█ Solvent Extraction

Selective Single-Step Separation of a Mixture of Three Metal Ions by a Triphasic Ionic-Liquid–Water–Ionic-Liquid Solvent Extraction System

Tom Vander Hoogerstraete, Jonas Blockx, Hendrik De Coster, and Koen Binnemans*[a]

Abstract: In a conventional solvent extraction system, metal ions are distributed between two immiscible phases, typically an aqueous and an organic phase. In this paper, the proof-of-principle is given for the distribution of metal ions between three immiscible phases, two ionic liquid phases with an aqueous phase in between them. Three-liquid-phase solvent extraction allows separation of a mixture of three metal ions in a single step, whereas at least two steps are required to separate three metals in the case of two-liquid-phase solvent extraction. In the triphasic system, the lower organic phase is comprised of the ionic liquid betainium- or choline bis(trifluoromethylsulfonyl)imide, whereas the upper organic phase is comprised of the ionic liquid trihexyl(tetra-decyl)phosphonium bis(trifluoromethylsulfonyl)imide. The triphasic system was used for the separation of a mixture of tin(II), yttrium(III), and scandium(III) ions.

Introduction

Ionic liquids (ILs) are solvents that consist entirely of ions.[1] In general, they have a melting point below 100 °C and some interesting physical properties such as negligible vapor pressure,[2] low flammability,[3] a broad liquidus range, and a broad electrochemical window.[4] In addition, their properties are highly tunable towards the desired applications. The tunable polarity, low flammability, and low volatility of ionic liquids make them interesting alternatives for conventional organic solvents used in solvent extraction experiments.[5]

Mutually immiscible ionic liquids were reported for the first time in 2006 by Arce et al.[6] They discovered that a mixture of the ionic liquids trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide [P_{66614}][Tf_2N] and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C_2mim][Tf_2N] had an upper critical solution temperature (UCST) of 115 °C. The UCST is defined by the lowest temperature at which the mixture is completely miscible in all possible proportions. Below the critical solution temperature, the solution separates into two phases. Since 2006, other mutually immiscible ionic liquid combinations have been reported.[7] To the best of our knowledge, only one report exists on the separation of molecular compounds by selective distribution between two mutually immiscible ionic liquids.[8] In this study, a mixture of [C_2mim][Tf_2N] and [P_{66614}][Tf_2N] was used for the separation of hexane and benzene. No significant improvement in selectivity was observed in the biphasic region in comparison with an extraction performed with only [C_2mim][Tf_2N].

Recently, a mixture of the two mutually immiscible ionic liquids 1-ethyl-3-methylimidazolium chloride and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) was used for the separation of metal ions.[7d, e] Ternary phase diagrams with a triphasic region between water, an organic solvent, and an ionic liquid have been described in the literature, but ternary phase diagrams consisting of water and two water-immiscible ionic liquids have not been reported yet.[9]

The formation of a third phase is considered as a disadvantage in solvent extraction systems.[10] The third phase is often formed at high metals loadings when the metal complex becomes partly insoluble in the organic phase. On the other hand, several authors have reported the distribution of metals between three different liquid phases. There are several examples where a third phase is used, consisting of a polymer and an additive.[11] Zhang et al. separated platinum(IV), palladium(II), and rhodium(III) by salting-out acetonitrile from the aqueous phase and introducing an aliphatic solvent containing an extractant as the third phase.[12] Triphasic extraction systems for metals that contain one ionic liquid phase have been reported only twice. The ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] in combination with water, cyclohexane, and two neutral extractants (8-quinolinol and tri-n-octylphosphine oxide) was successfully used in a triphasic extraction system. Nickel(II) was extracted towards the ionic liquid phase, whereas the other divalent metals manganese(II), zinc(II), cadmium(II), and lead(II) were extracted into the cyclohexane phase.[9b] The same group used a system consisting of [C_4mim][PF_6], diisopentyl sulfide/nonane, and water to separate platinum(IV), lead(II), and rhodium(III) from chloride media. In that case, platinum(IV) was extracted as the [$PtCl_6$]$^{2-}$

[a] *Dr. T. Vander Hoogerstraete, J. Blockx, H. De Coster, Prof. Dr. K. Binnemans*
Department of Chemistry
KU Leuven, Celestijnenlaan 200F
P.O. Box 2402, 3000 Heverlee (Belgium)
E-mail: koen.binnemans@chem.kuleuven.be

🖥 *Supporting information for this article is available on the WWW under*
http://dx.doi.org/10.1002/chem.201500825.

complex to the ionic liquid phase, palladium(II) to the nonane phase, and rhodium(III) remained in the aqueous phase.[13] Another example was described in the patent literature, where a triphasic extraction system containing an aqueous phase with a complexing agent, a salting-out agent, an ionic liquid, and a polymer phase was reported for the separation of rare-earth ions.[14]

In this paper, we present the binary phase diagrams of the ionic liquids betainium bis(trifluoromethylsulfonyl)imide [Hbet][Tf$_2$N] or choline bis(trifluoromethylsulfonyl)imide, [Chol][Tf$_2$N] with the ionic liquid trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide [P$_{66614}$][Tf$_2$N], the structures of which are given in Figure 1. Ternary phase diagrams containing
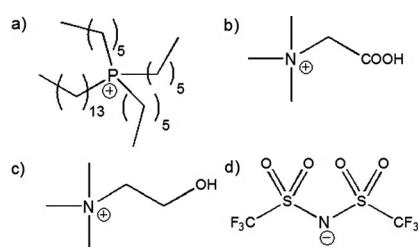


Figure 1. Chemical structures of the cations a) trihexyl(tetradecyl)phosphonium, b) betainium, c) choline and the anion d) bis(trifluoromethylsulfonyl)imide.

two immiscible ionic liquids and an aqueous phase are constructed. The proof-of-principle for a direct and selective separation of three different metal ions is given. Such a separation is clearly not possible with a biphasic solvent extraction system under similar conditions. Moreover, the physical separation of two strong metal-coordinating groups offers new opportunities for selective metals separations in solvent extraction studies.

Results and Discussions

Phase diagrams

The binary phase diagrams of [Hbet][Tf$_2$N]/[P$_{66614}$][Tf$_2$N] and [Chol][Tf$_2$N]/[P$_{66614}$][Tf$_2$N] are presented in Figure 2 and Figure 3. A mixture with a certain composition at a specific temperature located within the white area (biphasic region) separates into two phases, a [Hbet][Tf$_2$N]-rich or [Chol][Tf$_2$N]-rich phase (right side of the graph) and a [P$_{66614}$][Tf$_2$N]-rich phase (left side of the graph). The grey zones indicate the monophasic homogeneous region in which only one phase is formed. The [Hbet][Tf$_2$N]-rich phase contained less than 2 wt% of [P$_{66614}$][Tf$_2$N] at all considered temperatures (25 to 135 °C). A color change from transparent to yellow/brown of the mixture was observed above 135 °C, probably due to decomposition. The decomposition products could not be identified by NMR techniques because their concentrations were too low. Therefore, construction of the phase diagram [Hbet][Tf$_2$N]/[P$_{66614}$][Tf$_2$N] was stopped at 135 °C. The [Chol][Tf$_2$N]-rich phase contained less than 5 wt% of [P$_{66614}$][Tf$_2$N] at all measured temper-
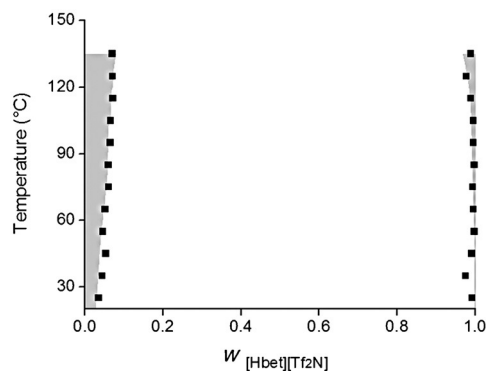
Figure 2. Temperature–composition diagram for the binary system [Hbet][Tf$_2$N]/[P$_{66614}$][Tf$_2$N]. The white area is the biphasic region and the grey area the monophasic region.
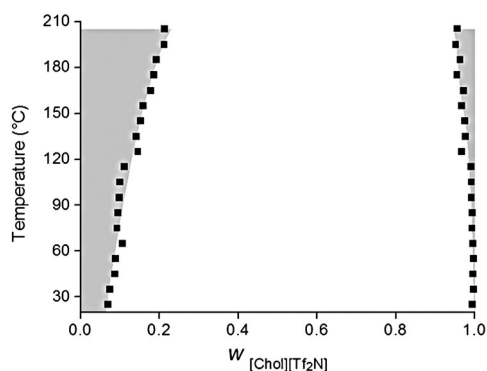

Figure 3. Temperature–composition diagram for the binary system [Chol][Tf$_2$N]/[P$_{66614}$][Tf$_2$N]. The white area is the biphasic region and grey area the monophasic region.

atures (25 to 205 °C). The [P$_{66614}$][Tf$_2$N] phase contains 3.5 and 7.2 wt% of [Hbet][Tf$_2$N] at 25 and 135 °C, respectively. The [P$_{66614}$][Tf$_2$N] phase in the [Chol][Tf$_2$N]/[P$_{66614}$][Tf$_2$N] system contained 7.0 and 21.3 wt% of [Chol][Tf$_2$N] at 25 and 205 °C, respectively.

