phase diagrams is visibly skewed toward low molar fractions of the ionic liquid. All the measured systems present solubility curves characterized by asymmetry with respect to equimolar composition. It is a consequence of much higher molar volumes of ionic liquids in comparison to that of alcohols. It is a typical behavior of systems with ionic liquids,

and this is similar to polymer solutions in which the asymmetry in the phase diagrams is due to the mixing entropy effect caused by the large difference between volumes occupied by the mixture's components.

It should be also noticed that the present results are compatible with the preliminary results reported by Wagner et al.⁸ The comparison of our results for the [bmim][BF₄] + 1,3-propanediol system with the results of Shiflett and Yokozeki⁹ shows excellent agreement between the two data sets using two different measurement techniques (Figure 2). A more detailed analysis of the results obtained presently shows very interesting behavior of the investigated systems and impact of the various characteristics of both ionic liquids and polyhydric alcohols on the mutual solubility.

The Influence of Ionic Liquid Anion ([BF₄[−]], [Tf₂N[−]], and [PF₆[−]]) on Miscibility with 1,2-Propanediol, 1,3-Propanediol, and 1,2-Ethanediol. Imidazolium ionic liquids based on 1-butyl-3-methylimidazolium cation with different anions have been mixed with 1,2-propanediol, and the results allowed us to determine the phase diagram shown in Figure 1. As can be noticed, the best miscibility was observed for tetrafluoroborate salt, and much higher phase transition temperatures were measured for bis(trifluoromethylsulfonyl)imide and hexafluorophosphate. Similar results are also obtained for [bmim][X] ([X] = [BF₄], [Tf₂N], [PF₆]) with other alcohols, such as 1,3-propanediol (Figure 2) and 1,2-ethanediol (Figure 3). Such behavior is different from that observed for monohydroxy alcohols reported until now, in which the best miscibility was observed for bis(trifluoromethylsulfonyl)imides.^{1,5} For dihydroxy alcohols mentioned above, that is, 1,2-propanediol, 1,3-pro-

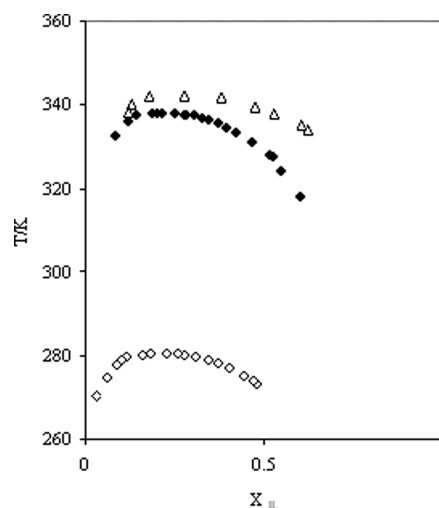


Figure 1. Miscibility of 1,2-propanediol with imidazolium ionic liquids; (\diamond) [bmim][BF₄], (\blacklozenge) [bmim][Tf₂N], and (Δ) [bmim][PF₆].

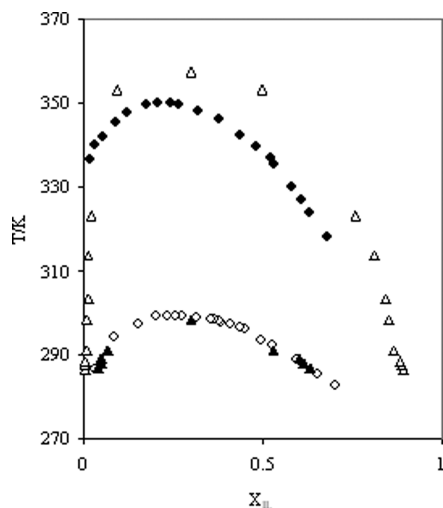


Figure 2. Miscibility of 1,3-propanediol with imidazolium ionic liquids: (\diamond) [bmim][BF₄], (\blacklozenge) [bmim][Tf₂N]. Comparison is made with data for [bmim][BF₄] (\blacktriangle) and [bmim][PF₆] (\triangle) from Shiftlett and Yokozeki.⁹

