

Solvent Extraction of Scandium(III) by an Aqueous Biphasic System with a Nonfluorinated Functionalized Ionic Liquid

Daphne Depuydt,[†] Wim Dehaen,[†] and Koen Binnemans^{*,†}

[†]KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Heverlee, Belgium

S Supporting Information

ABSTRACT: The use of ionic liquids (ILs) as solvents for extraction of metals is a promising development in separation science and technology; yet, the viscosities of ionic liquids (ILs) can be so high that long reaction times are required to reach the equilibrium state. An aqueous biphasic system (ABS) consisting of the nonfluorinated carboxyl-functionalized phosphonium IL [P₄₄₄C₁COOH]Cl and a 16 wt % NaCl solution is described. The IL-rich phase of the aqueous biphasic system has a very low viscosity, in comparison to the pure IL [P₄₄₄C₁COOH]Cl. This system has excellent extraction properties for scandium. Different extraction parameters were investigated, including contact time and metal loading. The influence of the pH on the solubility of the IL cation in the water-rich phase was determined via quantitative ¹H NMR. The stripping of scandium with oxalic acid from the IL phase was also investigated. A plausible extraction mechanism is proposed where three IL cations are deprotonated to form zwitterionic compounds that can coordinate scandium(III) ions.



1. INTRODUCTION

Ionic liquids (ILs) are solvents that consist entirely of ions.^{1–3} Because of their low flammability, negligible vapor pressure, and, thus, low volatility, they can be environmentally friendlier and safer to use than conventional volatile molecular solvents. The versatility of ILs, in which the chemical structure can be tuned to fit the requirements of any wanted application, is a great advantage of these solvents. Functionalized ILs contain a functional group in their structure and are also known as task-specific ILs.⁴ The carboxyl functional group has proven to be a good moiety for the extraction of metal ions.⁵ Carboxylic acids are used as extractants for the separation of copper from nickel and cobalt in hydrometallurgical processes.⁶ Given the fact that carboxylic acids are extractants for metal ions in solvent extraction processes, functionalization of an IL with a carboxylic acid was a logical step. Several examples of carboxyl-functionalized ILs have been described in the literature.^{7–11}

In most studies on solvent extraction processes with ILs, only hydrophobic ILs were considered. The number of hydrophobic ILs is limited and the majority of these ILs have fluorinated anions. Fluorinated ILs are expensive and persistent in nature, which makes them difficult to dispose of. Besides that, in the case of hexafluorophosphate anions, the hydrolysis of the anion, leading to the formation of hazardous hydrofluoric acid, is a major disadvantage.¹² A first step toward a greener process for solvent extraction of metals was already taken by the incorporation of nonfluorinated ILs in solvent extraction systems. ILs such as Cyphos IL 101 and Aliquat 336 are used in extraction systems, yet often with molecular solvents as diluents and thus, undermining the green character of the system.^{13–32}

Nonfluorinated ILs with long alkyl chains in their pure form are very viscous. A high viscosity hampers the mass transfer and

slows the kinetics. So, longer mixing times are needed for an exchange across the phase boundary. This can be solved by saturating the IL with water, by performing the extractions at elevated temperatures, and by lowering the concentrations of metal salts in the aqueous feed solution, since viscosity problems mainly arise with high metal loadings.³³ Another way to circumvent the issues related to highly viscous ILs in solvent extraction systems is by using ILs with *thermomorphic behavior*. A two-phase IL/solvent mixture is converted to one homogeneous phase by increasing the temperature in case of a system with an *upper critical solution temperature* (UCST). *Homogeneous liquid–liquid extraction* (HLL) takes advantage of the homogeneous phase above the UCST. Recently, HLL processes based on the use of thermomorphic ILs have been developed.^{34–36} In this way, the ILs that have a temperature-dependent miscibility with water can also be exploited for solvent extraction, since phase separation is controlled by temperature. Completely hydrophilic ILs have been neglected when it comes to extraction experiments, because they dissolve in water and do not form two phases. However, it is possible to use them in *aqueous biphasic systems* (ABS), which are also known as *aqueous two-phase systems* (ATPS). Conventional aqueous biphasic systems are polymer–polymer, polymer–salt, and salt–salt systems.³⁷ ABS has been extensively used for the separation and analytical studies of biomaterials since Albertsson developed the novel liquid–liquid extraction technique in the 1950s.³⁸ Aqueous biphasic systems are water-based and they show a large biocompatibility, so that

