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Towards an understanding of the mechanisms behind the formation of liquid-liquid systems formed by two ionic liquids

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Abstract

The identification of biphasic systems composed of aprotic ionic liquids (ILs) allows the development of new separation processes constituted only by non-volatile solvents. In this work, it is shown that mixtures of cholinium- and phosphonium-based ILs, either with common or different anions, lead to the formation of two-phase systems. Six pairs of ILs were found to be able to form biphasic systems, and the respective liquid-liquid phase diagrams were determined from (333.15 to 423.15) K. Although IL anions do not seem to control the phase separation phenomenon, they play, nevertheless, an important role on defining the size of the biphasic region. A linear dependence of the ILs mutual solubilities with the IL anions volume was found, therefore supporting the relevance of the entropy of mixing to create liquid-liquid systems formed by two ILs. With the exception of the liquid-liquid system formed by ILs with a common anion, the remaining systems display a significant ion exchange extent (from 21 to 50%, in mole fraction percentage) between the phases. Although not completely understood up to date, it is here demonstrated that the ion exchange extent inversely depends on the ILs cohesive energy, according to the determined dissociation energies of each ion pair, following a linear trend. These novel biphasic systems may be used in separation processes, and it is finally shown that four-phase systems can be prepared with a remarkable performance in the separation of mixtures of dyes.

Keywords

Liquid-liquid equilibria; ionic liquid; ion exchange; cation-anion interaction strength

Ionic liquids (ILs) are generally defined as organic salts with melting temperatures below 100 °C. Their unique properties, observed for most ILs, such as a negligible vapor pressure,¹ high chemical² and thermal³ stabilities, wide liquidus temperature range, and the possibility of tailoring their physicochemical properties through appropriate cation/anion combinations,^{4,5} make of them viable candidates to replace the organic and volatile solvents currently

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Notes

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used in industrial applications. In fact, there are *circa* 600 organic solvents used by industry nowadays, while there are more than one million of possible combinations of ions or different ILs.⁴ Due to their ionic and tailor-made nature, ILs have been studied as promising solvents to replace volatile organic ones in a wide variety of applications.^{6–11} However, even when employing non-volatile ILs, separation processes based on liquid-liquid extractions usually require the use of a volatile solvent (water or an organic solvent) to create two-phase systems. Therefore, the identification of novel liquid-liquid systems composed of two “immiscible” ILs allows the creation of new separation processes constituted only by non-volatile solvents. Although most ILs are completely miscible and do not allow this possibility, in 2006, Arce et al.¹² reported the existence of ILs not completely miscible, *i.e.*, ILs that split into two phases at given compositions and temperatures. The authors¹² determined the liquid-liquid phase equilibria of binary systems constituted by 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$) or 1-ethyl-3-methylimidazolium methane sulfonate ($[\text{C}_2\text{C}_1\text{im}][\text{CH}_3\text{SO}_3]$) and trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ($[\text{P}_{66614}][\text{NTf}_2]$), and further highlighted the presence of immiscibility domains in binary mixtures composed of $[\text{C}_n\text{C}_1\text{im}]\text{Cl}$ ($n = 1 - 5$) with $[\text{P}_{66614}]\text{Cl}$. They reported later¹³ a new binary liquid-liquid system formed by ethylpyridinium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{py}][\text{NTf}_2]$) and $[\text{P}_{66614}][\text{NTf}_2]$, and determined the ternary phase diagram of $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2] + [\text{C}_4\text{C}_1\text{im}][\text{NTf}_2] + [\text{P}_{66614}][\text{NTf}_2]$, in which $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ is complete miscible in the other two ILs.¹³ Afterwards, Annat et al.¹⁴ determined the phase diagram of *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[\text{C}_3\text{C}_1\text{pyr}][\text{NTf}_2]$) with $[\text{P}_{66614}][\text{NTf}_2]$, where a small biphasic region was identified.¹⁴ More recently, Palomar and co-workers¹⁵ reported a computational study based on the calculation of the excess enthalpies by COSMO-RS (COnductor like Screening MOdel for Real Solvents) aiming at identifying ILs pairs that could undergo phase separation. The authors found that liquid-liquid systems of partially immiscible ILs should be composed of notable different ions, *i.e.*, with a large deviation from ideality resulting from a strong endothermic mixing.¹⁵ More focused on the application of such type of systems, Binnemans and co-workers^{16,17} studied liquid-liquid systems formed by 1-ethyl-3-methylimidazolium chloride ($[\text{C}_2\text{C}_1\text{im}]\text{Cl}$) and trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate ($[\text{P}_{66614}][\text{Phosph}]\text{}$) to separate nickel from cobalt and rare earths. They also used¹⁸ a three-phase system formed by water and two ionic liquids ($[\text{P}_{66614}][\text{NTf}_2]$ with cholinium bis(trifluoromethylsulfonyl)imide or betainium bis(trifluoromethylsulfonyl)imide) to separate a mixture of tin(II), yttrium(III) and scandium(III). In general, it was found that liquid-liquid systems formed by partially immiscible ILs display some advantages, namely the possibility of changing the distribution ratios and separation factors of target solutes,¹⁶ and the use of ILs as leaching solutions to dissolve metal oxides and metal salts.^{19,20} Nevertheless, most of these works focused on mixtures of ILs with a common anion; only two works^{12,16} reported mixtures of ILs with different cations and anions, *i.e.*, with 4 ions in binary mixtures of ILs, and referred the possibility of ion exchange. For the two-phase system formed by $[\text{C}_2\text{C}_1\text{im}][\text{CH}_3\text{SO}_3] + [\text{P}_{66614}][\text{NTf}_2]$, the authors¹² demonstrated the presence of *circa* 10% of ion exchange, while for the system composed of $[\text{C}_2\text{C}_1\text{im}]\text{Cl}$ and $[\text{P}_{66614}][\text{Phosph}]$, they reported¹⁶ ion exchange, but no further discussion was carried out. Therefore, no conclusions were drawn on which factors rule the ions exchange in mixtures

