

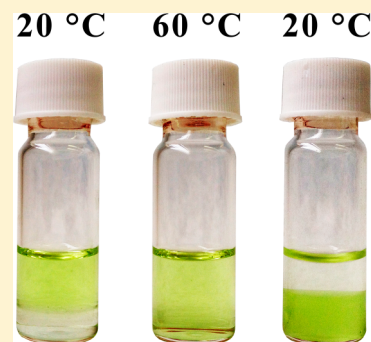
Homogeneous Liquid–Liquid Extraction of Metal Ions with a Functionalized Ionic Liquid

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S Supporting Information

ABSTRACT: Binary mixtures of the ionic liquid betainium bis(trifluoromethylsulfonyl)imide and water show an upper critical solution temperature. This solvent system has been used to extract metal ions by phase-transition extraction, using zwitterionic betaine as extractant. The system is efficient for the extraction of trivalent rare-earth, indium and gallium ions. This new type of metal extraction system avoids problems associated with the use of viscous ionic liquids, namely, the difficulty of intense mixing of the aqueous and ionic liquid phases by stirring.



SECTION: Liquids; Chemical and Dynamical Processes in Solution

The temperature-dependent miscibility of ionic liquids (ILs) with water or with organic solvents is an interesting phenomenon. Some IL/solvent mixtures have an upper critical solution temperature (UCST).^{1–6} Above the UCST, the components of the mixture are completely miscible in all proportions. Other IL/solvent mixtures have a lower critical solution temperature (LCST).^{5,7–11} They form one homogeneous phase below the LCST. ILs with an LCST or UCST are said to exhibit *thermomorphic behavior*. A two-phase IL/solvent mixture can be converted to one homogeneous phase by changing the temperature. Re-establishment of the two-phase equilibrium is possible by returning to the initial temperature. It has not been realized yet that IL/water mixtures with an UCST-type of phase transition can also be used for the extraction of metal ions. ILs are attractive as solvents for improved solvent extraction processes because of their negligible vapor pressure (and thus very low volatility) and their ability to solubilize metal complexes.^{12–18}

During solvent extraction, vigorous agitation is required to speed up the kinetics of the extraction process, because the metal ions have to pass the phase boundary between the two immiscible phases. However, ILs often have a high viscosity, and this makes efficient mixing of the aqueous and IL phase difficult. The need for intense stirring can be avoided by the formation of a homogeneous phase above the UCST. In the homogeneous phase, a fast reaction between the metal ion and the extractant can take place. Upon cooling, phase separation occurs with transfer of the metal complex to the IL phase. This separation technique is called *homogeneous liquid–liquid extraction*, *coalescence extraction*, or *phase-transition extraction*, and it is typically used for the extraction of natural products.^{19–21} The scarce examples of separation of metal ions via homogeneous liquid–liquid extraction make use of

nitriles (adiponitrile, glutaronitrile, succinonitrile, malononitrile), or propylene carbonate as organic phase.^{19,22–25}

In this Letter, we show the possibility to use ILs for the homogeneous liquid–liquid extraction of metal ions (Figure 1). The carboxyl-functionalized IL betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N], was selected as IL phase (Figure 2a).¹ The [Hbet][Tf₂N]–water mixture has an UCST of 55 °C. At the critical concentration, the mass fraction of the IL is 0.519. The extraction system was tested for

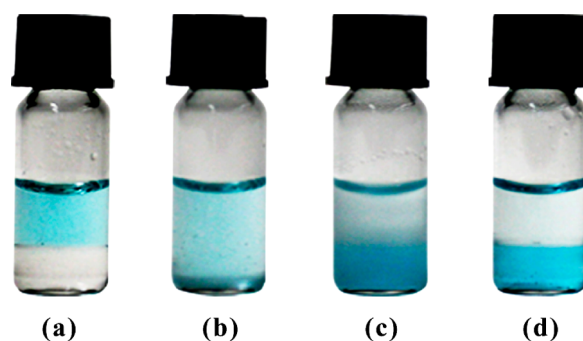


Figure 1. Homogeneous liquid–liquid extraction of Cu²⁺ ions (blue color) from an aqueous bis(trifluoromethylsulfonyl)imide medium with betaine as extractant in the [Hbet][Tf₂N]–water system: (a) initial stage, (b) homogeneous stage (60 °C), (c) settling stage, (d) after settling. The aqueous phase is the upper layer and the IL is the lower layer. The copper concentration in the aqueous feed solution was 2600 mg/kg.