Received: May 23, 2015

Revised: August 25, 2015

Accepted: August 26, 2015

Published: August 26, 2015

they are being used in the recovery and purification of proteins and nucleic acids,^{38,39} and for the preconcentration of solutes from small samples of metal chelates and porphyrins.^{40,41} Metal ions can also be extracted with the aqueous two-phase systems, although the number of examples is limited.^{42–45} Three different categories of ABS for extraction of metal ions can be defined: (i) extraction using a water-soluble extractant; (ii) extraction of metal ions as metal complexes with inorganic anions, and (iii) extraction by the polymer-rich phase.⁴⁶

The proof-of-principle for an IL-based ABS was reported by Rogers et al. in 2003,⁴⁷ and in the past decade, the literature on the theme has increased significantly, including polymer–IL-based ABS.^{48–57} The aqueous solution of an IL can undergo a liquid–liquid demixing upon addition of a salting-out agent. In this way, phase separation is chemically induced and a binary system consisting of an IL-rich phase and a salt-rich phase is formed. This implies complete control over the miscibility of the IL, which is essential for separation technologies. The advantages of IL-based ABS are 2-fold: the viscosity problem is solved because of the large water content of the IL-rich phase and the possibility to use water-miscible nonfluorinated ILs. The nonfluorinated ILs have great potential in this new separation technique. Moreover, they are less expensive and easier to dispose of than their fluorinated counterparts. The IL-based ABS opens the door to a new, greener solvent extraction system for metals. Although ABS is popular for the extraction of biomolecules,^{53,58–60} examples of the use of IL-based ABS for the extraction of metal ions are still rather scarce. Akama et al. have reported on ATPS with tetrabutylammonium bromide, for the extraction of cadmium and chromium(VI).^{61,62}

Scandium is a rare element, and of high technological interest. It can be used as an alloying metal for aluminum,⁶³ as well as in scandium-stabilized zirconia for solid oxide fuel cells,⁶⁴ and scandium(III) triflate is a recyclable Lewis acid catalyst used for the production of fine chemicals.⁶⁵ There are no scandium-rich deposits, but the element is produced as a byproduct during production of other metals (tin, tungsten, nickel, uranium, tantalum) or recovered from previously processed tailings or industrial process residues.⁶⁶ Solvent extraction is the most often used method for the recovery and purification of scandium.^{67–75}

In this paper, the solvent extraction of scandium was performed in an aqueous biphasic system with the water-miscible carboxyl-functionalized phosphonium IL [P₄₄₄C₁COOH]Cl (Figure 1), the aqueous miscibility of

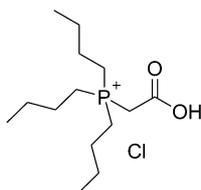


Figure 1. Structure of the ionic liquid (IL) tri-*n*-butyl(carboxymethyl)-phosphonium chloride, [P₄₄₄C₁COOH]Cl.

which was controlled by the addition of sodium chloride as a salting-out agent. The phase behavior of the ternary system was studied. Different extraction parameters, such as contact time, pH, and metal loading, were investigated. Furthermore, the extraction mechanism was examined, as well as the stripping of the metal from the IL.

2. EXPERIMENTAL SECTION

Chemicals. Tributylphosphine (99%), sodium chloride, and scandium(III) chloride hydrate (99.9%) were purchased from Sigma–Aldrich (Diegem, Belgium). Absolute ethanol and hydrogen chloride (37%) were obtained from VWR (Leuven, Belgium). Ethyl chloroacetate (99%) and phenol (99+%) were purchased from Acros Organics (Geel, Belgium). Sodium hydroxide was acquired from ChemLab (Zedelgem, Belgium). Acetonitrile (HPLC grade) was obtained from Fischer Chemicals (Geel, Belgium). Oxalic acid (>99.5%) was obtained from J.T. Baker. A 1000 ppm gallium ICP standard and 1000 ppm lanthanum ICP standard were obtained from Merck (Overijse, Belgium). The silicone solution in isopropanol was purchased from SERVA Electrophoresis GmbH (Heidelberg, Germany). All chemicals were used as received without further purification.