of ILs composed of different ions and, if present, on its impact upon the extraction performance of these systems.

In order to expand the range of liquid-liquid systems formed by two non-volatile ILs, and to foster the understanding of the factors ruling their immiscibility domains and ions exchange, a large number of partially immiscible ILs was here studied. The systems presenting liquid-liquid immiscibility include cholinium bis(trifluoromethylsulfonyl)imide ([Chol][NTf₂]) combined with six [P₆₆₆₁₄]-based ILs comprising the following anions: chloride (Cl⁻), bromide (Br⁻), dicyanamide ([N(CN)₂]⁻), bis(trifluoromethylsulfonyl)imide ([NTf₂]⁻), decanoate ([Deca]⁻) and bis(2,4,4-trimethylpentyl)phosphinate ([Phosph]⁻). The chemical structures of the investigated ILs are depicted in Figure 1.

Six liquid-liquid systems formed by two non-volatile ILs were identified. The liquid-liquid phase diagrams of the studied “binary” mixtures were determined from (333.15 to 423.15) K and are depicted in Figure 2 (detailed data are presented in the Supporting Information, as well as comparisons with literature data¹⁸). In Figure 2, IL compositions within each solubility curve form a two-phase system, whereas compositions outside the same solubility curve are completely miscible. Since some ion exchange between the ILs was observed, as will be discussed below, these phase diagrams are presented in a mole fraction basis of the IL cation (¹H NMR - Nuclear Magnetic Resonance – spectroscopy was used as an analytical method, namely to quantify the cations [Chol]⁺ and [P₆₆₆₁₄]⁺, using benzene as the internal standard; further details are given in the Supporting Information).