No large difference was found between the phase diagrams of both binary systems. This is probably due to the similar structure of both ionic liquids in comparison with the [P$_{66614}$][Tf$_2$N] ionic liquid. This was observed as well in the binary systems [Hbet][Tf$_2$N]/H$_2$O and [Chol][Tf$_2$N]/H$_2$O, systems that have similar phase diagrams too.[15] However, the phase diagrams are different from the reported ones for the binary systems [C$_2$py][Tf$_2$N]/[P$_{66614}$][Tf$_2$N] and [C$_2$mim][Tf$_2$N]/[P$_{66614}$][Tf$_2$N], which have a smaller biphasic area in the phase diagram.[6,7c] These ionic liquids are less polar owing to the absence of an alcohol or carboxylic acid group and therefore have higher solubility in the [P$_{66614}$][Tf$_2$N] phase in comparison with [Hbet][Tf$_2$N] or [Chol][Tf$_2$N].

Choice of the extraction system

The ternary phase diagrams of the systems [Hbet][Tf$_2$N]/H$_2$O/[P$_{66614}$][Tf$_2$N] and [Chol][Tf$_2$N]/H$_2$O/[P$_{66614}$][Tf$_2$N] are given in Figure 4 and Figure 5. In contrast to the binary phase dia-
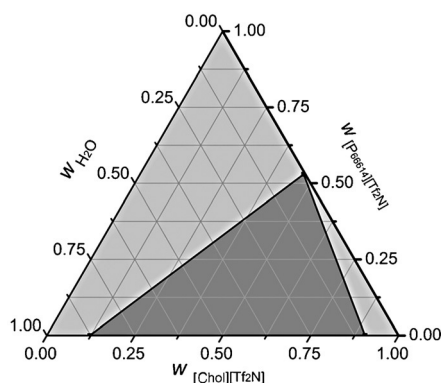
Figure 4. Ternary phase diagrams at room temperature for the mixture [Chol][Tf$_2$N]/H$_2$O/[P$_{66614}$][Tf$_2$N]. The black and grey zones are the triphasic and biphasic regions, respectively.
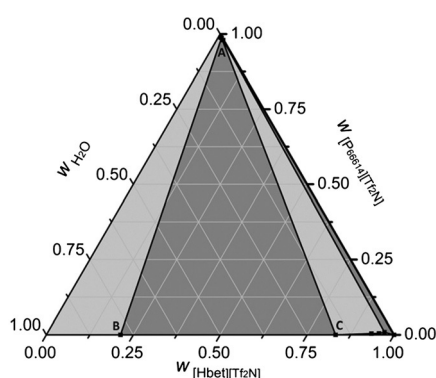
Figure 5. Ternary phase diagrams at room temperature for the mixture [Hbet][Tf$_2$N]/H$_2$O/[P$_{66614}$][Tf$_2$N]. The black and grey zones are the triphasic and biphasic regions, respectively.

grams, the ternary phase diagrams for the two systems showed remarkable differences. The area of the triphasic region for the [Chol][Tf$_2$N]/H$_2$O/[P$_{66614}$][Tf$_2$N] system was significantly smaller than that of the triphasic region in the [Hbet][Tf$_2$N]/H$_2$O/[P$_{66614}$][Tf$_2$N] system. From these results, it can be concluded that [Hbet][Tf$_2$N] system is of more interest than the [Chol][Tf$_2$N] system because the phases in the latter system are less pure and thus less interesting for solvent extraction systems. Moreover, choline is a very weak solvating ligand and extraction without the addition of an extra extractant is very difficult.[16]

The three phases of the [Hbet][Tf$_2$N]/H$_2$O/[P$_{66614}$][Tf$_2$N] system consist of almost pure [P$_{66614}$][Tf$_2$N] (A), and two less pure phases, namely [Hbet][Tf$_2$N] in H$_2$O (B) and H$_2$O in [Hbet][Tf$_2$N] (C) (Figure 5). Apart from the liquid–liquid–liquid triphasic region, also a second liquid–liquid–solid triphasic region was observed. In this region, the mixture separates into a liquid [Hbet][Tf$_2$N] phase containing a small amount of H$_2$O, a pure and solid [Hbet][Tf$_2$N] phase, and a [P$_{66614}$][Tf$_2$N] phase. The exact area of this region is difficult to determine and is due to the slow crystallization process of [Hbet][Tf$_2$N] (undercooled solution) when small amounts of water are present. There are also two small monophasic regions, one at the top

of the diagram when working with almost pure [P$_{66614}$][Tf$_2$N] and the other on the bottom right hand side of the graph when working with almost pure and solid [Hbet][Tf$_2$N].

The triphasic system [Hbet][Tf$_2$N]/H$_2$O/[P$_{66614}$][Tf$_2$N] was investigated for extraction. The extraction of metal ions by [Hbet][Tf$_2$N] or similar ionic liquids has been investigated elsewhere.[5p,q,17] The ionic liquid [Hbet][Tf$_2$N] can be classified as an acidic extractant. Some metal ions are extracted without the need for an increase in pH, whereas other metal ions need the addition of, for instance, betaine (causing an increase in pH) before they are extracted. The [P$_{66614}$][Tf$_2$N] phase has no strong coordination ability. Although it was shown that non-functionalized bis(trifluoromethylsulfonyl)imide ionic liquids can extract metals without the need of an additional extractants, this often requires very strong complexes and interactions with the cation and losses of the ionic liquid anion in the aqueous phase. Examples are the formation of metal nitrato or chloro complexes at high anion or acid concentrations.[18] Unfortunately, the use of nitric acid is not an option because very low pH values inhibit the transfer of metal ions to the [Hbet][Tf$_2$N] phase. Another option could be the formation of anionic chloro complexes.[19] These complexes are formed by the addition of chloride salts or hydrochloric acid, often in high concentration, to solutions of metal ions. It has been shown before that stable chloro complexes can be extracted towards a Tf$_2$N-based ionic liquid.[20] The mechanism often occurs through ion exchange and one or more Tf$_2$N$^-$ anions are exchanged for the charged metal chloro complex. The exchange of double- or even triple-charged species is quite contradictory to the Hofmeister series,[21] which predicts that the Tf$_2$N$^-$ anion is very weakly solvated in the aqueous phase, whereas higher charged species such as SO$_4^{2-}$ and PO$_4^{3-}$ are very strongly hydrated and difficult to extract towards basic extractants.[22] Therefore, the exchange of double-charged species and strongly hydrated species for Tf$_2$N$^-$ anions in the aqueous phase is unlikely. However, the interaction between the ionic liquid cation and the metal anion is a second driving force for extraction. It has been shown already that strong and highly charged metal complexes can be extracted towards Tf$_2$N ionic liquids.[20] Another option for extracting metals towards the [P$_{66614}$][Tf$_2$N] phase is the addition of a neutral extractant such as Cyanex 923 or tri-n-butyl phosphate (TBP), which can solvate metal ions. The addition of a strong solvating extractant to the upper phase will significantly increase the percentage extraction (%E) to the [P$_{66614}$][Tf$_2$N] phase. The addition of an extra component to the ternary IL/H$_2$O/IL system will of course change the phase diagram. The construction of quaternary phase diagrams was outside the scope of this article and volume changes were avoided by presaturation of the IL phases by the appropriate water phase as described in the Experimental Section of the article. Important to mention is the fact that mixtures of Cyanex 923 or TBP with water and [Hbet][Tf$_2$N] gave biphasic systems, which means that a third ionic liquid phase, immiscible with the two other phases, needs to be introduced for performing triphasic extractions.

