Liquid-liquid equilibria of mutually immiscible ionic liquids with a common anion of basic character

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ABSTRACT

Pairs of ionic liquids with the chloride or acetate anion as common ion and with largely different cations (namely a 1-alkyl-3-methylimidazolium cation and either methyltrioctylammonium or trihexyl(tetradecyl)phosphonium) were selected to investigate their mutual miscibility. Most of the pairs investigated were found to give rise to biphasic, non-volatile, totally liquid systems over wide temperature and composition ranges. An accurate determination of the liquid-liquid equilibria was carried out as a function of temperature, finding LCST-like behaviours for the systems with the phosphonium cation, and hourglass-shaped liquid-liquid domains for the systems with the ammonium cation. Enthalpies and entropies of mixing, calculated from the liquid-liquid equilibrium values, revealed that the first type of liquid-liquid equilibria was entropically driven, whereas for the second type a transition from enthalpically to entropically driven occurred with an increase in temperature.

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1. Introduction

Research on ionic liquids (currently definable as salts with a glass transition or melting temperature below 373 K) has grown formidably in the early years of this century, due to the attractiveness of their properties for a large number of widely varied applications [1]. Besides an extremely low volatility resulting from their inherent ionic character, one of the strengths of ionic liquids is the possibility of controlling their properties to a considerable extent by judicious choice and structural tuning of their constituent ions [1,2]. Many ionic liquids exhibit additionally other desirable characteristics for their use as solvents in reaction and separation processes; for instance: great solvation ability, wide liquid range, and good chemical and thermal stabilities [1].

In different separation techniques, two or more solvents are used simultaneously. Depending on the specific application, this mixture of solvents is miscible or presents mutual immiscibility. A classical example of the latter case is fractional extraction, where a mixture with two solutes is separated by fractional distribution between two partially miscible solvents [3,4]. In this regard, the liquid-liquid equilibria of many binary systems comprising an ionic liquid and a classical solvent, such as water or a volatile organic compound, have been investigated [1]. However, these biphasic solvent systems will not maintain integrally some of the

advantages of using an ionic liquid, for example a negligible vapour pressure. An alternative is the use of two or more ionic liquids exhibiting mutual immiscibility [5].

The mixture of ionic liquids that are totally miscible in any proportion, to create new ionic fluids involving three or more different ions and with sets of properties not achievable by means of 'single' ionic liquids, has gained important attention from the scientific community in recent years [6,7]. In contrast, mixtures of ionic liquids showing partial solubility still remain largely unexplored. To date, only the liquid-liquid equilibrium values of some pairs of ionic liquids (and of one mixture of three different ionic liquids) with a common anion have been reported, namely with the chloride or bis(trifluoromethylsulfonyl)amide ([NTf$_2$]$^-$) anions [5,8]. On the basis of this limited previous knowledge, the existence of immiscibility in liquid systems constituted by two ionic liquids seems to be connected with the combination of ions with sufficiently different structural features. A possible example would be the combination of a 1,3-dialkylimidazolium cation substituted with short alkyl chains and a tetraalkylphosphonium cation with long ones. With this in mind, in this work the liquid-liquid equilibria of several pairs of ionic liquids with a largely different cation and a common anion have been investigated. The fact of having a common anion reduces the complexity of the systems (a total of three different ions instead of four) and facilitates the interpretation of the results. In particular, the common anions selected were the basic ions chloride and acetate, which are ions of interest in

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applications of significant potential of ionic liquids (for instance, in the pre-treatment of lignocellulosic biomass) [9,10].

The pairs of ionic liquids selected have been envisaged to allow an analysis of the influence of different structural features of the involved ions on the liquid-liquid equilibrium, and the effect of temperature has been evaluated. A thermodynamic analysis has been carried out, in order to get valuable information for a better understanding of the liquid-liquid equilibria in systems of mixed ionic liquids.

2. Experimental

2.1. Ionic liquids

A description of the sources and purity of the chemical substances handled in this work is provided in Table 1. The ionic liquids 1-ethyl-3-methylimidazolium chloride ([C$_2$mim]Cl), 1-ethyl-3-methylimidazolium acetate ([C$_2$mim][OAc]), 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl), 1-methyl-3-octylimidazolium chloride ([C$_8$mim]Cl), 1-butyl-3-methylimidazolium acetate ([C$_4$mim][OAc]), Aliquat 336® ([Aliquat]Cl, trialkylmethylammonium chloride, where the alkyl chains are octyl or decyl, with octyl predominating in a 2:1 molar ratio [11]), and trihexyl(tetradecyl)phosphonium chloride ([P$_{6\ 6\ 6\ 14}$]Cl) were obtained from commercial vendors. 1-Hexyl-3-methylimidazolium chloride ([C$_6$mim]Cl) was synthesised in-house by alkylation of 1-methylimidazole with 1-chlorohexane, following an analogous procedure to that reported elsewhere for other 1-alkyl-3-methylimidazolium chlorides [12]. The syntheses of Aliquat acetate ([Aliquat][OAc]) and trihexyl(tetradecyl)phosphonium acetate ([P$_{6\ 6\ 6\ 14}$][OAc]) were conducted by a metathesis reaction between potassium acetate and the corresponding chlorides of the desired cations, according to the procedure reported by Mikkola et al. for the synthesis of several tetraalkylphosphonium acetates [13]. The concentration of spectator ions in the final products was found to be in the range 1600–1700 ppm for chloride (as determined by ion chromatography) and in the range (100–200) ppm for potassium (as determined by inductively coupled plasma optical emission spectroscopy, ICP-OES); which was considered acceptable for the purposes of this work (although it should be noted that, due to a large difference in formula weights between the spectator ions and the desired ionic liquids, these small mass-basis impurities are more relevant on a molar basis). The chemical structures of the constitutive ions of the mentioned ionic liquids are shown in Fig. 1.

