

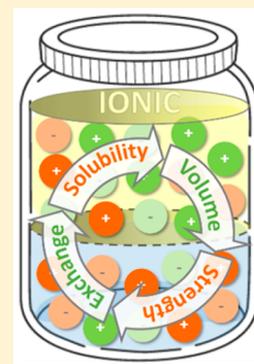
Toward an Understanding of the Mechanisms behind the Formation of Liquid–liquid Systems formed by Two Ionic Liquids

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S Supporting Information

ABSTRACT: Biphasic systems composed of aprotic ionic liquids (ILs) allow the development of new separation processes constituted only by nonvolatile solvents. Six pairs of cholinium- and phosphonium-based ILs were found to be able to form biphasic systems, and the respective liquid–liquid phase diagrams were determined. Although IL anions do not seem to control the phase separation phenomenon, they play an important role in defining the size of the biphasic region. A linear dependence of the ILs mutual solubilities with the IL anions volume was found, supporting the relevance of the entropy of mixing. With the exception of the system formed by ILs with a common anion, the remaining liquid–liquid systems display a significant ion exchange extent between the phases, which inversely depends on the ILs cohesive energy. It is finally shown that four-phase systems with a remarkable performance in the separation of mixtures of dyes can be prepared.



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 used in industrial applications. In fact, there are circa 600 organic solvents used by industry nowadays, while there are more than one million 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 nonvolatile 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 nonvolatile 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 ([C₂C₁im][NTf₂]) or 1-ethyl-3-methylimidazolium methanesulfonate ([C₂C₁im][CH₃SO₃]) and trihexyltetradecylphosphonium bis-(trifluoromethylsulfonyl)imide ([P₆₆₆₁₄][NTf₂]), and further highlighted the presence of immiscibility domains in binary

mixtures composed of [C_nC₁im]Cl (*n* = 1–5) with [P₆₆₆₁₄]Cl. They reported later¹³ a new binary liquid–liquid system formed by ethylpyridinium bis(trifluoromethylsulfonyl)imide ([C₂py][NTf₂]) and [P₆₆₆₁₄][NTf₂], and determined the ternary phase diagram of [C₂C₁im][NTf₂] + [C₄C₁im][NTf₂] + [P₆₆₆₁₄][NTf₂], in which [C₄C₁im][NTf₂] is completely miscible in the other two ILs.¹³ Afterward, Annat et al.¹⁴ determined the phase diagram of *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C₃C₁pyr][NTf₂]) with [P₆₆₆₁₄][NTf₂], 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) aimed at identifying ILs pairs that could undergo phase separation. The authors found that liquid–liquid systems of partially immiscible ILs should be composed of notably 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 ([C₂C₁im]Cl) and trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate ([P₆₆₆₁₄][Phosph]) to separate nickel from cobalt and rare earths. They also used¹⁸ a three-phase system formed by water and two ionic liquids ([P₆₆₆₁₄][NTf₂] with cholinium bis-(trifluoromethylsulfonyl)imide or betainium bis-(trifluoromethylsulfonyl)imide) to separate a mixture of tin(II),

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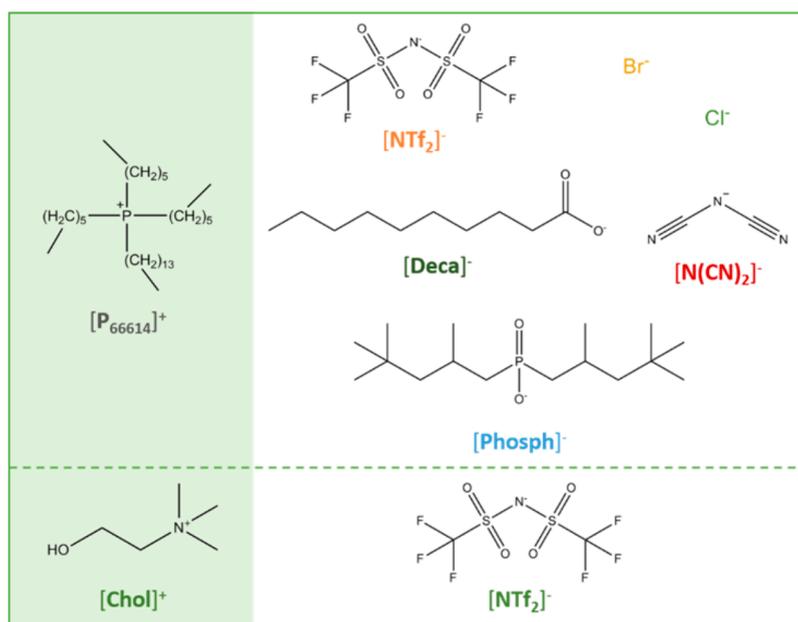


Figure 1. Chemical structures of the investigated IL ions: [Chol]⁺, cholinium; [P₆₆₆₁₄]⁺, trihexyltetradecylphosphonium; [NTf₂]⁻, bis(trifluoromethylsulfonyl)imide; Br⁻, bromide; Cl⁻, chloride; [Deca]⁻, decanoate; [N(CN)₂]⁻, dicyanamide; [Phosph]⁻, bis(2,4,4-trimethylpentyl)phosphinate.