A mixture of ions of three metals (tin, scandium, and yttrium) was chosen to demonstrate the proof-of-principle of a tri-

phasic IL/H$_2$O/IL extraction for two different reasons. First, it is known that tailings of tin mines contain relatively large amounts of scandium and yttrium, which could therefore be an interesting secondary source for these rare-earth metals.[23] Secondly, it is known that tin(II) and scandium(III) are extremely difficult to separate with carboxylic extractants because of the very similar pH dependence of the extraction of both elements. Preston et al. reported a difference of merely 0.2 units in terms of pH between 50% extraction of tin(II) and scandium(III).[24] A proper overview of the triphasic extraction system is given in Figure 6.
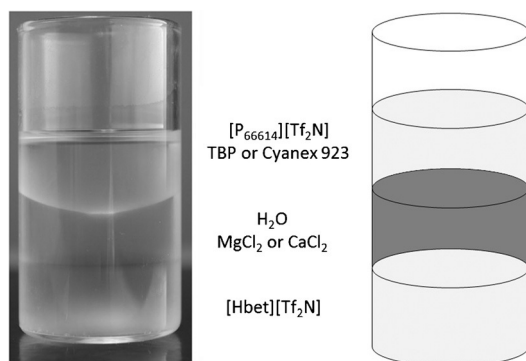

[P$_{66614}$][Tf$_2$N]
TBP or Cyanex 923

H$_2$O
MgCl$_2$ or CaCl$_2$

[Hbet][Tf$_2$N]

Figure 6. Visual representation of the triphasic extraction system.

Extraction results

First, the biphasic aqueous/ionic liquid extraction systems were investigated. [Hbet][Tf$_2$N] is an acidic extractant and its extraction behavior as function of the pH was studied. It was observed that about 80% of tin(II) and scandium(III) were extracted to the ionic liquid phase, whereas only 4% of yttrium(III) was extracted at an equilibrium pH of 1.01 (Figure 7). This means that it is possible to separate scandium(III) and tin(II) from yttrium(III), whereas the separation of scandium(III) from tin(II) is almost impossible, which is in agreement with literature data.[24] It was observed that the %E of all elements increased when the equilibrium pH was increased by the addition of betaine. However, a precipitate was formed at a pH
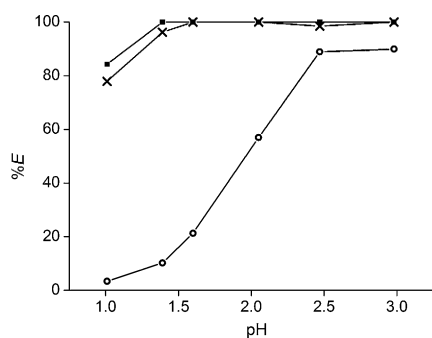
value of 1.6, which was deduced to be due to the hydrolysis of tin(II), as its recovery rate (the amount present in the IL phase and water phase together) was only 51% of the added amount. This is in agreement with the solubility product of Sn(OH)$_2$ ($K_{sp} = 3 \times 10^{-27}$).[25] At higher pH values, the percentage recoveries of tin(II) were again close to 100% and no precipitate formation was observed. This is probably due to the formation of very strong coordination complexes of the metals with the betaine inner salt in which no metal is available for the formation of hydrolysis species in the aqueous phase.

The extraction of the metal mixtures of scandium(III), tin(II) and yttrium(III) towards the [P$_{66614}$][Tf$_2$N] phase with TBP as extractant was tested as well. Attempts were made to extract the metals under conditions similar to that of the triphasic extraction systems. Unfortunately, the mixture TBP in [P$_{66614}$][Tf$_2$N] with H$_2$O formed strong emulsions and precipitates, which could not be removed by centrifugation or by temperature changes. When using higher salt concentrations, emulsions could be prevented, but a precipitate still formed. This is probably due to the higher pH and the formation of metal hydroxides. Both precipitation and emulsion formation could be avoided by using 1 M MgCl$_2$ in combination with a sufficiently high HCl concentration (pH 0.63 $\pm$ 0.02). Under these conditions, it was observed that yttrium(III) remained entirely in the water phase even at higher TBP concentrations. Over 80% of tin(II) was extracted in the [P$_{66614}$][Tf$_2$N] phase without significant extraction improvements at higher TBP concentrations. Scandium(III) remained mainly in the water phase. However, the %E increased slightly to 17% at 20 wt% TBP concentration. The results are shown in Figure 8. Perhaps, the separation could be modified by changing the concentration of the salting-out agent, but it is clear that it is impossible to separate three metals in a two-phase extraction system.
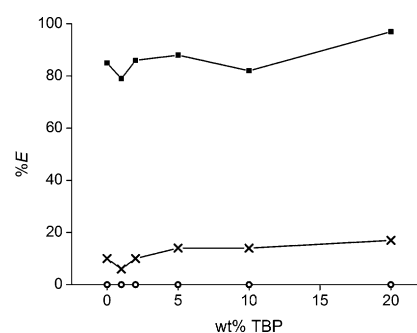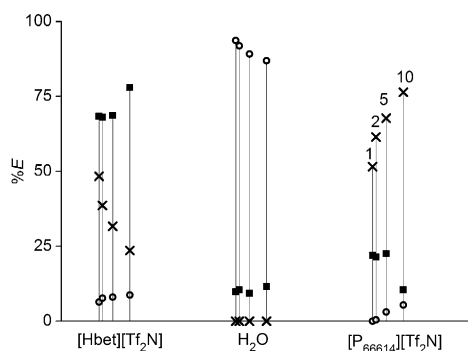

Figure 8. Percentage extraction (%E) of tin(II) (■), yttrium(III) (○), and scandium(III) (×) from chloride media to the [P$_{66614}$][Tf$_2$N] as a function of the TBP concentration (0 to 20 wt%). The aqueous phase contained 1 M MgCl$_2$ and the pH was adjusted to 0.63 $\pm$ 0.02.

After investigation of the biphasic extraction systems, a third phase was introduced. Tables with exact data and the recovery rates can be found in the Supporting Information. Two different types of molecular extractants with concentrations ranging between 1 and 10 wt% in the [P$_{66614}$][Tf$_2$N] phase were tested in combination with the [Hbet][Tf$_2$N] and water phase containing 0.5 M CaCl$_2$ (Figure 9 and Figure 10). It was observed that
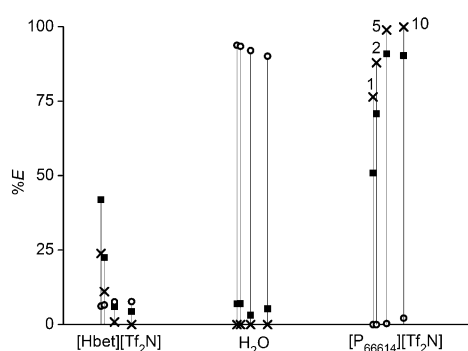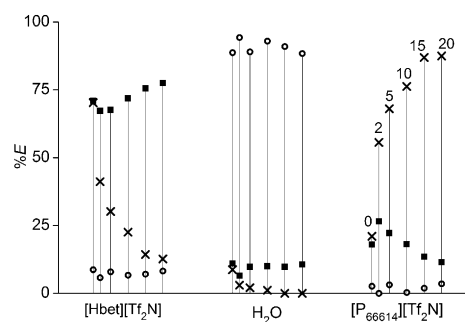

Figure 7. Percentage extraction (%E) of tin(II) (■), yttrium(III) (○), and scandium(III) (×) from chloride media towards [Hbet][Tf$_2$N] as a function of the equilibrium pH.

