



Phase behavior of imidazolium and phosphonium tetrafluoroborates with dihydroxy alcohols



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ABSTRACT

Liquid–liquid equilibrium curves for 1-ethyl-3-methylimidazolium tetrafluoroborate $-\text{[C}_2\text{MIM, BF}_4\text{]}$, 1-butyl-3-methylimidazolium tetrafluoroborate $-\text{[C}_4\text{MIM, BF}_4\text{]}$ and trihexyl(tetradecyl) phosphonium tetrafluoroborate $-\text{[P}_{6,6,6,14}\text{, BF}_4\text{]}$ with chosen dihydroxy alcohols and their deuterated analogues have been determined. All fourteen obtained phase diagrams are described by the upper critical solution temperature (UCST) type behavior. The mutual solubility of 1-ethyl-3-methylimidazolium tetrafluoroborates decreases with the increase in alkyl chain of 1,2-dihydroxy alcohols but the opposite effect was observed for the ionic liquid with phosphonium cation. The impact of the hydroxyl group position in butanediol molecule on miscibility with trihexyl(tetradecyl) phosphonium tetrafluoroborate was examined. The results lead to the conclusion that vicinal(1,2 and 2,3)-butanediols are much better miscible than more polar (1,3) and (1,4) isomers. Deuterium substitution in both hydroxyl groups of investigated diols generates downward isotope shift of UCST both for phosphonium and imidazolium based ionic liquids thus making the miscibility better in each case.

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1. Introduction

The ability to design ionic liquids in terms of their usefulness in chemical processes causes that the attractiveness of these materials is constantly high. In addition these substances attract much attention of many researchers because of their unique properties. There are many applications of ionic liquids especially as solvents in different organic reactions [1–3]. The knowledge of the thermo-physical and thermodynamic properties of solution is very important to understand and predict the phase behavior. Hydrophobic properties of some of them allow us to use them in the extraction of many organic substances from aqueous solutions [4–6]. Liquid phase behavior of mixtures containing ionic liquids with molecular solvents such as hydrocarbons [7–9], monohydroxy alcohols [10–14] and polyhydroxy alcohols [15–18] has been intensively studied in the recent years. Among numerous ionic liquids those with imidazolium cation are the most popular, however we can also find recently published reports on miscibility with phosphonium ionic liquids [19,20]. Independent of the kind of a cation in most of those cases the diagrams with the upper critical solution temperature (UCST) were observed. Only in a few cases interesting behavior

showing the lower critical solution temperature (LCST) type diagram have been found for systems containing ionic liquids [21,22].

It was noted that miscibility of ionic liquids with organic solvents is closely related to their structure. However in the case of diols and other polyhydroxy alcohols there is still much to be done in order to formulate clear rules describing impact of the structure of cation and anion on the their miscibility with ionic liquids. The study of the H/D isotope effect (IE) on miscibility of ionic liquids with different compounds is rather rare [23–29]. Theory of the isotope effects formulated and tested by Rabinovich [23] was based on the phase behavior of organic solvents and contains no data for solutions with ionic liquids. More advanced quantitative theoretical treatment by Van Hook and Rebelo was also dedicated to the molecular solvents. To the best of our knowledge only a few studies [26–28] were focused on investigation of influence of hydrogen/deuterium substitution in hydroxyl group on miscibility with ionic liquid. Some interesting results were obtained for $[\text{C}_4\text{MIM, PF}_6]$ with $\text{C}_2\text{H}_5\text{OH}/\text{C}_2\text{H}_5\text{OD}$ [27] or $[\text{C}_4\text{MIM, BF}_4]$ with isomeric butanols [26] systems. In these solutions isotopic substitution in polar group of alcohol generates the improvement of miscibility and this behavior is opposite to that expected for systems containing alcohols. For the mixtures of ionic liquids with arenes the miscibility is also improving upon deuterium substitution in the aromatic solvent [29]. These observations became the additional inspiration for continuation the study on phase behavior

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of ionic liquids with diols and to undertake the research of the isotope effects on miscibility in these systems.

2. Materials and method

The list of ionic liquids and dihydroxy alcohols used in experiments (together with the stated purity and water contents after drying procedure) is placed in Table 1. Ionic liquids were dried under vacuum at 60 °C (in presence of P₂O₅ keeping in separate chamber) during at least three days. All dihydroxy alcohols were dried over molecular sieves 5 Å. The water content was systematically checked by coulometric titration (Karl Fischer method) using KF Trace Titroline. Deuterated diols have been synthesized in triple exchange reaction with D₂O. The remaining water was removed by distillation. To dry them further, diols have been kept over molecular sieves 5 Å (previously treated with heavy water and activated). The NMR analysis was done for all deuterated diols and showed high rate of exchange reaction. The minimal deuterium content was 89% for 1,2-butanediol-d₂ and 92% for 1,2-hexanediol-d₂.