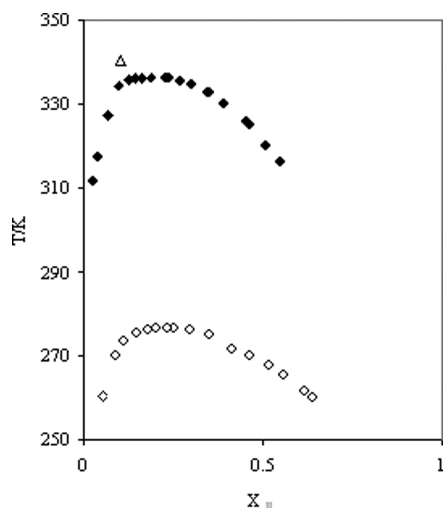


Figure 3. Miscibility of 1,2-ethanediol with imidazolium ionic liquids: (\diamond) [bmim][BF₄], (\blacklozenge) [bmim][Tf₂N]. Comparison is made with data for (\triangle) [bmim][PF₆] from Wagner et al.⁸

panediol and 1,2-ethanediol, miscibility with 1-butyl-3-methylimidazolium ionic liquids is the best for tetrafluoroborate and follows the order [BF₄][−] > [Tf₂N][−] > [PF₆][−].

For those three ionic liquids considered here, we can also notice a jump in the critical temperatures when comparing tetrafluoroborate with the both more hydrophobic ionic liquids. The strength of anion coordination is dependent on the hydrogen-bond basicity of the anion¹⁵ and is summarized from the IR band shifts as [PF₆][−] < [Tf₂N][−] < [BF₄][−]. Analysis of these findings leads us to conclude that the miscibility of the ionic liquids is likely related to the hydrogen-bond acceptor strength of the anion. Ionic liquids with anions that are assigned higher hydrogen bond basicity are more miscible with the analyzed diols. This relationship is best illustrated by Figure 4.

The Influence of Alkyl Side Chain Length of Cation in Imidazolium Bis(trifluoromethylsulfonyl)imide on Miscibility with 1,2-Ethanediol. To investigate the influence of the alkyl side chain length of imidazolium cation on the miscibility with polyhydroxy alcohols, ionic liquids with bis(trifluoromethylsulfonyl)imide anions as a model object were chosen. Phase diagrams for solutions of 1,2-ethanediol with three bis(trifluo-

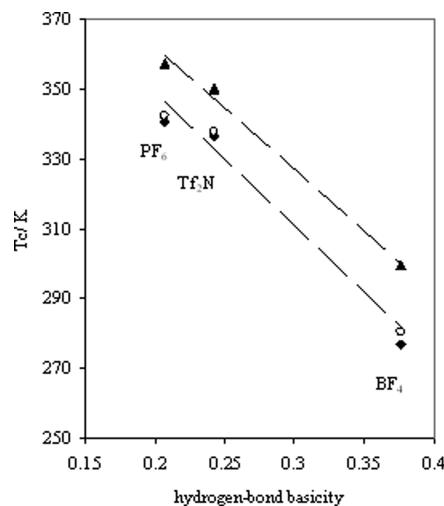


Figure 4. Relationship between upper critical solution temperatures of the investigated systems: ([bmim][BF₄], [bmim][Tf₂N], [bmim][PF₆] + 1,2-ethanediol (\blacklozenge), 1,2-ethanediol (\circ), and 1,3-propanediol (\blacktriangle) and the hydrogen-bond basicity of the anion.

romethylsulfonyl)imides are presented in Figure 5. Surprisingly, we observe that it is [emim][Tf₂N] for which we find the best miscibility with 1,2-ethanediol. Further analysis leads to the conclusion that the UCST increases for more hydrophobic cations with a longer side alkyl chain ($T_{c,EMIM^+} < T_{c,BMIM^+} < T_{c,HMIM^+}$). This trend is opposite that observed for systems with monohydroxy alcohols presented in the literature¹ but confirms the “screening” observations made by Wagner⁸ for transition temperatures of tetrafluoroborates containing [bmim]⁺, [hmim]⁺, and [omim]⁺ cations with 1,3-propanediol and ethylene glycol or hexafluorophosphates containing [bmim]⁺, [hmim]⁺, and [omim]⁺ cations with ethylene glycol. The reason for such behavior may be that diols have very small alkyl portions (in ethylene glycol it does not exist at all), and hence, van der Waals interactions between alkyl chain on the cation with the hydrophobic part of diols is highly ineffective. For monohydroxy alcohols, this type of interaction is considered an important factor affecting their miscibility with ILs. All of these findings lead us to the conclusion that the systems of ionic liquids with dihydroxy alcohols are more similar to systems with water.^{1,8,16} A slight decrease in the critical molar fraction is observed for a set with the longer side chain of the cation (Figure 5), which is a typical behavior observed for other systems.