Figure 9. Percentage extraction (%E) of tin(II) (■), yttrium(III) (○), and scandium(III) (×) to the [Hbet][Tf$_2$N]-, H$_2$O-, and [P$_{66614}$][Tf$_2$N]-rich phases as a function of the TBP concentration (1 to 10 wt%) in the [P$_{66614}$][Tf$_2$N] phase. The aqueous phase contained 0.5 M of CaCl$_2$ and the pH ranged between 1.11 and 1.15.

Figure 10. Percentage extraction (%E) of tin(II) (■), yttrium(III) (○), and scandium(III) (×) to the [Hbet][Tf$_2$N]-, H$_2$O-, and [P$_{66614}$][Tf$_2$N]-rich phases as a function of the Cyanex 923 concentration (1 to 10 wt%) in the [P$_{66614}$][Tf$_2$N] phase. The aqueous phase contained 0.5 M of CaCl$_2$ and the pH ranged between 1.15 and 1.22.

a changing concentration of TBP only slightly changed the %E of tin(II) and yttrium(III) in the three different phases. However, increasing the TBP concentration increased the concentration of scandium(III) in the [P$_{66614}$][Tf$_2$N] phase significantly without significant changes in pH values. In case of Cyanex 923, it was observed that the %E of scandium(III) and tin(II) towards the [P$_{66614}$][Tf$_2$N] phase remained almost equal. The values increased with increasing Cyanex 923 concentration but without any significant selectivity. The %E of yttrium(III) towards the water phase was always above 90%. In fact, increasing the Cyanex 923 concentration transferred more tin(II) and scandium(III) from the [Hbet][Tf$_2$N] phase towards the [P$_{66614}$][Tf$_2$N] phase at equal pH values. From these results, it can also be concluded that the addition of TBP gave better metal selectivity than using Cyanex 923.

In a second series of experiments, the salting-out agent was changed from 0.5 M CaCl$_2$ to 0.5 M MgCl$_2$ and the influence of the TBP concentration was monitored (Figure 11). The concentration of scandium(III) in the [P$_{66614}$][Tf$_2$N] phase increased with increasing TBP concentration, whereas the concentrations of yttrium(III) in the aqueous phase and tin(II) in the [Hbet][Tf$_2$N] remained more or less constant. The percentage extrac-

Figure 11. Percentage extraction (%E) of tin(II) (■), yttrium(III) (○), and scandium(III) (×) to the [Hbet][Tf$_2$N]-, H$_2$O-, and [P$_{66614}$][Tf$_2$N]-rich phases as a function of the TBP concentration in the [P$_{66614}$][Tf$_2$N] phase (0 to 20 wt%). The aqueous phase contained 0.5 M MgCl$_2$.

tion values for scandium(III) in the [P$_{66614}$][Tf$_2$N] phase and tin(II) in the [Hbet][Tf$_2$N] phase are slightly higher when using CaCl$_2$ at the same TBP concentrations.

In a third series of experiments, the effect of the concentration of the salting-out agent was studied (Figure 12). In this case, the concentration of MgCl$_2$ in the aqueous phase was varied between 0.25 and 2.5 M at constant TBP concentration
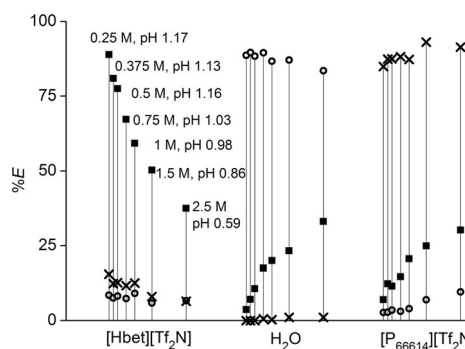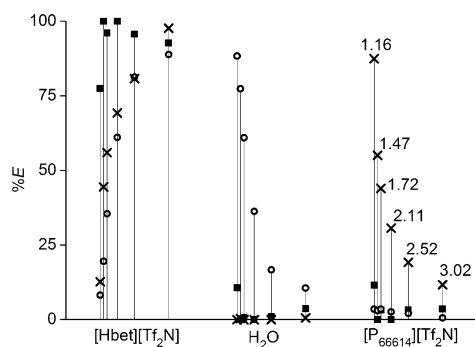

Figure 12. Percentage extraction (%E) of tin(II) (■), yttrium(III) (○), and scandium(III) (×) to the [Hbet][Tf$_2$N]-, H$_2$O-, and [P$_{66614}$][Tf$_2$N]-rich phases as a function of MgCl$_2$ concentration (0.25 to 2.5 M) in the aqueous phase. The [P$_{66614}$][Tf$_2$N] phase contained 20 wt% TBP.

in the [P$_{66614}$][Tf$_2$N] phase (20 wt%). It was observed that the percentage extraction of yttrium(III) and scandium(III) in the water phase slightly decreased with increasing chloride concentrations. In general, it seems that both metals are more strongly extracted to the [P$_{66614}$][Tf$_2$N] phase, which is probably due to the increasing salting-out effect at higher MgCl$_2$ concentrations. On the other hand, the percentage extraction values of all metals decreased in the [Hbet][Tf$_2$N] phase. This is probably not due to the salting-out agent but rather caused by the decreasing pH of the aqueous phase when working with higher MgCl$_2$ concentrations, an effect that was difficult to control during the experiment. During the investigation of this triphasic extraction system, it was concluded that the systems with the lowest chloride concentrations had better separation properties. At these conditions (20 wt% TBP, 0.25 M MgCl$_2$), 89% of tin(II) could be extracted to the [Hbet][Tf$_2$N]

phase, 89% of yttrium(III) remained in the aqueous phase, and 85% of scandium(III) was extracted to the $[P_{66614}][Tf_2N]$ phase. Unfortunately, due to the formation of emulsions, it was impossible to further decrease the chloride concentration. Important to mention here is that lower concentrations of $MgCl_2$ could be used in comparison with $CaCl_2$, which is probably because Mg^{II} is more kosmotropic than Ca^{II} and smaller amounts can be used to break the emulsion. Therefore, $MgCl_2$ was preferred over $CaCl_2$ in other experiments.

In a final series of experiments, the pH was increased by addition of betaine (Figure 13). When the pH was increased from

Figure 13. Percentage extraction (%E) of tin(II) (■), yttrium(III) (○), and scandium(III) (×) to the $[Hbet][Tf_2N]$-, H_2O-, and $[P_{66614}][Tf_2N]$-rich phases as a function of the pH, adjusted by the addition of betaine to the aqueous phase. The aqueous phase contained 0.5 M of $MgCl_2$ and the $[P_{66614}][Tf_2N]$ phase contained 20 wt% TBP.

1.16 to 1.47, an increase in percentage extraction values in the $[Hbet][Tf_2N]$ phase was observed. This behavior is expected for an acidic extractant. Unfortunately, a precipitate was formed at pH values of 1.72 and 2.11, due to hydrolysis of tin(II) and similar to that observed in the biphasic extraction systems. The percentage recovery was higher with 10 and 20 wt% of added betaine and no precipitate was visually observed. However, a stable emulsion was observed between the phases after centrifugation. Similar observations were made in the biphasic extraction system described above.

Conclusion

Two IL/IL combinations ($[Hbet][Tf_2N]$ or $[Chol][Tf_2N]$ with $[P_{66614}][Tf_2N]$) are presented and have very low mutual solubility. The same hydrophobic ionic liquids were used for the construction of IL/H_2O/IL ternary phase diagrams. The $[Hbet][Tf_2N]$/H_2O/$[P_{66614}][Tf_2N]$ system showed a very large triphasic region, which is interesting for separation processes. A proof-of-principle for the separation of tin(II), yttrium(III), and scandium(III) in a triphasic IL/H_2O/IL system was given. A few extraction parameters such as the pH, the salting-out agent, and the type of molecular extractant in the $[P_{66614}][Tf_2N]$ were varied. It was shown that the separation of scandium(III) from tin(II) in the biphasic extraction system $[Hbet][Tf_2N]$/H_2O is difficult due to the very similar pH dependence of the extraction behavior of these two metal ions. However, the introduction of a third

ionic liquid phase, containing a neutral extractant, significantly increases the separation of the three metal ions. The best separation was obtained at low chloride concentrations, without pH adjustment, and at high molecular extractant concentrations in the $[P_{66614}][Tf_2N]$ phase. At these conditions, 89% of tin(II) could be extracted to the $[Hbet][Tf_2N]$ phase, 89% of yttrium(III) remained in the aqueous phase, and 85% of scandium(III) was extracted to the $[P_{66614}][Tf_2N]$ phase.