Equipment and Characterization. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ¹H, 75 MHz for ¹³C). ³¹P NMR (255 MHz) spectra were recorded on a Bruker AMX 600 MHz spectrometer. ⁴⁵Sc NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer (operating at 97.2 MHz for ⁴⁵Sc). The chemical shifts are noted in parts per million (ppm), referenced to tetramethylsilane for ¹H and ¹³C, to 85% H₃PO₄ for ³¹P NMR, and to ScCl₃ (1 M) for ⁴⁵Sc NMR (see Figure S1 in the Supporting Information). All solutions were made in CDCl₃, except for the ⁴⁵Sc NMR, where D₂O was used. The spectra were analyzed with SpinWorks software. The Fourier transform infrared (FTIR) spectrum of the IL was recorded by a Bruker Vertex 70 spectrometer via the attenuated total reflectance (ATR) technique with a Bruker Platinum ATR accessory. The OPUS software package was used for analysis of the FTIR spectra. The elemental analysis of carbon, hydrogen, and nitrogen (CHN analysis) was performed on a CE Instruments Model EA-1110 elemental analyzer. The water content was determined by coulometric Karl Fischer titration, using a Mettler–Toledo DL39 titrator. The viscosity of the ILs was measured using an automatic plate-cone viscometer (Model LVDV-II CP, Brookfield Engineering Laboratories, USA). The error on the viscosity measurements is estimated to be <5%. The density of the IL was measured using a 5 mL pycnometer. ESI-MS was performed on a Thermo Electron LCQ Advantage ion trap mass spectrometer connected to Agilent Model 1100 HPLC system coupled to Xcalibur data system. The pK_a of the acidic IL was measured with a Mettler–Toledo T90 titrator with LabX titration software. Extraction experiments were performed in a TMS-200 thermoshaker (Nemux Life). A Bruker Model S2 Picofox total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal concentrations in both aqueous and organic (IL) phase. The lower limit of detection for Sc(III) is 2 ppm. Extraction mixtures were centrifuged using a Heraeus Labofuge 200. pH measurements were performed with a pH/ion meter (Mettler–Toledo, Model S220 SevenCompact) and a Slimtrode (Hamilton) electrode.

Synthesis of Functionalized IL [P₄₄₄C₁COOH]Cl. The synthesis of the IL [P₄₄₄C₁COOH]Cl was partly based on literature procedures.^{76,77} A solution of ethyl chloroacetate (50 mmol) in acetonitrile was purged with argon for 10 min. Tributylphosphine (50 mmol) was added dropwise, and the mixture was refluxed for 24 h. The solvent was evaporated and a 15 vol % aqueous solution of HCl was added, and the solution

was refluxed for 5 h. Next, the solvent was evaporated again and the IL fully dried on a high vacuum line (50 °C). A light yellow viscous liquid was formed (14.38 g, 92%). ¹H NMR (300 MHz, δ, CDCl₃): 9.57 (1H, s, COOH), 3.97 (2H, d, 13.0 Hz, CH₂), 2.37 (6H, m, 3 CH₂), 1.51 (12H, m, 6 CH₂), 0.95 (9H, t, 7.0 Hz, 3 CH₃). ¹³C NMR (75 MHz, δ, CDCl₃): 165.89 (C=O), 27.77 (CH₂), 23.98 (CH₂), 23.52 (CH₂), 19.65 (CH₂), 19.01 (CH₂), 13.39 (CH₃). ³¹P NMR (255 MHz, δ, CDCl₃): 32.20. FTIR-ATR: (ν/cm⁻¹): 2960, 2933, 2873, 1713 (C=O), 1464, 1097, 909. CHN analysis (calculated for C₁₄H₃₀ClO₂P·2H₂O): C 50.36% (50.30%), H 10.83% (10.30%), N 0% (0%). ESI-MS (MeOH): *m/z* 283.5 (100%) [P₄₄₄C₁COO]Na⁺.

Measurement of the Phase Diagram. The mutual coexistence curve for the [P₄₄₄C₁COOH]Cl/NaCl system was determined via the cloud point method at room temperature.⁷⁸ To an aqueous solution of the IL, the aqueous solution of NaCl was added until turbidity appeared. Then, pure Milli-Q water was added until this cloudiness disappeared again.