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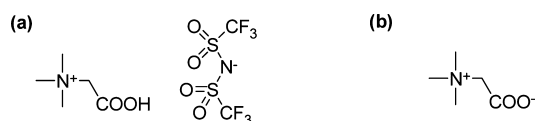


Figure 2. Structures of (a) [Hbet][Tf₂N] and (b) zwitterionic betaine.

different metals, including rare earths. It will be shown that the [Hbet][Tf₂N]–water system, in combination with the betaine as extractant, is very suitable for the extraction of scandium, gallium, and indium.

It is common practice to perform solvent extraction experiments with the organic and aqueous phase in a given volume ratio. However, for the homogeneous liquid–liquid extraction experiments described in this Letter, a given mass ratio was used. [Hbet][Tf₂N] is a solid at room temperature or a viscous liquid after presaturation with water, so that it is difficult to dispense an exact volume correctly by pipetting. On the other hand, weighing of the IL is easy and precise. The mutual solubility of the IL [Hbet][Tf₂N] and water results in a change in mass of the phases during extraction. [Hbet][Tf₂N] takes up ca. 12 wt % of water at room temperature and dissolves in water for ca. 15 wt %. The mass of the organic phase (= IL) decreases during the extraction. By presaturation of the IL with water, further uptake of water during the extraction step is prevented. The IL still partly dissolves in the aqueous phase, resulting in a volume increase of the aqueous phase and a corresponding decrease of the organic phase. In a typical extraction experiment, 1 g of the IL [Hbet][Tf₂N] (presaturated with water) was mixed in a 1:1 mass ratio with an aqueous solution of a metal ion. The mixture was heated above the UCST of the solvent system (homogeneous stage) in an oil bath at 60 °C. The homogenization of the system was accelerated by gentle shaking of the mixture, and a one-phase system was obtained in less than 1 min. Subsequently, the mixture was allowed to cool to room temperature and to re-establish the two-phase equilibrium. After approximately one hour of equilibration at room temperature (or at a lower temperature), the aqueous phases were sampled and its metal content was determined by total reflection X-ray fluorescence (TXRF) spectrometry. The metal concentrations are expressed in mg/kg. The efficiency of the extraction process can be expressed by the *distribution ratio* (D), which is defined as the ratio of the total concentration of a compound in the organic phase (c_{org}) to the total concentration of the compound in the aqueous phase (c_{aq}): $D = c_{\text{org}}/c_{\text{aq}}$. Although the use of the distribution ratio is preferred for the thermodynamical study of distribution equilibria, the extraction process is often expressed in terms of the *percentage extraction* (% E), which is defined as the ratio of the amount of metal extracted to the total amount of metal present in the system, times 100. Due to the mutual solubility between the water phase and the IL phase, the distribution ratio D and the extraction percentage % E are slightly underestimated.

The initial extraction experiments were carried out with pure [Hbet][Tf₂N], without the addition of an extractant. It is known that [Hbet][Tf₂N] is a very powerful solvent for dissolution of metal oxides or hydroxides. Given the fact that carboxylic acids are being used as extractant of metal ions,²⁶ it was assumed that the [Hbet][Tf₂N]–water system is a very good starting point for the development of a separation process for metal ions based on phase-transition extraction. The extraction experiments were performed with metal bis-

(trifluoromethylsulfonyl)imide salts (metal bistriflimides), to avoid anion exchange with the IL [Hbet][Tf₂N]. Very low distribution ratios ($D < 1$) were found for the trivalent lanthanide ions, showing that pure [Hbet][Tf₂N] cannot efficiently extract these ions from an aqueous phase. Therefore, it was decided to add zwitterionic betaine as an extractant to this system (Figure 2b). It is known that lanthanide ions can form complexes with betaine.¹ After having obtained promising preliminary results with betaine as extractant, it was decided to investigate the influence of different extraction parameters on the extraction of neodymium(III). It is important to notice that in conventional solvent extraction systems, the extractant is dissolved in the organic phase. However, in the homogeneous liquid–liquid extraction experiments described in this Letter, betaine was dissolved in the aqueous phase. First, the influence of the ratio of extractant to metal ion in the aqueous solution was examined. Extraction mixtures with the following composition were prepared: 1 g of the IL [Hbet][Tf₂N], 1 g of Nd(Tf₂N)₃ solution (with a neodymium concentration of 1500 mg/kg), and a certain amount of betaine ranging between 0 and 250 mg. The mixtures were heated to 60 °C to form one homogeneous phase and were then allowed to cool to room temperature.