Experimental Section

Materials

Choline chloride (99%) and tri-*n*-butyl phosphate (TBP, 98%) were purchased from Alfa Aesar (Karlsruhe, Germany) and betaine chloride (99%) from Acros Organics (Geel, Belgium). Lithium bis(trifluoromethylsulfonyl)imide (99%) was obtained from IoLiTec (Heilbronn, Germany). Trihexyl(tetradecyl)phosphonium chloride ($>97\%$) (Cyphos IL 101) and Cyanex 923 were purchased from Cytec Industrial Materials (St Jean, Toulouse, France). Absolute ethanol and HCl (37 wt%) were obtained from VWR (Leuven, Belgium). $CaCl_2$ (95%) and $MgCl_2\cdot6H_2O$ (99%) were purchased from ChemLab (Zedelgem, Belgium). $ScCl_3\cdot xH_2O$ was synthesized,[26] $YCl_3\cdot6H_2O$ (99.9%) was obtained from Strem Chemicals (Kehl, Germany), a 1000 ppm Cerium standard and $SnCl_2\cdot2H_2O$ ($>98\%$) were obtained from Merck (Overijse, Belgium). The silicon solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). Deuterated DMSO was obtained from Sigma–Aldrich (Diegem, Belgium). All chemicals were used as received, without further purification.

Equipment

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer (Bruker Biospin, Rheinstetten, Germany), operating at 300 MHz for ^1H and 75 MHz for ^{13}C. The melting points of the ionic liquids were recorded on a power compensation DSC (DSC 882e, Mettler–Toledo, Greifensee, Switzerland) under a helium atmosphere. A Mettler–Toledo DL39 coulometric Karl Fischer titrator (Mettler–Toledo, Greifensee, Switzerland) was used to determine the water content in the synthesized ionic liquids. CHN analysis (carbon, hydrogen, nitrogen) was performed on a CE Instruments EA-1110 element analyzer (Interscience, Louvain-la-Neuve, Belgium) and FTIR spectra were recorded on a Bruker Vertex 70 spectrometer and analyzed with OPUS software (Bruker Optics, Ettlingen, Germany). The ionic liquids were examined directly, without further preparation, using a Platinum ATR single-reflection diamond attenuated total reflection (ATR) accessory (Bruker Optics, Ettlingen, Germany). A Nemus Life Thermo Shaker TMS-200 (Nemus LIFE AB, Lund, Sweden) was used for constructing the phase diagrams and the extraction experiments. A Heraeus Labofuge 200 centrifuge (Thermo Fisher Scientific, Asse, Belgium) was used to accelerate phase separation. pH measurements were performed with a S220 SevenCompact™ pH/Ion meter (Mettler–Toledo) and a Slimtrode (Hamilton) electrode. A GC-MS (TraceGC Oven, ITQ9000, Thermoscientific) was used to quantify the composition of the Cyanex 923 mixture. A total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metals concentrations (S2 PICOFOX, Bruker).

Extractions

Prior to the extractions, a spike metal salt mixture was created. $ScCl_3 \cdot x H_2O$ (342.8 mg), $SnCl_2 \cdot 2H_2O$ (177.5 mg) and $YCl_3 \cdot 6H_2O$ (338.2 mg) were dissolved in water (150 mL) and stirred for 1 h. Water was removed on the rotary evaporator at 70 °C to obtain a solid metal salt mixture. The solid was then crushed to a powder and three random samples were measured with TXRF to check the homogeneity of the obtained powder. For 8 mg of metal salts (the standard amount used in the extractions) there was 13.30 ± 0.24 mmol scandium(III), 8.30 ± 0.15 mmol tin(II), and 11.36 ± 0.15 mmol yttrium(III) present. A slightly different metal salt mixture was used for the $[P_{66614}][Tf_2N]$ biphasic system: 8 mg contained 16.92 ± 0.9 mmol scandium(III), 8.84 ± 0.8 mmol tin(II), and 12.23 ± 0.9 mmol yttrium(III). Low concentrations were chosen instead of high concentrations to avoid large volume changes upon addition of the metal salts.

The molecular extractant (Cyanex 923 or TBP) was dissolved in $[P_{66614}][Tf_2N]$ to obtain the desired concentration. The water phase was prepared by dissolving the salting-out agent ($CaCl_2$ or $MgCl_2$) in water and the $[Hbet][Tf_2N]$ phase was made liquid by presaturation with water. Before performing the extractions, the three phases were equilibrated with each other to prevent volume changes during extraction. To achieve this, 4 mL of $[P_{66614}][T_{f2}N]$ containing Cyanex 923 or TBP (top phase), 4 mL of water containing $CaCl_2$ or $MgCl_2$ (middle phase), and 4 mL of water-saturated $[HBet][Tf_2N]$ (bottom phase) were brought into contact with each other and shaken for 20 min at 70 °C. After cooling down and phase separation by centrifugation at 3000 rpm for 5 min, the water phase was removed with a syringe and a new water phase (4 mL) was added. This saturation procedure was performed four times until two ionic liquid phases were obtained, which were in equilibrium with each other and the aqueous phase. However, the water phase was still taking up $[Hbet][Tf_2N]$ during the last saturation step. Therefore, the actual $MgCl_2$ or $CaCl_2$ concentration will be slightly lower than the reported ones. The errors made in the reported chloride concentrations depend on the salting-out effect of the cation and the concentration and is in all cases lower than 11 %.

An aliquot (1 g) of each pre-equilibrated phase was taken and 8 mg of the metal salts mixture was added. The salt mixture was added to the extraction system as a solid because of practical considerations. The addition of metal chlorides to a presaturated aqueous stock could salt-out part of the dissolved $[Hbet][TF_2N]$ phase, causing partial loss of the metals in this phase, even before extraction. The triphasic system was shaken at 3000 rpm at 70 °C for 1 h. After cooling down, the system was centrifuged (5300 rpm, 5 min) to improve phase separation and the pH of the aqueous phase was measured. Afterwards, about 50 mg was taken from each phase for metal quantification. 20 µL of a 1000 ppm cerium standard was added to the $[P_{66614}][Tf_2N]$-phase, whereas 200 µL of the 1000 ppm cerium standard was added to the aqueous and $[Hbet][Tf_2N]$ phases. These mixtures were further diluted to 1 mL with absolute ethanol. The addition of different amounts of standard volumes was done because of the poor solubility of $[P_{66614}][Tf_2N]$ in ethanol in the presence of a significant amount of water coming from the standard solution. Afterwards, 2 µL of the solution was transferred to a Quartz TXRF carrier, dried for 30 min at 60 °C in a hot air oven and measured by TXRF for 1000 s. The biphasic extractions were performed in a similar way as the triphasic extractions. An aliquot of 2 mL of an aqueous phase containing the desired $MgCl_2$ and betaine concentration was brought into contact with 2 mL of $[Hbet][Tf_2N]$. Similarly, 2 mL of an aqueous phase containing 1 M $MgCl_2$ was adjusted with HCl until a pH of 0.5 was ob-

tained. Afterwards, the solution was used to pre-equilibrate the $[P_{66614}][Tf_2N]$ phase containing 0 to 20 wt % of TBP. The mixtures were shaken for 20 min at 70 °C and after cooling down and phase separation by centrifugation at 5300 rpm for 5 min, the water phase was removed with a syringe and a new water phase (2 mL) was added. This saturation step was performed four times until both phases were in equilibrium with each other. From the equilibrated phases, 1 g was taken and 8 mg of the metal salt mixture was added to the solvent mixture. The mixtures were shaken at 3000 rpm at 70 °C for 1 h. After cooling down to room temperature, the systems were centrifuged (5300 rpm, 5 min) to improve the phase separation, followed by measurement of the pH of the aqueous phase. Quantification of the metal concentrations was performed in the same way as described for the triphasic system. The percentage extraction (%E) of a metal, i, in each phase a ($a = x[Hbet][Tf_2N]$, $y[H_2O]$, and $z[P_{66614}][Tf_2N]$) was calculated by using Equation (1):

$$(\%E)_{i,a} = \frac{[M_i]_x \cdot m_x}{[M_i]_x \cdot m_x + [M_i]_y \cdot m_y + [M_i]_z \cdot m_z} \times 100\% \qquad (1)$$

where x, y, and z are the abbreviations for the three phases, $[M_i]$ is the concentration (in $moles\,kg^{-1}$ or $mg\,kg^{-1}$) of one specific metal 'i' in one of the three phases, and m_x is the used mass (in kg) of the x phase in the extraction system (≈ 1 g). Three metals in three different phases give nine values. Notice that for practical reasons, the concentrations used to calculate the %E values are expressed in $mg\,kg^{-1}$ rather than in $mol\,L^{-1}$.