Since the IL [P₄₄₄C₁COOH]Cl is completely miscible with water and can be salted out with NaCl, the experimental conditions for phase separation were investigated first. Starting from the pure IL (0.5 g), 0.5 g of aqueous phase was added, so the mass to mass ratio was always 1:1. The IL was contacted with a solution containing a certain weight percentage of NaCl. The total concentration of salt is always half of the initial weight percentage since the mass ratio of IL and aqueous phase is equal. As a first test, a 10 wt % solution of NaCl was added to the pure IL and shaken. After settling, it could be seen that the volumes of the phases were not equal; much water had dissolved in the IL so that the volume of the IL phase was greater than that of the aqueous phase. So an overall NaCl concentration of 5 wt % was not enough for good phase separation. The addition of a 20 wt % NaCl solution to the IL resulted in the unwanted precipitation of NaCl; it was concluded that this overall concentration of 10 wt % NaCl in the aqueous biphasic system is too high. It was decided to use an average of 16 wt % NaCl solutions as aqueous phases in all systems, thus obtaining an overall concentration of 8 wt % NaCl.

Procedure for Extraction and Stripping Experiments.

Prior to the extraction, the IL was brought into contact with the 16 wt % NaCl solution in order to presaturate the IL and avoid changes in the phase volume. In a typical extraction experiment, 500 mg of this presaturated IL was mixed with 500 mg of aqueous feed solution also containing 16 wt % NaCl. The metal concentration in the aqueous feed was 5 mmol kg⁻¹, unless otherwise stated. The extraction mixture was shaken in a thermoshaker at 2500 rpm at room temperature for 15 min, unless otherwise stated. A sample of 100 mg was taken from the aqueous phase to determine the metal concentration in this phase with a TXRF spectrometer. A small amount (100 mg) of gallium (measurements of aqueous phases) or lanthanum (measurements of IL phases) ICP standard solution (1000 mg L⁻¹) was added to the sample as a reference for quantification. The sample was further diluted to 1 mL with Milli-Q water for aqueous samples, and with ethanol for the IL-rich phase. The prepared sample solutions were homogenized by vortex mixing and a small droplet (5 μL) was dispensed on a quartz sample carrier. Finally, the carrier containing the sample was dried at 60 °C for 30 min. Prior to dispensing the sample droplet, the quartz carrier was pretreated with a SERVA silicone solution in isopropanol (20 μL), in order to make the surface more

hydrophobic and keep the sample droplet in the middle of the carrier.

The extraction and stripping were evaluated by calculating the values for the distribution ratio, percentage extraction, and percentage stripping, respectively.

The distribution ratios (*D*) were calculated by the following equation:

$$D = \frac{c_{\text{org}}}{c_{\text{aq}}} \quad (1)$$

where *c*_{org} and *c*_{aq} are the metal concentration in the organic phase (i.e., IL phase, in mg/kg) and in the aqueous phase, respectively.

The percentage extraction (%*E*) of a metal is defined as

$$\%E = \frac{\text{amount of extracted metal}}{\text{total amount of metal}} \times 100 \quad (2)$$

or

$$\%E = \frac{c_{\text{org}}m_{\text{org}}}{c_{\text{org}}m_{\text{org}} + c_{\text{aq}}m_{\text{aq}}} \times 100 \quad (3)$$

After the extraction of scandium, the IL was regenerated by stripping with oxalic acid. For the stripping of the scandium, a larger extraction experiment was performed. For a stripping experiment, 500 mg of the loaded IL was taken and known amounts of oxalic acid were added to vary the molar ratios of oxalic acid over scandium.

The percentage stripping (%*S*) is defined as

$$\%S = \frac{\text{amount of stripped metal}}{\text{total amount of extracted metal}} \times 100 \quad (4)$$

or

$$\%S = \frac{c_{\text{org},0} - c_{\text{org},s}}{c_{\text{org},0}} \times 100 \quad (5)$$

where *c*_{org,0} is the metal concentration in the IL before stripping and *c*_{org,s} is the metal concentration in the IL phase after the stripping process (both in mg/kg).

Quantitative ¹H NMR. The amount of IL that is lost into the salt-rich phase during the extraction was determined by quantitative ¹H NMR. A certain amount of phenol (10 mg) was added in approximately equimolar concentrations to an aliquot of water, saturated with the IL. Phenol was chosen as internal standard, since there is no overlap with the ¹H NMR spectrum of the IL. The ¹H NMR spectrum of the water sample was recorded, and the relative concentration versus phenol and the absolute concentration of [P₄₄₄C₁COOH]Cl was calculated by integration of the peaks.