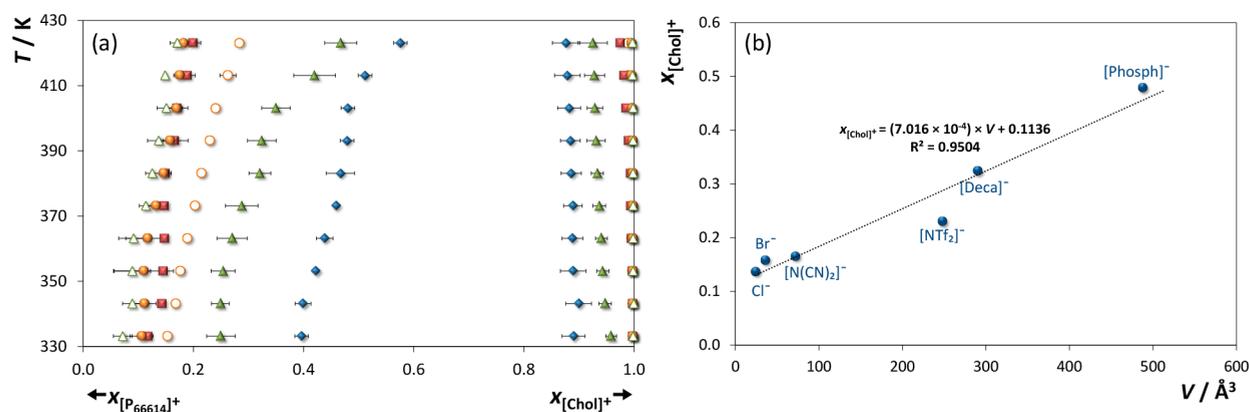


Figure 2. (a) Liquid–liquid phase diagrams of [Chol][NTf₂] and phosphonium-based ILs in a mole fraction basis corresponding to the IL cation: ◆, [P₆₆₆₁₄][Phosph]; ▲, [P₆₆₆₁₄][Deca]; ○, [P₆₆₆₁₄][NTf₂]; ■, [P₆₆₆₁₄][N(CN)₂]; ●, [P₆₆₆₁₄]Br; △, [P₆₆₆₁₄]Cl. (b) Correlation between the molar solubility of the cholinium cation in the phosphonium-rich phase at 393.15 K and the anion volume, V .²¹ This correlation was performed for all temperatures with a squared correlation coefficient, R^2 , ranging from 0.9239 to 0.9504.

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 four ions in binary mixtures of ILs, and referred the possibility of ion exchange. For the two-phase system formed by [C₂C₁im][CH₃SO₃] + [P₆₆₆₁₄][NTf₂], the authors¹² demonstrated the presence of circa 10% of ion exchange, while for the system composed of [C₂C₁im]Cl and [P₆₆₆₁₄]-[Phosph], they reported¹⁶ ion exchange, but no further discussion was carried out. Therefore, no comprehensive discussions were given 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 nonvolatile 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 nonvolatile 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

Table 1. Mole Fraction Solubility (x) of Each Ion in Each Phase and Mole Fraction Percentage Data Corresponding to Ion Exchange^a

system	phase	$x[\text{NTf}_2]^-$	$x[\text{Chol}]^+$	$x[\text{Phosph, Deca, Cl, Br or N}(\text{CN})_2]^-$	$x[\text{P}_{66614}]^+$	ion exchange/%
[Chol][NTf ₂] + [P ₆₆₆₁₄][Phosph]	top	0.325	0.074	0.175	0.426	49.7
	bottom	0.175	0.426	0.325	0.074	
[Chol][NTf ₂] + [P ₆₆₆₁₄][Deca]	top	0.365	0.048	0.135	0.452	36.5
	bottom	0.135	0.452	0.365	0.048	
[Chol][NTf ₂] + [P ₆₆₆₁₄]Cl	top	0.396	0.001	0.104	0.499	21.0
	bottom	0.104	0.499	0.396	0.001	
[Chol][NTf ₂] + [P ₆₆₆₁₄]Br	top	0.384	0.001	0.116	0.499	23.4
	bottom	0.116	0.499	0.384	0.001	
[Chol][NTf ₂] + [P ₆₆₆₁₄][N(CN) ₂]	top	0.356	0.018	0.144	0.482	32.4
	bottom	0.144	0.482	0.356	0.018	

^aThe top phase is enriched in the phosphonium, while the bottom phase is majorly composed of [Chol]-based ILs.