All liquid-liquid systems here studied display an UCST (Upper Critical Solution Temperature) type behavior, in agreement with the remaining IL-IL binary systems reported in the literature.^{12–14,18} In all systems, the bottom and more dense phase corresponds to the [Chol][NTf₂]-rich phase, being the phosphonium-based ILs in the top, less dense, phase. The solubility of [Chol][NTf₂] in the [P₆₆₆₁₄]-rich phase is of the same order of magnitude (10⁻¹ in mole fraction) in all phosphonium-based ILs investigated, while the solubility of these in the cholinium-rich phase ranges between 10⁻³ and 10⁻¹ (in mole fraction). At a fixed temperature, the mutual miscibility between [Chol][NTf₂] and each [P₆₆₆₁₄]-based IL decreases according to the following anions rank: [Phosph]⁻ > [Deca]⁻ > [NTf₂]⁻ > [N(CN)₂]⁻ > Br⁻ > Cl⁻. Taking into account the data gathered in this work and those obtained from the literature,^{12–18} in which mixtures of two ILs with a common cation are hardly able to form two-phase systems while mixtures of ILs of common anions are able to undergo liquid-liquid demixing, it is evident that it is the IL cation which controls the existence of liquid-liquid equilibria. Therefore, IL anions have a minor impact on the formation of biphasic systems; yet, they do play a role in the mutual solubility magnitude. Contrarily to what has been found in the liquid-liquid phase behavior of IL-water binary mixtures,^{22,23} in which hydrogen-bonding and the IL anion basicity are primordial features, the trend presented does not reflect the ability of each anion for hydrogen-bonding, as defined by their hydrogen-bond basicity,²⁴ nor a significant correlation with the cation-anion interaction strength has been observed (*cf.* the Supporting Information). Remarkably, the rank presented above shows a linear dependency on the IL anions volume,²¹ as depicted in Figure 2, supporting therefore the relevance of the entropy of mixing on the large deviations from ideality. The larger the volume of the [P₆₆₆₁₄]-based IL, the higher is the solubility of the

cholinium-based IL, *i.e.* the lower the deviation to the ideality due to the favorable mixing entropy effect. Despite the IL anion contribution, when considering all the data obtained as well as those taken from the literature,^{12–18} the main requirement to create liquid-liquid systems formed by two ILs is still based on having two ILs composed of two cations of very different polarity,²⁵ and not straightly depending on the IL cation volume as verified with the IL anion. ILs with the cations cholinium and trihexyltetradecylphosphonium form the pair more able to form two-phase systems, as shown by the larger immiscibility regimes reported in this work, being indeed at extremes in terms of hydrogen-bond acidity.²⁵ Based on an extended compilation of hydrogen-bond acidity data,²⁵ it is expected that other IL cations functionalized with hydroxyl or amino groups also will be able to create two-phase systems with trihexyltetradecylphosphonium-based ILs, as also proposed by Palomar and co-workers¹⁵ using a different approach.

With the exception of the system composed of [Chol][NTf₂] + [P₆₆₆₁₄][NTf₂], with a common anion, the remaining systems are created by two ILs with different cations and anions. Therefore, depending on the cohesive energies of each cation-anion pair, ion exchange between the two ILs is expected to occur. To appraise this possibility and to better understand this phenomenon, mixtures of all IL-IL combinations investigated in this work were prepared, equilibrated at 298 K, and at least 3 ions in each phase quantified. ¹H NMR was used to quantify the cations [Chol]⁺ and [P₆₆₆₁₄]⁺, using benzene as the internal standard, while ¹⁹F NMR was used to quantify the [NTf₂][−] anion, using perfluorobenzene as the internal standard. Further experimental details are given in the Supporting Information. The amount of each ion in the phases and mole fraction percentage of ion exchange are given in the Supporting Information.

With the exception of the liquid-liquid system formed by a common anion, all remaining systems show a significant exchange of ions between the ILs/phases. The system composed of [Chol][NTf₂] + [P₆₆₆₁₄][Phosph] displays the largest ion exchange (49.7%), while the [Chol][NTf₂] + [P₆₆₆₁₄]Cl system is the one with the lowest ion exchange (21.0%). The trend obtained in the ions exchange according to the IL anion correspond to the trend observed on the solubility data; however, it was not found a significant correlation between the two parameters (*cf.* the Supporting Information). It is expected that the ions exchange will mainly depend on the ILs cohesive energy. To appraise this possibility, the relative binding energies of the ions in the gas-phase were semi-quantitatively determined by electrospray tandem mass spectrometry (ESI-MS-MS) – experimental details given in the Supporting Information. The variable collision energies in the ESI-MS-MS spectra are taken from the relative abundances of precursor and fragment ions, while the energy value corresponding to a relative abundance of the precursor ion at 50% can be used as a measure of the relative dissociation energy, as shown before with ILs.²⁶ The determined dissociation energies, $E_{\text{cm},1/2}$, are given in the Supporting Information.