3. RESULTS AND DISCUSSION

Synthesis and Characterization of [P₄₄₄C₁COOH]Cl.

The IL [P₄₄₄C₁COOH]Cl was synthesized by reaction of tributyl phosphine with ethyl chloroacetate, followed by hydrolysis of the formed ester-functionalized IL by hydrochloric acid. The structure of the product was confirmed by ¹H and ¹³C NMR, ATR-FTIR spectroscopy, and CHN analysis. The IL is completely miscible with water and polar solvents such as ethanol in all volume ratios, yet totally immiscible with nonpolar solvents such as toluene and heptane. The dried IL still contained 0.12 wt % of water, equivalent to 1159 ppm. This was used as the pure IL. The viscosity of this IL is very high:

>20 000 cP at room temperature. A high viscosity is typical for many functionalized ILs, since the presence of the functional group gives rise to extra intermolecular interactions (e.g., hydrogen bonds) in the IL. The viscosity of the IL-rich phase of the aqueous biphasic system was much lower (400 cP) at room temperature, which is beneficial for extractions (Figure 2). The

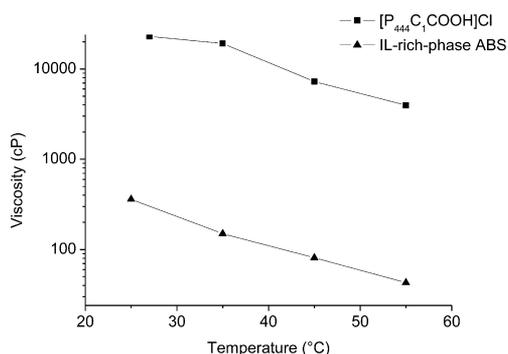


Figure 2. Temperature dependence of the viscosities of the pure IL $[P_{444}C_1COOH]Cl$ and the IL phase that was contacted with a 16 wt % NaCl solution in Milli-Q water.

pK_a of the carboxyl functional group is 2.32 in this IL. The density of the pure IL is 0.9648 g cm^{-3} at room temperature. After phase separation in water by the salting-out with NaCl, the IL-rich phase will be the upper phase. Even after presaturation, an amount of the IL still dissolves in the salt-rich water phase; this loss was determined by quantitative 1H NMR to be 5.79 wt %.

Characterization of Aqueous Biphasic System. The mutual coexistence curve for the $[P_{444}C_1COOH]Cl$ –NaCl system was determined via the cloud point method at room temperature.⁷⁸ Since it is virtually impossible to stir the very viscous pure IL, the IL was dissolved in a small amount of water to facilitate the stirring process. To this aqueous solution of 80 wt % IL, the 16 wt % aqueous solution of NaCl was added until turbidity appeared. Pure Milli-Q water then was added until this cloudiness disappeared again. This procedure was repeated several times until turbidity was no longer observed. The ternary phase diagram of the ABS composed of the IL, NaCl, and water is given in Figure 3. In this orthogonal representation, the water fraction is omitted so that pure water becomes the origin of the axes. Although, in the literature, the salts K_3PO_4 or K_2HPO_4 are used most often,⁵¹ in case of the rare earths, these salts cannot be used since

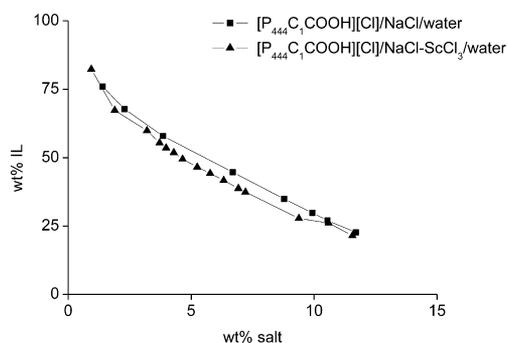


Figure 3. Ternary phase diagrams of ABS composed of (■) $[P_{444}C_1COOH]Cl + NaCl + water$ and (▲) $[P_{444}C_1COOH]Cl + NaCl-ScCl_3 + water$ at 298 K (values given in units of wt %).