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 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 upper critical solution temperature (UCST)-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 that 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 has a significant correlation with the cation–anion interaction strength (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 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 depends 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/phases 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 each phase and mole fraction percentage of ion exchange are given in [Table 1](#).

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 anions trend obtained in the ions exchange is in agreement with 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, however, expected that the ions exchange will mainly depend on the ILs cohesive energy and enthalpic contributions. To appraise this possibility, the relative binding energies of the ions in the gas-phase were semiquantitatively 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 were 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% was used as a measure of the relative dissociation energy, as shown before with ILs.^{2,6} The determined dissociation energies, $E_{\text{cm},1/2}$, are given in the Supporting Information.

To prove our hypothesis, the percentage of ion exchange was correlated against the experimentally obtained relative cation–anion interaction energy (Figure 3) in which a linear

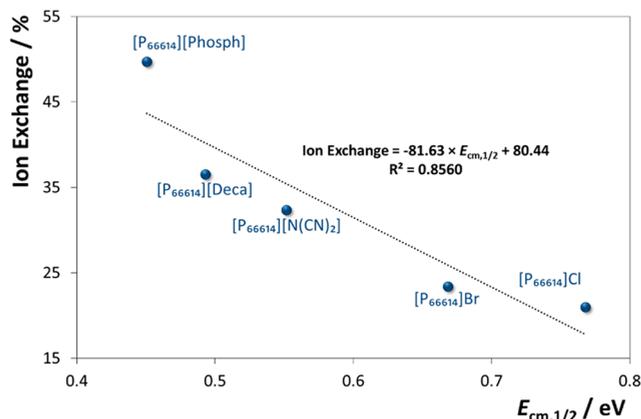


Figure 3. Ion exchange extent in IL–IL liquid–liquid systems as a function of relative cation–anion interaction energies ($E_{\text{cm},1/2}$).

dependence has been found. The ion exchange extent 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 [P₆₆₆₁₄][Cl], show a lower probability to undergo ion exchange, i.e., to replace Cl[−] by [NTf₂][−].

In summary, a new combination of mutually “immiscible” ILs showing liquid–liquid equilibria was identified. The systems studied comprise [Chol][NTf₂] combined with [P₆₆₆₁₄]-based ILs, in which their mutual miscibilities decrease according to the following IL anions rank: [Phosph][−] > [Deca][−] > [NTf₂][−] > [N(CN)₂][−] > Br[−] > Cl[−]. The solubility of [Chol][NTf₂] in the [P₆₆₆₁₄]-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%), which straightly correlates with the ILs 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 nonvolatile solvents and may be used in liquid–liquid separation processes. Although the ions exchange occurs, these systems can be applied in separation processes and recycled, yet keeping in mind that the recycled phases do not correspond to “pure” ILs but instead to multi-ionic phases. Nevertheless, by knowing in advance the phase equilibrium data and the ion exchange extent it is possible to design separation processes in which the ILs and respective phases can be reused.

Taking advantage of the ILs tunable properties and their miscibility/immiscibility with molecular solvents, these binary liquid–liquid systems can be designed to create multiphase systems targeting the separation of complex mixtures, as shown in Figure 4. Water and dodecane were added to the

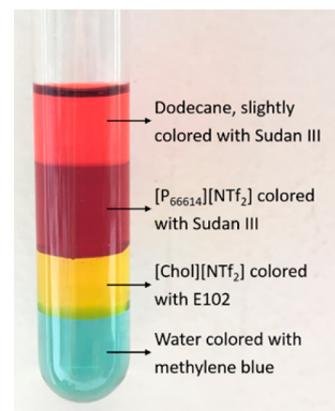


Figure 4. Four-phase system composed of dodecane + [P₆₆₆₁₄][NTf₂] + [Chol][NTf₂] + H₂O used in the separation of dyes.

[Chol][NTf₂] + [P₆₆₆₁₄][NTf₂] system, allowing the creation of four-phase systems, found to be efficient in the separation of mixtures of dyes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.7b01234.

Details on materials and experimental procedure, comparison with literature data, and detailed results of solubility, ions exchange, and relative cation–anion interaction strengths (PDF)

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Notes

The authors declare no competing financial interest.

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