The distribution ratio and extraction efficiency were found to increase as a function of the extractant-to-metal ratio (Figure 3). At a betaine-to-neodymium molar ratio of 200, nearly 99%

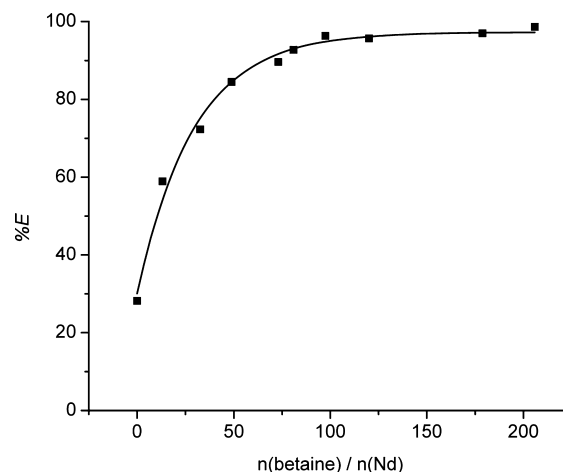


Figure 3. Extraction efficiency as a function of the ratio of the number of moles of betaine to the number of moles of neodymium in the aqueous feed solution for the extraction of Nd³⁺ from bis-(trifluoromethylsulfonyl)imide medium in the [Hbet][Tf₂N]–H₂O system, with zwitterionic betaine as an extractant.

of the Nd³⁺ ions were extracted to the IL phase. This ratio corresponds to a betaine concentration of ca. 200 mg/g in the starting aqueous solution. It should be noted that the addition of betaine to the binary [Hbet][Tf₂N]–water mixture has a lowering effect on the UCST of approximately 10 °C for 10 wt % of betaine, but the mutual solubility at room temperature is not increased significantly and does not influence the extraction yields. Since the mutual solubility of [Hbet][Tf₂N] and water depends on the temperature, it can be expected that the temperature to which the extraction mixtures are cooled down after the homogeneous stage of the extraction process (and at which the sampling of the phases is done) has an influence on the distribution ratio of the metal ions. Experiments were done at different temperatures ranging from 6 to 50 °C. Every

extraction mixture contained 1 g of [Hbet][Tf₂N], 1 g of Nd(Tf₂N)₃ solution (1500 mg/kg Nd), and 200 mg of betaine. Both the distribution ratio and the extraction efficiency were found to have nearly constant values over the entire temperature range (%E = 99%), except at 50 °C, where the value is substantially lower (%E = 92%). Therefore, room temperature is an ideal temperature for reinstalling the two-phase equilibrium after cooling down the homogeneous extraction mixture. Small changes in temperature will not result in large differences in distribution ratios or extraction efficiencies. The lower values at 50 °C can be rationalized by the fact that [Hbet][Tf₂N] has a higher solubility in the aqueous phase at that temperature, and as a consequence, the metal–betaine complex is also more soluble in the aqueous phase. No correlation could be found between the extraction efficiency and the time that the solution was kept above the UCST (between 0.5 and 60 min at 65 °C). The distribution ratios remained virtually constant for the different heating times. However, it is important to complete the settling stage to reobtain a well-separated two-phase mixture before analysis of organic and aqueous phase. In practice, one has to wait until the turbidity of the solutions has disappeared and two transparent phases are obtained. This can take 1 h or longer. The settling time was reduced from 1 h to only a few minutes by centrifugation.