All ionic liquids were stirred and heated at *ca.* (330–340) K under reduced pressure (<1 Pa) to reduce the level of possible vola-tile impurities, in particular of water, given their hygroscopic character and the strong influence that water can have on their performance [14]. The chemical identity and absence of significant levels of impurities of the purified products were confirmed by ^{1}H and ^{13}C NMR spectroscopy (spectra available as Supplementary Material). Their final water content was measured by Karl-Fischer titration in a Metrohm 737 KF coulometer, and is reported in Table 1. (As commented above for the halide impurities, please note that the small mass-basis water contents obtained become more relevant if considered in a molar basis as a result of the large difference in formula weights between water and the investigated ionic liquids.)

2.2. Thermal analyses

To determine the temperature ranges to be investigated in each particular system, thermal analyses were carried out to identify the range in which the ionic liquids remained liquid.

Thermal stability of the ionic liquids was determined by thermogravimetric analysis (TGA) using a TA Instruments Q500 thermogravimetric analyser with a weight precision of 0.01%. An open platinum pan loaded with *ca.* 15–20 mg of sample was used in each case. The TGA runs were carried out at a heating rate of 5 K·min^{-1}, from ambient temperature up to 773 K, using N$_2$ (Praxair, 99.999%) as balance purge gas and sample purge gas (with flow rates of 40 mL·min^{-1} and 60 mL·min^{-1}, respectively). Analysis of the obtained TGA curves was made by means of the Universal Analysis 2000 software, version 4.5.0.5, by TA Instruments. For each ionic liquid, the regular onset decomposition temperature T_d and the 5% onset decomposition temperature $T_{d,5\%}$ (corresponding to the onset using a tangent to the TGA curve at a sample mass loss of 5% of the original sample mass) were calculated, and reported in Table 2. The $T_{d,5\%}$ magnitude constitutes a more conservative and better estimation, as compared to T_d, of the maximum temperature at which the substances can be used practically [29]. For the experimental T_d values, a comparison with representative literature values by other authors was possible (Table 2); except for [Aliquat][OAc], for which no numerical value was found in the literature. A reasonably good degree of agreement between experimental and literature values sets was observed, particularly if taking into account the rather high dispersion of literature values for some of the ionic liquids (as exemplified by the groups of references selected for certain ionic liquids). Such dispersion may be attributed to the presence in the samples of different (levels of) impurities, as well as to the fact of having carried out the experiments under somewhat different conditions (e.g. at a different heating rate), which affects the T_d value finally obtained. Regarding the

Table 1
CAS number, source, initial mass fraction purity (w_i), purification method and final mass fraction purity (w_f) of the chemical samples used in this work, including all ionic liquids along with their corresponding abbreviations and final water contents expressed as mass fractions (w_{H2O}).

Name	Abbreviation	CAS number	Source	w_i	Purification method	w_f [a]	w_{H2O}
1-Methylimidazole	–	616-47-7	Aldrich	>0.99	None	–	–
1-Chlorohexane	–	544-10-5	Aldrich	0.995	None	–	–
Potassium acetate	–	127-08-2	Sigma Aldrich	>0.99	None	–	–
1-Ethyl-3-methylimidazolium chloride	[C$_2$mim]Cl	65039-09-0	Iolitec	>0.98	High vacuum, heating	>0.98	0.0020
1-Butyl-3-methylimidazolium chloride	[C$_4$mim]Cl	79917-90-1	Fluka	>0.95	High vacuum, heating	>0.98	0.0004
1-Hexyl-3-methylimidazolium chloride	[C$_6$mim]Cl	171058-17-6	Synthesis	–	High vacuum, heating	>0.98	0.0006
1-Octyl-3-methylimidazolium chloride	[C$_8$mim]Cl	64697-40-1	Fluka	>0.98	High vacuum, heating	>0.98	0.0006
1-Ethyl-3-methylimidazolium acetate	[C$_2$mim][OAc]	143314-17-4	Iolitec	>0.95	High vacuum, heating	>0.98	0.0008
1-Butyl-3-methylimidazolium acetate	[C$_4$mim][OAc]	284049-75-8	Fluka	>0.95	High vacuum, heating	>0.98	0.0012
Aliquat 336®	[Aliquat]Cl	63393-96-4	Sigma	0.85–0.95	High vacuum, heating	>0.98	0.0002
Aliquat acetate	[Aliquat][OAc]	–	Synthesis	–	High vacuum, heating	>0.98	0.0005
Trixeyl(tetradecyl)phosphonium chloride	[P$_{6\ 6\ 6\ 14}$]Cl	258864-54-9	Cytec	>0.97	High vacuum, heating	>0.98	0.0007
Trixeyl(tetradecyl)phosphonium acetate	[P$_{6\ 6\ 6\ 14}$][OAc]	872700-58-8	Synthesis	–	High vacuum, heating	>0.98	0.0023

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