Eutectic mixtures of pyrrolidinium-based ionic liquids

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The solid−liquid equilibria of five systems consisting of different pairs of pyrrolidinium-based ionic liquids were investigated. For all five tested systems the solid−liquid phase behaviour was found to be of eutectic type, and the eutectic compositions and temperatures were determined. Additional experiments were carried out to determine thermal stability of the resulting mixtures in comparison to the corresponding parent salts. Compared to the latter, melting point depression of the eutectic mixtures as large as 151 K are achievable for the system $[C_2MPyrr][NTf_2] + [C_4MPyrr][BF_4]$. At the same time, this is the first detailed analysis of eutectic mixture of ionic liquids involving four different ions that is reported in the literature.
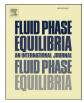
1. Introduction

Simple ionic liquids (ILs), a class of organic salts that melt at a temperature below 373.15 K [1–3], are commonly referred to as designer solvents. This is due to the possibility of fine-tuning their properties to a considerable extent by judicious and independent selection of the constituting cation and anion, in order to prepare the optimum solvent for a given application [4]. As a result of this versatility, ILs are the subject of intensive research oriented towards a variety of industrial applications [5,6]. The melting point (or glass transition temperature) of an IL is, in this context, one of its most relevant properties, and is obviously related to the structures of the cation−anion combination [7,8], in particular to the size and symmetry of the ions [9,10]. Attempts are being made to obtain ionic liquids with lower melting temperatures, so that they can be applied in liquid state over wider and less energy-demanding temperature ranges. Besides the variation of the combination of cation and anion, a possibility to achieve this could be through the addition of co-solvents [11–13]. The solid−liquid phase behaviour for this kind of systems has been studied intensely [14–18]. Unfortunately the disadvantage of this approach is that such mixtures do not always preserve desired properties of ILs like e.g. non-

volatility or aprotic character. A different strategy to depress the melting point is the addition of another IL instead of a molecular solvent. This can lead to the creation of a eutectic mixture of ILs; i.e. to a global minimum in melting point of the mixture at an appropriate molar ratio [19].

Thermodynamic exploration of eutectic mixtures of ILs was the subject of several articles in the literature [10,20−24], which focused almost entirely on mixtures of imidazolium-based ILs. Pyrrolidinium-based ILs are another popular family of ILs, somewhat cheaper than their imidazolium analogues, and with favourable properties such as wide electrochemical windows, of great interest for e.g. electrochemical applications [25]. However, their melting temperatures are typically higher than the corresponding imidazolium ILs with the same anion and equivalent cationic alkyl substituents. Thus, pyrrolidinium ILs could largely benefit from being components of eutectic mixtures with lower melting temperatures, consequently improving their potential for applications. Therefore, the aim of this work was to increase the body of knowledge of eutectic behaviour in mixtures of ILs, beyond imidazolium-based ILs, and particularly focusing on pyrrolidinium-based ILs.

The strategy in the previous studies of eutectic points of mixtures of ILs was to mix two different ILs with one common ion (either the cation or the anion). This simplifies the interpretation of the results, since there are only three types of ions involved. In the present work we report a number of eutectic systems comprising exclusively of salts with a pyrrolidinium cation, having a common

ion. In particular, the following mixtures with a common cation (namely 1-butyl-1-methylpyrrolidinium ([C_4MPyrr]$^+$) or 1-ethyl-1-methylpyrrolidinium ([C_2MPyrr]$^+$)) are investigated: [C_4MPyrr]Cl + [C_4MPyrr]Br; [C_4MPyrr]Br + [C_4MPyrr][BF_4]; [C_4MPyrr]Cl + [C_4MPyrr][BF_4]; and [C_2MPyrr][NTf_2] + [C_2MPyrr][BF_4] (where [NTf_2]$^-$ stands for bis(trifluoromethylsulfonyl) amide). Additionally, and similarly to a strategy as presented by Kunze et al. [26] for the calorimetric study of equimolar mixtures of pyrrolidinium ionic liquids, one more system was investigated in which the parent compounds do not have any ions in common and thus four different ions are involved: [C_2MPyrr][NTf_2] + [C_4MPyrr][BF_4]. Not all of the salts selected as parent compounds meet the conventionally accepted definition of ILs, but the idea was to obtain eutectic mixtures with a temperature below 373.15 K (therefore meeting such definition).

For each of the systems mentioned above, experiments for the determination of eutectic temperatures and composition, as well as characterisation of their thermal stability in comparison to the corresponding parent salts, were carried out and reported below.

2. Materials and methods

2.1. Materials

1-Methylpyrrolidine (Fluka, 98%), 1-chlorobutane (Sigma−Aldrich, 99%), 1-bromobutane (Sigma−Aldrich, 99%), 1-bromoethane (Sigma−Aldrich, 98%), potassium tetrafluoroborate (Sigma−Aldrich, 96%), and lithium bis(trifluoromethylsulfonyl) amide (Sigma−Aldrich, 99%) were used as received. The solvents acetonitrile (Sigma−Aldrich, 99%), ethyl acetate (Sigma−Aldrich, 99%), and dichloromethane (Sigma−Aldrich, 99%) were of reagent grade.