Phase diagrams were determined using visual cloud-point method based on appearance of turbidity in slowly cooled solution. All samples have been prepared gravimetrically in special, very tight glass cell equipped with Rotaflow needle valve at atmospheric pressure. The cells were immersed in appropriate bath – for temperatures between 0 °C and 90 °C – mixture of ethylene glycol plus water, at temperatures higher than 90 °C in glycerol or oil bath. Then it was placed on magnetic stirrer and heated. All mixtures were heating about 5 K above the expected phase transition temperature to obtain homogenous system. After about 10 min of thermostating, the system was cooling slowly (with a rate about 0.1 K/min), until turbidity of solution appeared. The measurements were repeated at least three times so the overall uncertainty is no more than 0.1 K far from the critical concentration and even better up to 0.05 K close to the critical region.

Data of dielectric constant for alcohols at 298 K have been taken from The Landolt–Bornstein Database [30], for 1,2-hexanediol was estimated [18].

3. Results and discussion

Phase diagrams of binary mixtures containing tetrafluoroborate ionic liquids and dihydroxy alcohols were determined for 14 following systems:

- [C₂MIM, BF₄] with 1,2-ethanediol, 1,2-propanediol, 1,2-butanediol, 1,2-hexanediol, 1,2-butanediol-d₂, 1,2-hexanediol-d₂.

- [C₄MIM, BF₄] with 1,2- butanediol-d₂, 1,2-hexanediol-d₂.
- [P_{6,6,6,14}, BF₄] with 1,2-propanediol, 1,2-butanediol, 1,2-pentanediol, 1,3-butanediol, 2,3-butanediol, 1,2-butanediol-d₂.

All measured transition temperatures for samples of given concentrations are placed in Table 2. The results were fitted to nonlinear fits based on the scaling Eq. (1). (including first Wegner correction): [31–33]

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

where $t = 1 - T/T_c$, x -mole fraction, T -phase transition temperature, x_c, T_c - critical concentration and critical temperature, A_1, A_2 - amplitudes, β - universal critical exponent.

All the obtained fitting parameters are presented in Table 3.

3.1. The impact of alkyl chain length in dihydroxy alcohols on miscibility with ionic liquids

3.1.1. Miscibility of 1-ethyl-3-methylimidazolium tetrafluoroborate

Miscibility results of imidazolium [C₂MIM, BF₄] with 1,2-diols: 1,2-ethanediol, 1,2-propanediol, 1,2-butanediol and 1,2-hexanediol are presented in Fig. 1. They show phase behavior characteristic for UCST type diagrams. The best miscibility was observed for the shortest diol – 1,2-ethanediol. This system presents complete miscibility at room temperature. The elongation of alkyl chain in alcohol worsens the miscibility and finally for the system with 1,2-hexanediol, the UCST is shifted up to 374.36 K.

Comparing phase behavior of [C₂MIM, BF₄] to other imidazolium tetrafluoroborates in dihydroxy alcohol solutions investigated earlier [15] one can notice the higher values of critical temperatures (worse miscibility) for all systems containing [C₂MIM, BF₄] with C₃–C₆ (1,2) diols. On the other hand, the best miscibility has been observed for the samples with ethylene glycol.

Fig. 2 nicely illustrates this behavior. As it can be observed the longer alkyl chain length in imidazolium cation of ionic liquid, the better miscibility with 1,2-propanediol, 1,2-butanediol and 1,2-hexanediol. As can be seen the critical temperatures for 1,2-ethanediol with [C₂MIM, BF₄] (277.05 K) and [C₄MIM, BF₄] (276.81 K) are very close, and one may also observe the significant deterioration in miscibility with elongation of side chain in cation.

3.1.2. Miscibility of trihexyl(tetradecyl) phosphonium tetrafluoroborate

Phase transition temperatures as a function of molar fraction of trihexyl(tetradecyl) phosphonium tetrafluoroborate solution for system with vicinal (1,2) diols have been presented in Fig. 3. The

Table 1
Table of pure components used in this work.

Name of the component	Abbreviation	Source	Purity stated (% mass)	Method of purification	Water content (ppm)
Trihexyl(tetradecyl) phosphonium tetrafluoroborate	[P _{6,6,6,14}][BF ₄]	Merck	98	Dried under vacuum (0.1 Pa) at 330.15 K	80
1-Ethyl-3-methylimidazolium tetrafluoroborate	[C ₂ MIM, BF ₄]	Sigma –Aldrich	98	Dried under vacuum (0.1 Pa) at 330.15 K	70
1-Butyl-3-methylimidazolium tetrafluoroborate	[C ₄ MIM, BF ₄]	Fluka	98.5	Dried under vacuum (0.1 Pa) at 330.15 K	150
1,2-Ethanediol		Sigma–Aldrich	99.8	Dried over molecular sieves 5 Å	100
1,2-Propanediol		Fluka	99.5	Dried over molecular sieves 5 Å	50
1,3-Butanediol		Sigma–Aldrich	99	Dried over molecular sieves 5 Å	30
1,2-Butanediol		Fluka	98	Dried over molecular sieves 5 Å	60
2,3-Butanediol		Aldrich	98	Dried over molecular sieves 5 Å	130
1,2-Pentanediol		Aldrich	99.5	Dried over molecular sieves 5 Å	50
1,2-Hexanediol		Aldrich	98	Dried over molecular sieves 5 Å	230
1,2-Butanediol- d ₂		Deuterated in our lab	88.4 at.D	Dried over molecular sieves 5 Å	60
1,2-Hexanediol- d ₂		Deuterated in our lab	91.5 at.D	Dried over molecular sieves 5 Å	70

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