Structure of Alcohols: The Influence of Alkyl Chain Length in Glycols on Miscibility with 1-Butyl-3-methylimidazolium Tetrafluoroborate. Alcohols, polar solvents, are well-known to form a hydrogen bonded network with both high enthalpies and constants of association. Comparing the critical temperatures, we find an increase in the UCST with an increase in the hydrophobicity of an alcohol. The systems with different ionic liquids (hydrophilic (Figure 6) and hydrophobic (Figure 7)) were investigated, and in both cases, the longer the alkyl chain of the glycol, the less miscible the system was. These observations are consistent with previous results collected in the literature for different ionic liquids with primary or secondary alcohols.^{1–7} It may also be of some interest to compare the miscibility of the selected ILs + monohydroxy alcohols with ILs + corresponding diol systems. Comparing, for example, the systems of [bmim][BF₄] with alcohols we find the following behavior: (1) [bmim][BF₄]/ethanol ($T_c = 281.65$ K)⁸ and [bmim][BF₄]/1,2-ethanediol ($T_c = 276.81$ K), (2) [bmim][BF₄]/propanol ($T_c = 316.9$ K)¹ and [bmim][BF₄]/1,2-propanediol

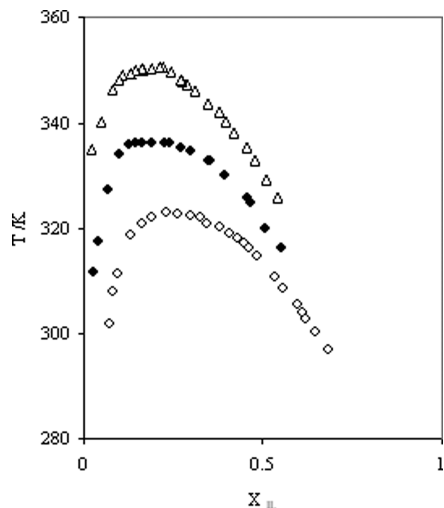


Figure 5. Miscibility of 1,2-ethanediol with bis(trifluoromethylsulfonyl)imides: (\diamond) [emim][Tf₂N], (\blacklozenge) [bmim][Tf₂N], and (Δ) [hmim][Tf₂N].

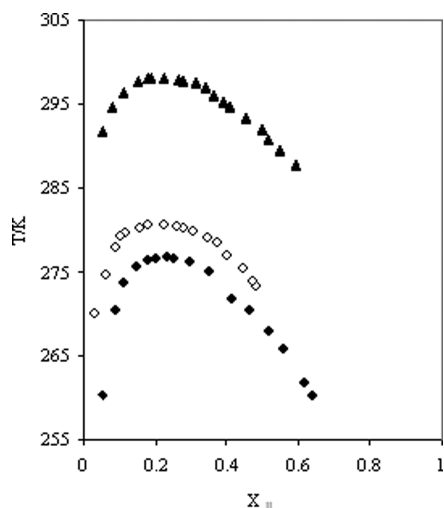


Figure 6. Miscibility of [bmim][BF₄] with glycols: (\blacklozenge) 1,2-ethanediol, (\diamond) 1,2-propanediol, and (\blacktriangle) 1,2-butanediol.

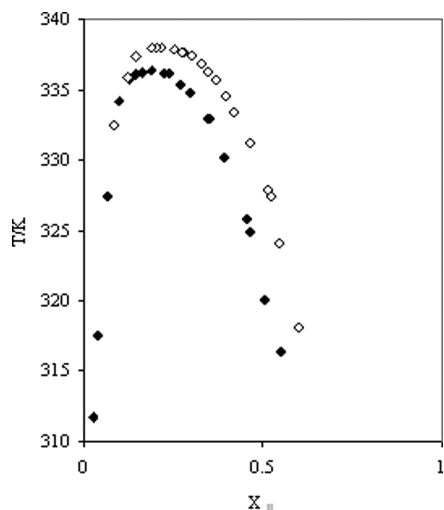


Figure 7. Miscibility of [bmim][Tf₂N] with glycols: (\blacklozenge) 1,2-ethanediol and (\diamond) 1,2-propanediol.

($T_c = 280.62$ K), and (3) [bmim][BF₄]/butanol ($T_c = 334.95$ K)¹ and [bmim][BF₄]/1,2-butanediol ($T_c = 298.17$ K).