The percentage recovery (%R)$_i$ is calculated by Equation (2):

$$(\%R)_{i,a} = \frac{[M_i]_x \cdot m_x + [M_i]_y \cdot m_y + [M_i]_z \cdot m_z}{m_{i,added}} \times 100\% \qquad (2)$$

Where m_i is the amount of metal added to the extraction mixture. The percentage recovery represents the quality of the data points and includes all errors. Three measurement errors are made in the concentrations of each of the three phases. Also, the metal concentrations measured in the stock solutions contain an error. Moreover, the measurements were often made in large ionic liquid matrices and the dried salt mixture was taking up water when transferring from the sealed stock vial to the extraction mixture, both of which influence the concentration accuracies.

Synthesis of betainium bis(trifluoromethylsulfonyl)-imide, [Hbet][Tf$_2$N]

Betainium hydrochloride ([Hbet]Cl, 153.61 g mol^{-1}, 30 g, 0.195 mol) was dissolved in distilled water (80 mL). Lithium bis(trifluoromethylsulfonyl)imide (Li[Tf$_2$N], 287.05 g mol^{-1}, 56.2 g, 0.195 mol) was added while the solution was stirred. The solution was then stirred for a further 1 h. The ionic liquid (IL) phase phase-separated from the aqueous phase. The water phase was removed and the IL phase was washed three times with water (10 mL) to remove all remaining LiCl. The remaining chloride concentration was checked by TXRF measurements, but no chlorine peak could be detected.[27] The solution was dried on a rotary evaporator (50 °C, 2 h) under vacuum and overnight on the Schlenk line at 60 °C. A white solid was obtained (yield: 92 %, 71.696 g, 0.180 mol). m.p.: 56.6 °C (literature: 57 °C);[28] ^{1}H NMR (300 MHz, [d$_6$]DMSO) δ: 4.29 (s, 2H, CH$_2$), 3.21 ppm (s, 9H, 3×CH$_3$); ^{13}C NMR (75.48 MHz, [d$_6$]DMSO) δ: 166.3 (s, COO), 119.4 (q, 3×CF$_3$, $J = 4.27$), 62.6 (s, CH$_2$), 52.9 ppm (s, 3× CH$_3$); elemental analysis calcd. (%) for $C_7H_{12}N_2O_6F_6S_2 \cdot H_2O$ (416.3): C

20.20, H 3.39, N 6.73; found: C 20.57, H 3.61, N 6.85; density (water-saturated, 25 °C): 1.453 g cm^{-3}; FTIR (ATR) ν: 1767 (COOH), 1479 (CH$_2$), 1423, 1350 (SO$_2$), 1325 (SO$_2$), 1170 (CF$_3$), 1139 (SO$_2$), 1049 (SO$_2$), 741 (CF$_3$), 608 (CF$_3$) 570 (CF$_3$), 513 cm^{-1} (CF$_3$).

Synthesis of choline bis(trifluoromethylsulfonyl)imide, [Chol][Tf$_2$N]

Choline chloride ([Chol]Cl, 139.6 g mol^{-1}, 20.165 g, 0.144 mol) and lithium bis(trifluoromethylsulfonyl)imide (Li[Tf$_2$N], 287.05 g mol^{-1}, 41.353 g, 0.144 mol) were added to distilled water (250 mL). The mixture was stirred for 1 h at room temperature. The resulting ionic liquid phase-separated from the aqueous layer and was washed with distilled water to remove any remaining LiCl. The ionic liquid was checked for the presence of chloride impurities by TXRF, but no chlorine peak could be detected.[27] The ionic liquid was then dried on the rotary evaporator (50 °C, 2 h) under vacuum and overnight on the Schlenk line. White crystals were obtained (yield 50%, 27.735 g, 0.072 mol). m.p.: 30 °C (literature: 30 °C);[28] ^{1}H NMR (300 MHz, [d$_6$]DMSO) δ: 5.27 (t, 1H, OH, $J = 5.0$ Hz), 3.83 (m, 2H, CH$_2$), 3.39 (m, 2H, CH$_2$-OH), 3.10 ppm (s, 9H, CH$_3$); ^{13}C NMR (75.47 MHz, [d$_6$]DMSO) δ: 121.35 (q, 2×CF$_3$, $J = 4.24$ Hz), 66.90 (N-CH$_2$), 55.10 (CH$_2$-OH), 53.11 ppm (3×CH$_3$); elemental analysis calcd. (%) for C$_7$H$_{14}$F$_6$N$_2$O$_5$S$_2$·1/2 H$_2$O (393.3): C 21.38, H 3.84, N 7.12; found: C 21.45, H 3.67, N 7.29; FTIR (ATR) ν: 3537 (OH), 2915 (CH$_2$), 1478 (CH$_2$), 1420 (OH), 1347 (SO$_2$), 1181 (CF$_3$), 1132 (SO$_2$), 1055 (SNS), 791 (CS), 764 (SNS), 741 (CF$_3$), 655 (SNS), 613 (SO$_2$), 570 (CF$_3$), 512 (CF$_3$), 409 cm^{-1} (SO$_2$).

Synthesis of trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide, [P$_{66614}$][Tf$_2$N]

Trihexyl(tetradecyl)phosphonium chloride ([P$_{66614}$]Cl, 519.31 g mol^{-1}, 34 g, 0.0654 mol) was added to a solution of lithium bis(trifluoromethylsulfonyl)imide (Li[Tf$_2$N], 287.05 g mol^{-1}, 56.2 g, 0.195 mol) in distilled water (50 mL) while the solution was stirred. This mixture was stirred for 8 h. Another equivalent of Li[Tf$_2$N] was added and stirred for another 4 h. Two phases formed after centrifugation (2900 rpm, 5 min). The IL was separated from the water and washed three times with water (10 mL), each time using the centrifuge to get quicker separation. The liquid was dried on the rotary evaporator (50 °C, 4 h) under vacuum and overnight on the Schlenk line (65 °C). White crystals were obtained (yield: 71%, 35.52 g, 0.046 mol). ^{1}H NMR (300 MHz, [d$_6$]DMSO) δ: 2.16 (m, 8H, 4×P-CH$_2$), 1.34 (m, 48H, 24×CH$_2$), 0.88 ppm (m, 12H, 4×CH$_3$); ^{13}C NMR (75.48 MHz, [d$_6$]DMSO) δ: 119.5 (q, 3×CF$_3$, $J = 4.27$ Hz), 31.3, 30.3, 30.0, 29.8, 29.6, 29.0, 28.9, 28.7, 28.6, 28.0, 22.0, 21.8, 20.5, 20.4, 17.8, 17.1, 13.8, 13.7 ppm; elemental analysis calcd. (%) for C$_{34}$H$_{68}$F$_6$NO$_4$PS$_2$·2 H$_2$O (800.0): C 51.04, H 9.07, N 1.75; found: C 51.08, H 8.94, N 2.05; density (water-saturated, 25 °C): 1.065 g cm^{-3}; FTIR (ATR) ν: 2926 (CH$_2$), 2857 (CH$_3$), 1464 (CH$_2$), 1349 (SO$_2$), 1183 (CF$_3$), 1136, (SO$_2$), 1056 (SO$_2$), 616 (CF$_3$), 570 (CF$_3$), 512 cm^{-1} (CF$_3$).