After extraction, it is important that the extracted metal ion can be removed from the IL as a water-soluble salt (stripping process), in order to reuse the IL for new extractions and to enable further processing of the extracted or separated metals. Stripping can be achieved by addition of acid to the organic phase. The use of hydrogen bis(trifluoromethylsulfonyl)imide (HTf₂N) as a stripping agent is limited to the solubility of the organic phase in the aqueous phase. If, for example, 50 wt % of a HTf₂N solution (80 wt % in water, approximately 2.8 M) was added to the organic phase after extraction, a homogeneous solution was obtained, and phase separation did not occur. For HTf₂N concentrations of 1 M or lower, phase separation could be induced at low temperatures (e.g., at 6 °C). The influence of HTf₂N on the stripping efficiency was measured by stripping the organic phase, resulting from the extraction of 6 mL of Nd(Tf₂N)₃ solution (1500 mg/kg Nd) with 1.250 g of betaine in 5 g of [Hbet][Tf₂N]. HTf₂N solutions (500 μL) with concentrations varying between 0.1 and 1 M were mixed with 500 mg of organic phase. Similar to the extraction process, the mixtures were heated above the UCST (to 65 °C) and cooled down to 6 °C to induce phase separation. More concentrated HTf₂N stripping solutions resulted in higher stripping efficiencies, with a value of ca. 95% for a 1 M HTf₂N solution. HCl solutions were found to be better stripping agents than HTf₂N. This was shown by stripping an organic phase of [Hbet][Tf₂N], loaded with 1000 mg/kg of Er and 800 mg/kg of La, with HCl solutions, with concentrations varying between 0.01 and 2 M. The mixture was heated to 65 °C and allowed to cool to room temperature. Phase separation was very easily obtained, and there was no need for cooling to 6 °C, even for the higher HCl concentrations. The UCST increased with higher HCl concentrations, and no homogeneous phase was formed during the heating/mixing stage with HCl concentrations of 0.25 M and higher. Stripping efficiencies of almost 100% were obtained for HCl concentrations of 0.5 M and higher. The increasing UCST by the addition of chloride anions (HCl) and also the decrease in UCST by adding Tf₂N⁻ anions to the mixture is similar to what has been observed in the

literature and is due to salting in/salting out phenomena.^{27–29} Dissolution of IL in water can have toxic effects on the aqueous environment, and it leads to undesirable losses of IL. Addition of inorganic salts to the IL–water system decreases the mutual solubility. This behavior will be used in the future to reduce unavoidable losses of [Hbet][Tf₂N] in the aqueous phase.²⁹

The extraction of different metal ions was tested to explore the possibilities of homogeneous liquid–liquid extraction with the [Hbet][Tf₂N]–H₂O solvent system. The aqueous feed solutions for the extraction contained a metal bis(trifluoromethylsulfonyl)imide salt (metal concentration of approximately 1000 mg/kg) and 13 wt % of betaine. Of this feed solution, 1 g was mixed with 1 g of [Hbet][Tf₂N] and the mixture was heated to 65 °C with shaking. After 10 min, the extraction mixture was allowed to cool to induce phase separation, and the aqueous phase was analyzed with TXRF to determine the metal content. The results for the extraction of La³⁺, Pr³⁺, Nd³⁺, Dy³⁺, Ho³⁺, Er³⁺, Y³⁺, Sc³⁺, Ga³⁺, In³⁺, Mn²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Ag⁺ are shown in Figure 4. Sc³⁺, Ga³⁺, and

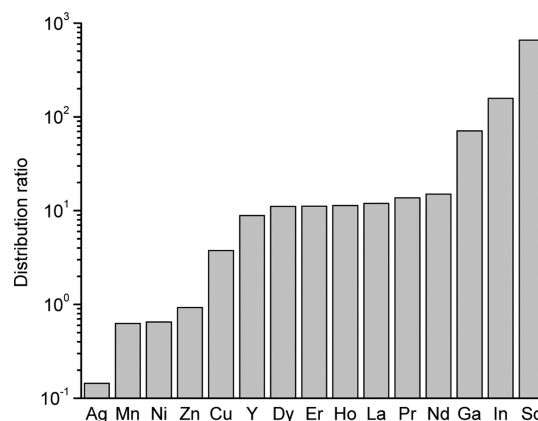


Figure 4. Distribution ratios for the extraction of different metal bis(trifluoromethylsulfonyl)imide salts with betaine as an extractant, for the [Hbet][Tf₂N]–water system under homogeneous liquid–liquid extraction conditions.