To prove our hypothesis, the experimentally obtained relative cation-anion interaction energies were correlated against the percentage of ion exchange – Figure 3 – in which a linear dependence has been found. The ion exchange in IL-IL liquid-liquid systems increases with the decrease on the cation-anion interaction strength. Phosphonium-based ILs

with stronger cohesive energies, such as $[P_{66614}]Cl$, show a lower probability to undergo ion exchange, *i.e.* to replace Cl^- by $[NTf_2]^-$.

In summary, a new combination of mutually “immiscible” ILs showing liquid-liquid equilibria was identified. The systems studied comprise $[Chol][NTf_2]$ combined with $[P_{66614}]$ -based ILs, in which their mutual miscibilities decrease according to the following IL anions rank: $[Phosph]^- > [Deca]^- > [NTf_2]^- > [N(CN_2)]^- > Br^- > Cl^-$. The solubility of $[Chol][NTf_2]$ in the $[P_{66614}]$ -rich phase is *ca.* 10^{-1} in mole fraction, while the solubility of phosphonium-based ILs in the cholinium-rich phase ranges between 10^{-3} and 10^{-1} . Although IL anions display a relevant role on defining the mutual solubilities magnitude, which linearly depends on the IL anion volume, they do not have a significant impact on the creation of liquid-liquid systems. Only mixtures of two ILs with significantly structurally different IL cations or of highly different hydrogen-bond acidity are able to undergo liquid-liquid demixing, highlighting therefore the primordial role of the IL cation. With the exception of the liquid-liquid system formed by ILs with a common anion, all the remaining systems display a significant ions exchange (ranging between 21 and 50%). It was here demonstrated that the ion exchange extent in IL-IL systems straightly correlates with their cohesive energy. ILs with stronger cation-anion interactions strength have lower probability to undergo ions exchange. In spite of the ions exchange, these novel biphasic systems are still formed by two non-volatile solvents and may be used in liquid-liquid separation processes.

Taking advantage of the ILs tunable properties and their miscibility/immiscibility with molecular solvents, these binary liquid-liquid systems can be designed to create multiphasic systems targeting the separation of complex mixtures, as shown in Figure 4. Water and dodecane were added to the $[Chol][NTf_2] + [P_{66614}][NTf_2]$ system, allowing the creation of four-phase systems, found to be efficient in the separation of mixtures of dyes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Chemical structures of the investigated IL ions: $[Chol]^+$, cholinium; $[P_{66614}]^+$, trihexyltetradecylphosphonium; $[NTf_2]^-$, bis(trifluoromethylsulfonyl)imide; Br^- , bromide; Cl^- , chloride; $[Deca]^-$, decanoate; $[N(CN)_2]^-$, dicyanamide; $[Phosph]^-$, bis(2,4,4-trimethylpentyl)phosphinate.

Figure 2.

(a) Liquid-liquid phase diagrams of $[\text{Chol}][\text{NTf}_2]$ and phosphonium-based ILs in a mole fraction basis corresponding to the IL cation: $\blacklozenge$, $[\text{P}_{66614}][\text{Phosph}]$; $\blacktriangle$, $[\text{P}_{66614}][\text{Deca}]$; $\circ$, $[\text{P}_{66614}][\text{NTf}_2]$; $\blacksquare$, $[\text{P}_{66614}][\text{N}(\text{CN})_2]$; $\bullet$, $[\text{P}_{66614}]\text{Br}$; $\triangle$, $[\text{P}_{66614}]\text{Cl}$. (b) Correlation of ionic volumes, V , and molar solubility of cholinium in the phosphonium-rich phase at 393.15 K. This correlation was performed for all temperatures and the squared correlation coefficient, R^2 , ranging from 0.9239 to 0.9504.

Figure 3. Ion exchange in IL-IL liquid-liquid systems as a function of relative cation–anion interaction energies ($E_{cm,1/2}$).

Figure 4.

Four-phase system composed of dodecane + $[P_{66614}][NTf_2]$ + $[Chol][NTf_2]$ + H_2O used in the separation of dyes.