Cyanex 923

^{1}H NMR (300 MHz, [d$_6$]DMSO) δ: 1.56 (6H, m), 1.27 (30H, m), 0.87 (9H, m); GC-MS: weight ratio of main components: [CH$_3$(CH$_2$)$_7$]$_3$P=O: 16.98%, [CH$_3$(CH$_2$)$_7$]$_2$[CH$_3$(CH$_2$)$_5$]P=O, 38.53%, [CH$_3$(CH$_2$)$_7$][CH$_3$(CH$_2$)$_5$]$_2$P=O: 32.86%, [CH$_3$(CH$_2$)$_5$]$_3$P=O: 11.63%, other impurities: <8% of total weight.

Construction of the phase diagrams

The phase diagrams are expressed in terms of weight percentages (wt%). Expressing the phase diagram in terms of mole percentages (mol%) would compress the most interesting part of the ternary phase diagram in one corner of the triangle because the number of moles of water are much higher than the number of moles of the ionic liquids when using equal volumes during the extraction experiments. The binary phase diagram of the mixture [Hbet][Tf$_2$N]/[P$_{66614}$][Tf$_2$N], for instance, was constructed by mixing the ionic liquids in weight ratios of 70:30. All mixtures were heated and stirred in sealed vials for 2 h. Then, they were allowed to settle overnight at a specific temperature ranging between 25 and 205 °C. An aliquot of both phases was removed with a syringe and quantitatively dissolved in deuterated DMSO. The concentrations of the ionic liquids in both phases were analyzed by ^{1}H NMR spectroscopy. For [Hbet][Tf$_2$N], the peak at 4.25 ppm was used, which corresponds to the two hydrogen atoms on the carbon atom between the nitrogen atom and the carboxylic group of betaine. The peak at 0.93 ppm was used in the case of [P$_{66614}$][Tf$_2$N], which corresponds to the 12 hydrogen atoms standing at the end of the alkyl chains. The mole fraction of the ionic liquids in both phases can be calculated from the integrated values. The area under the [Hbet][Tf$_2$N] peak was integrated and calibrated as 2. The weight percentage (wt%) of [Hbet][Tf$_2$N] ($w_{[Hbet][Tf_2N]}$) in each phase can be calculated by using Equation (3):

$$w_{[Hbet][Tf_2N]} = \frac{MM_{[Hbet][Tf_2N]}}{MM_{[Hbet][Tf_2N]} + (y/12) \cdot MM_{[P_{66614}][Tf_2N]}} \qquad (3)$$

where MM corresponds to the molecular mass of the ionic liquids. The value $y/12$ is equal to the integrated area under the peak at 0.9 ppm (y) divided by the number of hydrogen atoms that are giving this signal (12). The weight percentage of [P$_{66614}$][Tf$_2$N] in each phase was calculated by using a similar formula, Equation (4):

$$w_{[P_{66614}][Tf_2N]} = \frac{(y/12) \cdot MM_{[P_{66614}][Tf_2N]}}{MM_{[Hbet][Tf_2N]} + (y/12) \cdot MM_{[P_{66614}][Tf_2N]}} \qquad (4)$$

or Equation (5)

$$w_{[P_{66614}][Tf_2N]} = 1 - w_{[Hbet][Tf_2N]} \qquad (5)$$

The triphasic phase diagram [Hbet][Tf$_2$N]/H$_2$O/[P$_{66614}$][Tf$_2$N] was constructed similarly, as reported earlier by Arce et al.[29] A mixture containing 1 g of water, [Hbet][Tf$_2$N], and [P$_{66614}$][Tf$_2$N] was shaken for 1 h at 1900 rpm and 25 °C. Afterwards, the mixture was centrifuged at 5300 rpm for 10 min to accelerate phase separation. Each phase was separated with a syringe and the molar and weight ratio of the ionic liquids in each of the three phases were determined by analyzing the ^{1}H NMR spectrum in the same way as for the binary system [Hbet][Tf$_2$N]/[P$_{66614}$][Tf$_2$N] (Equations (1) and (2)). The water content of [Hbet][Tf$_2$N] was determined gravimetrically by drying the phases overnight in vacuo at 100 °C and can be calculated from Equation (6):

$$w_{water} = \frac{m_b - m_a}{m_b} \qquad (6)$$

where m_b and m_a are the masses of the specific phase before and after the drying procedure, respectively. The weight percentage of

each ionic liquid in each of the three phases can be calculated by using Equation (7):

$$w_{IL} = (1 - w_{water}) \cdot w'_{IL} \qquad (7)$$

where w'_{IL} is the weight percentage of each ionic liquid in one of the three phases determined by using Equations (1) and (2) and $(1 - w_{water})$ is the correction factor for the presence of water in the ternary system. The binary and ternary phase diagrams containing [Chol][Tf$_2$N] were constructed in the same way as for the [Hbet][Tf$_2$N] systems. The peak around 3.42 ppm in the ^{1}H NMR spectrum, corresponding to the two hydrogen atoms on the carbon atom between the nitrogen atom and the alcohol group, was used for the integrations.

The precision and accuracy of the method was tested by dissolving known quantities of [Hbet][Tf$_2$N] and [P$_{66614}$][Tf$_2$N], in a weight ratio of 1:9, in deuterated DMSO. A weight ratio of 1:9 is similar to what was found in the upper [P$_{66614}$][Tf$_2$N] ionic liquid phase in the case of a binary ionic liquid system. The percentage accuracy was 100.2% and the precision 6.5%.

Acknowledgements

Keywords: hydrometallurgy · ionic liquids · rare earths · ternary phase diagram · three-liquid solvent extraction

[1] a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083; b) K. R. Seddon, *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351–356; c) R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792–793.

[2] M. J. Earle, J. M. S. S. Esperanca, M. A. Gilea, J. N. Canongia Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, J. A. Widegren, *Nature* **2006**, *439*, 831–834.

[3] D. M. Fox, W. H. Awad, J. W. Gilman, P. H. Maupin, H. C. De Long, P. C. Trulove, *Green Chem.* **2003**, *5*, 724–727.

[4] a) P. A. Z. Suarez, V. M. Selbach, J. E. L. Dullius, S. Einloft, C. M. S. Piatnicki, D. S. Azambuja, R. F. de Souza, J. Dupont, *Electrochim. Acta* **1997**, *42*, 2533–2535; b) F. Endres, *J. Phys. Chem.* **2004**, *108*, 255–283; c) *Electrochemical windows of room-temperature ionic liquids (RTILs)*, H. Matsumoto, in *Electrochemical Aspects of Ionic Liquids* (Ed.: H. Ohno), Hoboken, New Jersey, John Wiley & Sons, **2011**, pp. 35–54.

[5] a) G. Huddleston, D. Rogers, *Chem. Commun.* **1998**, 1765–1766; b) P. R. Vasudeva Rao, K. A. Venkatesan, A. Rout, T. G. Srinivasan, K. Nagarajan, *Sep. Sci. Technol.* **2012**, *47*, 204–222; c) S. Ha, R. Menchavez, Y. M. Koo, *Korean J. Chem. Eng.* **2010**, *27*, 1360–1365; d) A. E. Visser, R. P. Swatloski, S. T. Griffin, D. H. Hartman, R. D. Rogers, *Sep. Sci. Technol.* **2001**, *36*, 785–804; e) M. L. Dietz, *Sep. Sci. Technol.* **2006**, *41*, 2047–2063; f) *Ionic Liquids: New Hopes for Efficient Lanthanide/Actinide Extraction and Separation?* I. Billard, in *Handbook on the Physics and Chemistry of Rare Earths* (Eds.: J. C. G. Bünzli, V. Pescharsky), Amsterdam, Elsevier, **2013**, pp. 213–273; g) M. Sypula, A. Ouadi, C. Gaillard, I. Billard, *RSC Adv.* **2013**, *3*, 10736–10744; h) Y. Shen, X. Tan, L. Wang, W. Wu, *Sep. Purif. Technol.* **2011**, *78*, 298–302; i) A. Rout, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, *Radiochim. Acta* **2009**, *97*, 719–725; j) S. I. Nikitenko, P. Moisy, *Inorg. Chem.* **2006**, *45*, 1235–1242; k) M. Regel-Rosocka, M. Wisniewski, in *Applications of ionic liquids in science and technology* (Ed.: S. Handy), InTech, Rijeka, **2011**, pp. 375–398; l) M. V. Mancini, N. Spreti, P. Di Profio, R. Germani, *Sep. Purif. Technol.* **2013**, *116*, 294–299; m) T. J. Bell, Y. Ikeda, *Dalton Trans.* **2011**, *40*, 10125–10130; n) A. Stojanovic, B. K. Keppler, *Sep. Sci. Technol.* **2012**, *47*, 189–203; o) A. P. Abbott, G. Frisch, J. Hartley, K. S. Ryder, *Green Chem.* **2011**, *13*, 471–481; p) T. Vander Hoogerstraete, B. Onghena, K. Binnemans, *J. Phys. Chem. Lett.* **2013**, *4*, 1659–1663; q) T. Vander Hoogerstraete, B. Onghena, K. Binnemans, *Int. J. Mol. Sci.* **2013**, *14*, 21353–21377; r) X. P. Xuan, L. L. Chang, H. Zhang, N. Wang, Y. Zhao, *CrystEngComm* **2014**, *16*, 3040–3046; s) K. Sasaki, K. Takao, T. Suzuki, T. Mori, T. Arai, Y. Ikeda, *Dalton Trans.* **2014**, *43*, 5648–5651; t) W. Wang, Y. Liu, A. Xu, H. Yang, H. Cui, J. Chen, *Chin. J. Chem. Eng.* **2012**, *20*, 40–46; u) D. P. Fagnant, G. S. Goff, B. L. Scott, W. Runde, J. F. Brennecke, *Inorg. Chem.* **2013**, *52*, 549–551.