In³⁺ are almost completely extracted, leaving only a very small amount of metal in the aqueous phase. Extraction experiments with Sc³⁺, Ga³⁺, and In³⁺ were repeated for a concentration of 8000 mg/kg in the feed solution, because otherwise the concentration in the aqueous phase after extraction was too low for a reliable determination of the metal content. The distribution ratios of Mn²⁺, Ni²⁺, Zn²⁺, and Ag⁺ are very low. There is almost no extraction of these metal ions to the organic phase. Cu²⁺ is reasonably well extracted to the IL phase (Figure 1). This indicates the possibility for separation of Cu²⁺ from Ni²⁺, Zn²⁺ and Mn²⁺. The distribution ratios for the lanthanide ions are about 10, and there are no significant differences between the different lanthanide ions. The extractability of metal ions with the homogeneous [Hbet][Tf₂N]–H₂O is very comparable to the sequence that is observed for the solvent extraction of metal ions with carboxylic acids.²⁶ The UCST of 55 °C of the pure [Hbet][Tf₂N]–H₂O system was not found to be marginally altered at low loadings of rare-earth salts. However, Brennecke and co-workers recently observed a significant lowering of the UCST of the [Hbet][Tf₂N]–H₂O systems at high concentrations of dissolved Nd₂O₃.³⁰ Here, the question is whether the decrease in UCST is due to the formation of HTf₂N and H₂O during the dissolution process or

by the increase in metal concentration. It must be noted that the [Hbet][Tf₂N]-H₂O system shows some resemblance with the water-based two-phase systems consisting of mixtures of tetrabutylammonium bromide (TBAB) and (NH₄)₂SO₄ that have been used by Akama and co-workers for the extraction of metal complexes, since [Hbet][Tf₂N] is distributed after phase separation over the [Hbet][Tf₂N]-rich IL phase and the [Hbet][Tf₂N]-lean aqueous phase.^{31,32}

In conclusion, this Letter shows for the first time that ILs can be used for homogeneous liquid-liquid extraction of metal ions. The proof-of-principle is given with the functionalized IL [Hbet][Tf₂N] as the organic phase and zwitterionic betaine as the extractant. The IL forms a homogeneous solution with water above the upper critical temperature of 55 °C. In the single-phase mixture, the interaction between the metal ions and the extractant is fast. Cooling to room temperature induces phase separation, and the metal ions are distributed between the two phases. It was shown that this extraction system is suitable for the extraction of Cu²⁺, In³⁺ and the trivalent rare-earth ions. Especially Sc³⁺, Ga³⁺, and In³⁺ are very strongly extracted to the IL phase. The possibility of stripping the metal ions from the IL phase with a strong acid has been proven. Further work on homogeneous liquid-liquid extraction of metal ions with ILs is in progress, with emphasis on new extraction systems and speciation studies.