It means that we always observe the improvement of miscibility when we add one hydroxyl group more. One might

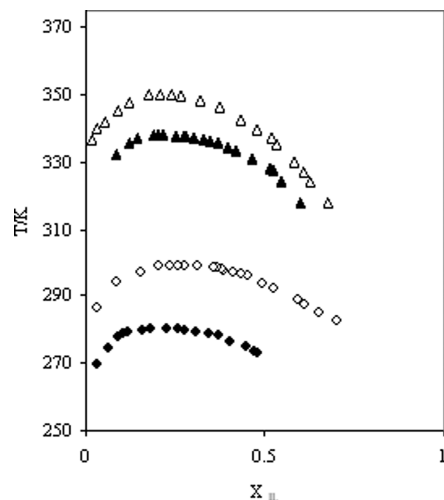


Figure 8. Miscibility of imidazolium ionic liquids with diols: (\blacklozenge) [bmim][BF₄]/1,2-propanediol, (\diamond) [bmim][BF₄]/1,3-propanediol, (\blacktriangle) [bmim][Tf₂N]/1,2-propanediol, and (Δ) [bmim][Tf₂N]/1,3-propanediol.

then anticipate stronger intermolecular interactions of ILs with the diols in comparison with monohydroxy alcohols. Although this qualitative conclusion is important, it is worth noting that although the difference between UCSTs for ethanol and 1,2-ethanediol is very small (<5 K than for the butanol–1,2-butanediol pair), this difference rises almost to 37 K. Furthermore, the impact of the alkyl chain length is much more pronounced in the case of monoalcohols than for diols: the difference between ethanol and butanol is more than 53 K, whereas for diols, it is only about 22 K.

The Effect of the Structure of the Polyhydroxy Alcohols on Miscibility with [bmim][BF₄] and [bmim][Tf₂N]. Comparing our miscibility results observed for ionic liquids based on 1-butyl-3-methylimidazolium cation with propanediol isomers (Figure 8), we can conclude that in both cases ([bmim][BF₄] and the more hydrophobic [bmim][Tf₂N]), the solvent with vicinal hydroxyl groups is a better solvent than its isomer. Interesting behavior has been noticed for [bmim][BF₄] with alcohols. Whereas for the monohydroxy alcohol (*n*-propanol) the immiscibility gap is quite big (UCST = 316.9 K),¹ the addition of one hydroxyl group improves the miscibility, and it occurs for both propanediol isomers, although the critical temperatures are different (for 1,2-propanediol UCST = 280.62 K, but for 1,3-propanediol, UCST = 299.50 K). Following this trend, one could expect further improvement of miscibility when we add one hydroxyl group more. However, increasing the number of hydroxyl groups in the alcohol molecule up to three (1,2,3-propanetriol), we observe (Figure 9) the rise of UCST of the system with [bmim][BF₄] (UCST = 347.80 K). It is also worth noting that the data obtained presently confirm the general observation made for monohydroxy alcohols:¹⁷ namely, that there is a correlation between critical temperatures and dielectric constants or the Reichardt–Dimroth $E_T(30)$ scale.¹⁸ The latter is the well-known empirical scale of solvent polarity widely used in various free-energy relationships (the $E_T(30)$ scale is defined as the molar electronic transition energy of dissolved negatively solvatochromic pyridinium *N*-phenolate betaine dye). Watching the present results, it can be seen that for polyhydroxy alcohols, miscibility is worse when the polarity of the alcohol rises (Figure 10).

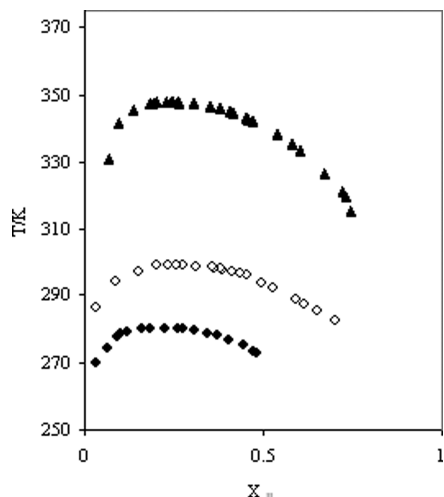


Figure 9. Miscibility of [bmim][BF₄] with polyhydroxy alcohols (◆) 1,2-propanediol, (◇) 1,3-propanediol, and (▲) 1,2,3-propanetriol.