The organic salts were prepared using standard synthetic protocols. [27] The following paragraphs describe the procedures in detail. The chemical identity and absence of remaining starting materials or other impurities in the final products were checked by ^{1}H and ^{13}C NMR spectroscopy.

1-Butyl-1-methylpyrrolidinium chloride ([C_4MPyrr]Cl) was synthesised by alkylation of 1-methylpyrrolidine with 1-chlorobutane. First, 1-methylpyrrolidine (0.11 mol, 9.4 g) was mixed with 70 mL acetonitrile and cooled to 273 K. To this stirred solution, a 10% molar excess of 1-chlorobutane (0.12 mol, 10.2 g) was added dropwise. The reaction mixture was heated to 338 K and stirred for 24 h at this temperature. Removal of the solvent under reduced pressure afforded crude 1-butyl-1-methylpyrrolidinium chloride. The product was purified by dissolution in a small amount of acetonitrile and gradual addition of ethyl acetate in order to initiate crystallisation. Finally, the product was dried under high vacuum for removal of water and other possible volatile impurities that might be present.

1-Butyl-1-methylpyrrolinium bromide ([C_4MPyrr]Br) and 1-ethyl-1-methylpyrrolidinium bromide ([C_2MPyrr]Br) were prepared in an analogous manner, using 1-bromobutane (0.12 mol,

15.1 g) or 1-bromoethane (0.12 mol, 13.1 g) as alkylating agents instead of 1-chlorobutane.

In order to prepare 1-butyl-1-methylpyrrolidinium tetrafluoroborate ([C_4MPyrr][BF_4]), a solution of [C_4MPyrr]Br (0.05 mol, 11.1 g) in distilled water (70 mL) was mixed with a solution of potassium tetrafluoroborate (0.06 mol, 7.6 g) in dichloromethane (70 mL). The mixture was stirred for one hour at room temperature to allow the metathesis reaction to proceed. The biphasic mixture was transferred to a separation funnel, and the organic layer was extracted with distilled water ($\times$6) with 0.1 mol equivalent of K[BF_4] in the first three portions. After separation of the dichloromethane phase, the solvent was removed by rotary evaporation. The product was dried under high vacuum for five days in order to remove any remaining water or other volatile impurities. Absence of significant levels of halides in the final product was assessed by the $AgNO_3$ test.

1-Ethyl-1-methylpyrrolidinium tetrafluoroborate ([C_2MPyrr][BF_4]) was prepared in an analogous manner to [C_4MPyrr][BF_4], simply using [C_2MPyrr]Br (0.05 mol, 9.7 g) as starting material instead of [C_4MPyrr]Br.

1-Ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) amide ([C_2MPyrr][NTf_2]) was also prepared by metathesis via a very similar procedure, with the initial addition of lithium bis(trifluoromethylsulfonyl) amide (Li[NTf_2]) (0.06 mol, 17.2 g) to a solution of [C_2MPyrr]Br (0.05 mol, 9.7 g) in distilled water (70 mL). The mixture was stirred for one hour at 303 K to allow the metathesis reaction to proceed. Then, the mixture was transferred to a separator funnel, and washed with distilled water ($\times$6) with 0.1 mol equivalent of Li[NTf_2] in the first three portions. The solvent was removed by rotary evaporation and the product was dried under high vacuum for five days in order to remove any remaining water or other volatile impurities. The $AgNO_3$ test was used to ensure that there were no significant levels of halide impurities in the final product.

The full names of all salts, their abbreviation, and information on the preparation of samples and their estimated final purity are summarised in Table 1.

2.2. Preparation of samples for DSC analysis

For each binary system, molar compositions were used to prepare the mixtures for determination of the eutectics. Each set of mixtures A + B was prepared at concentrations ranging gradually from 100% of component A to 0% of component A (i.e. 100% of component B) with a step of ~10% in molar fraction composition. For each mixture preparation, the corresponding amounts of the pure salts were weighed directly into aluminium DSC pans (previously tarred) to yield a sample with a total mass of 6−18 mg, approximately. Next, the DSC pans were immediately sealed with lids of the same material with a pin hole (that ensured removal of any possible remaining water during the first heating cycle of the DSC experiment, as well as equilibration of the pressure resulting from the potential expansion of any evolving gas), and submitted for DSC analysis.

Table 1
Prepared substances.

Chemical name	Abbreviation	Source	Purification method	Final molar fraction purity[a]
1-Butyl-1-methylpyrrolidinium chloride	[C_4MPyrr]Cl	Synthesis	Recrystallisation, high vacuum	>0.98
1-Butyl-1-methylpyrrolidinium bromide	[C_4MPyrr]Br	Synthesis	Recrystallisation, high vacuum	>0.98
1-Butyl-1-methylpyrrolidinium tetrafluoroborate	[C_4MPyrr][BF_4]	Synthesis	High vacuum	>0.98
1-Ethyl-1-methylpyrrolidinium tetrafluoroborate	[C_2MPyrr][BF_4]	Synthesis	High vacuum	>0.98
1-Ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) amide	[C_2MPyrr][NTf_2]	Synthesis	High vacuum	>0.98

[a] Estimated from ^{1}H NMR spectra.