ASSOCIATED CONTENT

Supporting Information

Experimental details, phase diagram, and graph with extraction efficiency as a function of the temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Nockemann, P.; Thijs, B.; Pittois, S.; Thoen, J.; Glorieux, C.; Van Hecke, K.; Van Meervelt, L.; Kirchner, B.; Binnemans, K. Task-Specific Ionic Liquid for Solubilizing Metal Oxides. *J. Phys. Chem. B* **2006**, *110*, 20978–20992.
- (2) Nockemann, P.; Thijs, B.; Parac-Vogt, T. N.; Van Hecke, K.; Van Meervelt, L.; Tinant, B.; Hartenbach, I.; Schleid, T.; Ngan, V. T.; Nguyen, M. T.; Binnemans, K. Carboxyl-Functionalized Task-Specific Ionic Liquids for Solubilizing Metal Oxides. *Inorg. Chem.* **2008**, *47*, 9987–9999.
- (3) Nockemann, P.; Binnemans, K.; Thijs, B.; Parac-Vogt, T. N.; Merz, K.; Mudring, A. V.; Menon, P. C.; Rajesh, R. N.; Cordoyannis, G.; Thoen, J.; Leys, J.; Glorieux, C. Temperature-Driven Mixing-Demixing Behavior of Binary Mixtures of the Ionic Liquid Choline Bis(trifluoromethylsulfonyl)imide and Water. *J. Phys. Chem. B* **2009**, *113*, 1429–1437.
- (4) Lachwa, J.; Szydłowski, J.; Makowska, A.; Seddon, K. R.; Esperanca, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N. Changing from an Unusual High-Temperature Demixing to a UCST-Type in Mixtures of 1-Alkyl-3-Methylimidazolium Bis((trifluoromethyl)sulfonyl)amide and Arenes. *Green Chem.* **2006**, *8*, 262–267.
- (5) Fukaya, Y.; Sekikawa, K.; Murata, K.; Nakamura, N.; Ohno, H. Miscibility and Phase Behavior of Water-Dicarboxylic Acid Type Ionic Liquid Mixed Systems. *Chem. Commun.* **2007**, 3089–3091.
- (6) Nockemann, P.; Pellens, M.; Van Hecke, K.; Van Meervelt, L.; Wouters, J.; Thijs, B.; Vanecht, E.; Parac-Vogt, T. N.; Mehdi, H.; Schaltin, S.; Franssaer, J.; Zahn, S.; Kirchner, B.; Binnemans, K. Cobalt(II) Complexes of Nitrile-Functionalized Ionic Liquids. *Chem.—Eur. J.* **2010**, *16*, 1849–1858.
- (7) Kohno, Y.; Ohno, H. Temperature-Responsive Ionic Liquid/Water Interfaces: Relation between Hydrophilicity of Ions and Dynamic Phase Change. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5063–5070.
- (8) Kohno, Y.; Arai, H.; Saita, S.; Ohno, H. Material Design of Ionic Liquids to Show Temperature-Sensitive LCST-Type Phase Transition after Mixing with Water. *Aust. J. Chem.* **2011**, *64*, 1560–1567.
- (9) Fukumoto, K.; Ohno, H. LCST-Type Phase Changes of a Mixture of Water and Ionic Liquids Derived from Amino Acids. *Angew. Chem., Int. Ed.* **2007**, *46*, 1852–1855.
- (10) Lachwa, J.; Szydłowski, J.; Najdanovic-Visak, V.; Rebelo, L. P. N.; Seddon, K. R.; da Ponte, M. N.; Esperanca, J. M. S. S.; Guedes, H. J. R. Evidence for Lower Critical Solution Behavior in Ionic Liquid Solutions. *J. Am. Chem. Soc.* **2005**, *127*, 6542–6543.
- (11) Xie, Z. L.; Taubert, A. Thermomorphic Behavior of the Ionic Liquids [C₄mim][FeCl₄] and [C₁₂mim][FeCl₄]. *ChemPhysChem* **2011**, *12*, 364–368.
- (12) Wellens, S.; Thijs, B.; Binnemans, K. An Environmentally Friendlier Approach to Hydrometallurgy: Highly Selective Separation of Cobalt from Nickel by Solvent Extraction with Undiluted Phosphonium Ionic Liquids. *Green Chem.* **2012**, *14*, 1657–1665.
- (13) Parmentier, D.; Metz, S. J.; Kroon, M. C. Tetraalkylammonium Oleate and Linoleate Based Ionic Liquids: Promising Extractants for Metal Salts. *Green Chem.* **2013**, *15*, 205–209.
- (14) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room Temperature Ionic Liquids as Novel Media for ‘Clean’ Liquid-Liquid Extraction. *Chem. Commun.* **1998**, 1765–1766.
- (15) Rao, P. R. V.; Venkatesan, K. A.; Rout, A.; Srinivasan, T. G.; Nagarajan, K. Potential Applications of Room Temperature Ionic Liquids for Fission Products and Actinide Separation. *Sep. Sci. Technol.* **2012**, *47*, 204–222.
- (16) Liu, Y.; Chen, J.; Li, D. Application and Perspective of Ionic Liquids on Rare Earths Green Separation. *Sep. Sci. Technol.* **2012**, *47*, 223–232.
- (17) Billard, I. Chapter 256 - Ionic Liquids: New Hopes for Efficient Lanthanide/Actinide Extraction and Separation? In *Handbook on the Physics and Chemistry of Rare Earths Including Actinides*; Bünzli, J. C. G., Pescharsky, V., Eds.; Elsevier: 2013; pp 213–273.
- (18) Vander Hoogerstraete, T.; Wellens, S.; Verachtert, K.; Binnemans, K. Removal of Transition Metals from Rare Earths by Solvent Extraction with an Undiluted Phosphonium Ionic Liquid: Separations Relevant to Rare-Earth Magnet Recycling. *Green Chem.* **2013**, *15*, 919–927.
- (19) Lamb, J. D.; Peterson, R. T. Coalescence Extraction - A Novel, Rapid Means of Performing Solvent Extractions. *Sep. Sci. Technol.* **1995**, *30*, 3237–3244.
- (20) Ullmann, A.; Ludmer, Z.; Shinnar, R. Phase-Transition Extraction Using Solvent Mixtures with Critical-Point of Miscibility. *AIChE J.* **1995**, *41*, 488–500.
- (21) Schaadt, A.; Bart, H. J. Coalescence Extraction — A Benign Extraction Tool. *Chem. Eng. Technol.* **2003**, *26*, 469–472.
- (22) Hosseini, M. H.; Alizadeh, N. Coalescence Extraction System for Rapid Efficient and Selective Separation of Zirconium and Hafnium. *Ind. Eng. Chem. Res.* **2010**, *49*, 7068–7073.
- (23) Alizadeh, N.; Ashtari, K. Coalescence Extraction of Silver(I) Using the Temperature-Induced Phase Separation (TIPS) Process. *Sep. Purif. Technol.* **2005**, *44*, 79–84.