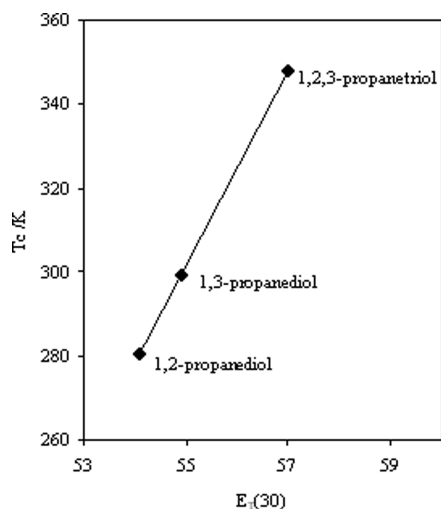


Figure 10. Correlation of UCSTs for [bmim][BF₄] + polyhydroxy alcohols systems with Reichardt–Dimroth $E_T(30)$ parameters of alcohol.

Conclusions

Liquid–liquid equilibria of 11 binary systems involving ILs ([bmim][BF₄], [bmim][PF₆], [emim][Tf₂N], [bmim][Tf₂N], or [hmim][Tf₂N]) and polyhydric alcohols (1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2,3-propanetriol, or 1,2-butanediol) have been reported. All phase diagrams are characterized by the upper critical solution temperature behavior. The results obtained show how the structure of both ionic liquid and alcohol affects the phase behavior. It was shown that the miscibility depends on the choice of an anion, and in the case of diols, the order observed is as follows: [BF₄][−] > [Tf₂N][−] > [PF₆][−]. This behavior is opposite that found for monohydroxy alcohols.

Another interesting result shows that the impact of the alkyl chain length on the miscibility is also opposite that for systems with monohydroxy alcohols. In the present case, the best mutual solubility is found for the imidazolium cation with an ethyl alkyl chain. In general, the miscibility behavior is similar to that observed for systems of ILs with water. The structure of alcohols affects the miscibility, as well. At first, one may observe the better miscibility for diols in comparison with the corresponding monohydroxy alcohols. The relative position of the OH groups within an alcohol molecule affects the miscibility as well: the vicinal position favors the miscibility. The length of the alkyl chain in alcohols influences the miscibility in the same manner as for monohydroxy alcohols. The results obtained presently also suggest some correlation between miscibility and acceptor/donor properties of the mixture components.

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Supporting Information Available: Experimental liquid–liquid data, Tables S1–S11. This material is available free of charge via the Internet at <http://pubs.acs.org>

References and Notes

- (1) Crosthwaite, J. M.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2004**, *108*, 5113–5119.
- (2) Domanska, U.; Mazurowska, L. *Fluid Phase Equilib.* **2004**, *221*, 73–82.
- (3) Domanska, U.; Marciniak, A. *J. Phys. Chem. B* **2004**, *108*, 2376–2382.
- (4) Heintz, A.; Lehmann, J. K.; Wertz, C.; Jacquemin, J. *J. Chem. Eng. Data* **2005**, *50*, 956–960.
- (5) Crosthwaite, J. M.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. *Fluid Phase Equilib.* **2005**, *228*–229, 303–309.
- (6) Lachwa, J.; Szydlowski, J.; Makowska, A.; Seddon, K. R.; Esperança, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N. *Green Chem.* **2006**, *8*, 262–267.
- (7) Lachwa, J.; Morgado, P.; Esperança, J. M. S. S.; et al. *J. Chem. Eng. Data* **2006**, *51*, 2215–2221.
- (8) Wagner, M.; Stanga, O.; Schroer, W. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3943–3950.
- (9) Shiflett, M. B.; Yokozeki, A. *J. Chem. Eng. Data* **2007**, *52*, 1302–1306.
- (10) Szydlowski, J.; Rebelo, L. P. N.; Van Hook, W. A. *Rev. Sci. Instrum.* **1992**, *63*, 1717–1725.
- (11) Szydlowski, J.; Szykula, M. *Fluid Phase Equilib.* **1999**, *154*, 79–87.
- (12) Greer, S. C. *Phys. Rev. A* **1976**, *14*, 1770–1780.
- (13) Wilson, K. G. *Phys. Rev. B* **1971**, *4*, 3174–3184.
- (14) Singh, R. R.; Van Hook, W. A. *J. Chem. Phys.* **1987**, *87*, 6097–6110.
- (15) Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, J. M.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2790–2794.
- (16) Freire, M. G.; Neves, C. M. S. S.; Carvalho, P. J.; Gardias, R. L.; Fernandes, A. M.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. *J. Phys. Chem. B* **2007**, *111*, 13082–13089.
- (17) Makowska, A.; Siporska, A.; Szydlowski, J. *J. Phys. Chem. B* **2006**, *110*, 17195–17199.
- (18) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319–2358.

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