[6] A. Arce, M. J. Earle, S. P. Katdare, H. Rodriguez, K. R. Seddon, *Chem. Commun.* **2006**, 2548–2550.

[7] a) S. Omar, J. Lemus, E. Ruiz, V. c. R. Ferro, J. Ortega, J. Palomar, *J. Phys. Chem. B* **2014**, *118*, 2442–2450; b) G. Annat, M. Forsyth, D. R. MacFarlane, *J. Phys. Chem. B* **2012**, *116*, 8251–8258; c) A. Arce, M. J. Earle, S. P. Katdare, H. Rodriguez, K. R. Seddon, *Fluid Phase Equilib.* **2007**, *261*, 427–433; d) A. Rout, S. Wellens, K. Binnemans, *RSC Adv.* **2014**, *4*, 5753–5758; e) S. Wellens, B. Thijs, C. Möller, K. Binnemans, *Phys. Chem. Chem. Phys.* **2013**, *15*, 9663–9669.

[8] A. Arce, M. J. Earle, S. P. Katdare, H. Rodriguez, K. R. Seddon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2538–2542.

[9] a) K. Anderson, H. Rodriguez, K. R. Seddon, *Green Chem.* **2009**, *11*, 780–784; b) T. Takata, N. Hirayama, *Anal. Sci.* **2009**, *25*, 1269–1270; c) S. A. Chowdhury, J. L. Scott, D. R. MacFarlane, *Pure Appl. Chem.* **2008**, *80*, 1325–1335.

[10] a) P. R. Vasudeva Rao, Z. Kolarik, *Solvent Extr. Ion Exch.* **1996**, *14*, 955–993; b) R. Chiarizia, M. P. Jensen, M. Borkowski, J. R. Ferraro, P. Thiyagarajan, K. C. Littrell, *Solvent Extr. Ion Exch.* **2003**, *21*, 1–27.

[11] a) P. Yu, K. Huang, C. Zhang, K. Xie, X. He, J. Zhao, F. Deng, H. Liu, *J. Colloid Interface Sci.* **2011**, *362*, 228–234; b) K. Xie, K. Huang, L. Yang, H. Liu, *J. Chem. Technol. Biotechnol.* **2012**, *87*, 955–960; c) N. Sui, K. Huang, H. Zheng, J. Lin, X. Wang, C. Xiao, H. Liu, *Ind. Eng. Chem. Res.* **2014**, *53*, 16033–16043; d) P. Yu, K. Huang, H. Liu, K. Xie, *Sep. Purif. Technol.* **2012**, *88*, 52–60; e) K. Xie, K. Zhao, L. Yang, P. Yu, H. Liu, *Sep. Purif. Technol.* **2010**, *76*, 191–197; f) P. Yu, K. Huang, C. Zhang, K. Xie, X. He, H. Liu, *Ind. Eng. Chem. Res.* **2011**, *50*, 9368–9376; g) N. Sui, K. Huang, C. Zhang, N. Wang, F. Wang, H. Liu, *Ind. Eng. Chem. Res.* **2013**, *52*, 5997–6008; h) F. Xun, L. Huan, C. Hui, W. Zhengshui, W. Debao, *Solvent Extr. Ion Exch.* **1999**, *17*, 1281–1293; i) G. Guohua, W. Yueshun, F. Xun, H. Xiaopeng, Y. Weirong, X. Yahong, *Solvent Extr. Ion Exch.* **2000**, *18*, 841–851.

[12] C. Zhang, K. Huang, P. Yu, H. Liu, *Sep. Purif. Technol.* **2011**, *80*, 81–89.

[13] C. Zhang, K. Huang, P. Yu, H. Liu, *Sep. Purif. Technol.* **2013**, *108*, 166–173.

[14] K. Huang, H. Liu, CN102382982, **2013**.

[15] a) P. Nockemann, K. Binnemans, B. Thijs, T. N. Parac-Vogt, K. Merz, A. V. Mudring, P. C. Menon, R. N. Rajesh, G. Cordoyiannis, J. Thoen, J. Leys, C. Glorieux, *J. Phys. Chem. B* **2009**, *113*, 1429–1437; b) P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen, K. Binnemans, *Inorg. Chem.* **2008**, *47*, 9987–9999.

[16] B. Onghena, J. Jacobs, L. Van Meervelt, K. Binnemans, *Dalton Trans.* **2014**, *43*, 11566–11578.

[17] a) D. Dupont, K. Binnemans, *Green Chem.* **2015**, *17*, 856–868.

[18] a) R. Schurhammer, G. Wipff, *J. Phys. Chem. B* **2006**, *110*, 4659–4668; b) N. Papaiconomou, I. Billard, E. Chainet, *RSC Adv.* **2014**, *4*, 48260–48266.

[19] a) T. Vander Hoogerstraete, S. Wellens, K. Verachtert, K. Binnemans, *Green Chem.* **2013**, *15*, 919–927; b) Y. Zuo, Y. Liu, J. Chen, D. Q. Li, *Ind. Eng. Chem. Res.* **2008**, *47*, 2349–2355; c) T. Vander Hoogerstraete, B. Blanpain, T. Van Gerven, K. Binnemans, *RSC Adv.* **2014**, *4*, 64099–64111.

[20] N. Papaiconomou, I. Billard, E. Chainet, *RSC Adv.* **2014**, *4*, 48260–48266.

[21] R. Leberman, A. K. Soper, *Nature* **1995**, *378*, 364–366.

[22] S. Shahriari, C. M. S. S. Neves, M. G. Freire, J. A. P. Coutinho, *J. Phys. Chem. B* **2012**, *116*, 7252–7258.

[23] W. Wang, Y. Pranolo, C. Y. Cheng, *Hydrometallurgy* **2011**, *108*, 100–108.

[24] J. S. Preston, *Hydrometallurgy* **1985**, *14*, 171–188.

[25] S. Zumdahl, D. J. DeCoste, *Chemical Principles*, Cengage Learning, Belmont, **2012**.

[26] B. Onghena, K. Binnemans, *Ind. Eng. Chem. Res.* **2015**, *54*, 1887–1898.

[27] T. Vander Hoogerstraete, S. Jamar, S. Wellens, K. Binnemans, *Anal. Chem.* **2014**, *86*, 3931–3938.

[28] P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner, K. Binnemans, *J. Phys. Chem. B* **2006**, *110*, 20978 – 20992.

[29] a) A. Arce, M. J. Earle, H. Rodriguez, K. R. Seddon, *Green Chem.* **2007**, *9*, 70 – 74; b) A. Arce, M. J. Earle, H. Rodriguez, K. R. Seddon, *J. Phys. Chem. B* **2007**, *111*, 4732 – 4736; c) A. Arce, O. Rodriguez, A. Soto, *J. Chem. Eng. Data* **2004**, *49*, 514 – 517.