(24) Xu, J. Z.; Rajapakse, N.; Finston, H. L. Homogeneous Liquid–Liquid-Extraction of Uranium from Fission-Products. *Radiochim. Acta* **1990**, *49*, 135–140.

(25) Murata, K.; Ikeda, S.; Yokoyama, Y. Homogeneous Liquid–Liquid Extraction Method - Extraction of Iron(III) Thenoyltrifluoroacetate by Propylene Carbonate. *Anal. Chem.* **1972**, *44*, 805–810.

(26) Preston, J. S. Solvent-Extraction of Metals by Carboxylic-Acids. *Hydrometallurgy* **1985**, *14*, 171–188.

(27) Freire, M. G.; Neves, C. M. S. S.; Silva, A. M. S.; Santos, L. M. N. B.; Marrucho, I. M.; Rebelo, L. P. N.; Shah, J. K.; Maginn, E. J.; Coutinho, J. A. P. ¹H NMR and Molecular Dynamics Evidence for an Unexpected Interaction on the Origin of Salting-In/Salting-Out Phenomena. *J. Phys. Chem. B* **2010**, *114*, 2004–2014.

(28) Saita, S.; Kohno, Y.; Ohno, H. Detection of Small Differences in the Hydrophilicity of Ions Using the LCST-Type Phase Transition of an Ionic Liquid–Water Mixture. *Chem. Commun.* **2013**, *49*, 93–95.

(29) Freire, M. G.; Carvalho, P. J.; Silva, A. M. S.; Santos, L. M. N. B.; Rebelo, L. P. N.; Marrucho, I. M.; Coutinho, J. A. P. Ion Specific Effects on the Mutual Solubilities of Water and Hydrophobic Ionic Liquids. *J. Phys. Chem. B* **2009**, *113*, 202–211.

(30) Fagnant, D. P.; Goff, G. S.; Scott, B. L.; Runde, W.; Brennecke, J. F. Switchable Phase Behavior of [HBet][Tf₂N]–H₂O upon Neodymium Loading: Implications for Lanthanide Separations. *Inorg. Chem.* **2013**, *52*, 549–551.

(31) Akama, Y.; Ito, M.; Tanaka, S. Selective Separation of Cadmium from Cobalt, Copper, Iron(III) and Zinc by Water-Based Two-Phase System of Tetrabutylammonium Bromide. *Talanta* **2000**, *53*, 645–650.

(32) Akama, Y.; Sali, A. Extraction Mechanism of Cr(VI) on the Aqueous Two-Phase System of Tetrabutylammonium Bromide and (NH₄)₂SO₄ Mixture. *Talanta* **2002**, *57*, 681–686.