insoluble rare-earth phosphates would be formed. NaCl is preferred as the salting-out agent in the aqueous biphasic system for three reasons: (1) it is an inexpensive and readily available salt with good salting-out behavior, (2) there is no possibility of mixing of anions between the IL and the salt, and (3) no anionic complexes with rare-earth ions are formed at medium chloride concentrations, which avoids complication of the extraction mechanism. In the extraction itself, not only pure NaCl, but also $ScCl_3$ is present in the system. Therefore, the influence of the addition of 5 mmol kg^{-1} of $ScCl_3$ salt to the ABS was investigated. The $ScCl_3$ solution has a pH of 3, so no hydrolysis of this solution occurs.⁷⁹ Taking the amount of scandium(III) chloride salt in the aqueous phase into account, there is definitely a shift to the left in the orthogonal phase diagram (Figure 3). This is obvious when looking at the salting-out effect: the higher charge density of Sc^{3+} , in comparison to that of Na^+ , causes a higher hydration energy for Sc^{3+} , since a higher charge density means more strongly hydrated cations. Water molecules form a hydration shell around the cations of the added salt and no longer around the IL cations, which favors the phase separation of the IL.

Extraction Experiments. The aqueous biphasic system was used for the solvent extraction of scandium(III). Given the fact that carboxylic acids are extractants for metal ions in solvent extraction processes, and are known to be excellent extractants for scandium(III),³⁴ a carboxyl-functionalized IL was the IL of choice. In this way, the extracting group is covalently tethered to the cationic part in the IL. Prior to the extraction, the IL was brought into contact with the 16 wt % NaCl solution in order to presaturate the IL and minimize changes in the phase volume. In every extraction experiment, 500 mg of $[P_{444}C_1COOH]Cl$ (presaturated with 16 wt % NaCl) was mixed with 500 mg of aqueous feed solution (containing 16 wt % NaCl). The metal concentration in the aqueous feed was 5 mmol kg^{-1} , unless otherwise stated. The extraction mixture was shaken in a thermoshaker at 2500 rpm at room temperature for 15 min, unless otherwise stated. The two phases were allowed to settle, a process that was accelerated by centrifugation. A sample of 100 mg was taken from the aqueous phase to determine the metal concentration in this phase with a TXRF spectrometer. To express the efficiency of the extraction system, the distribution ratio (D) can be used (eq 1). Another possible way is to use the percentage extraction (%E) (eq 2).

First, the conditions necessary to obtain extraction equilibrium were determined. An aliquot of 0.5 g of $ScCl_3$ (5 mmol kg^{-1}) solution containing 16 wt % NaCl was contacted with 0.5 g of IL (presaturated with 16 wt % of NaCl). Even after 1 min of shaking, 90% of the scandium was already extracted, and 100% extraction was achieved after 10 min (Figure 4). To ensure full equilibrium was reached, 15 min of shaking at room temperature with a shaking speed of 2500 rpm was maintained for all extraction measurements. The fast kinetics of this extraction system is most likely due to the low viscosity of the water-saturated IL, even when loaded with metals.

The influence of the pH on the solubility of the IL cation in the water-rich phase was tested. The pH was varied from 3.33 to 0 in the aqueous feed solution containing 5 mmol kg^{-1} of Sc and 16 wt % of NaCl, similar to that of a regular extraction feed. Five hundred milligrams (500 mg) of the presaturated IL was brought in contact with 500 mg of the aqueous layer. The mixtures were shaken for 15 min to ensure equilibrium after

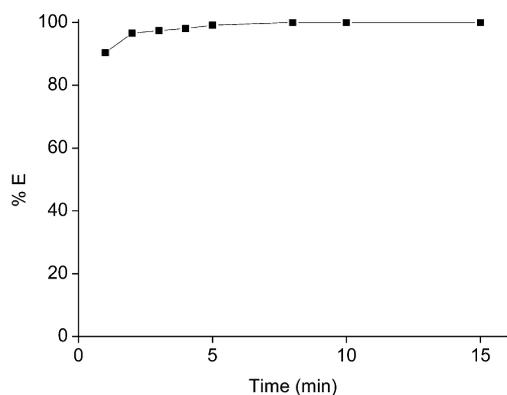


Figure 4. Percentage extraction as a function of time ($[P_{444}C_1COOH]Cl$ (presaturated with 16 wt % NaCl), scandium concentration = 5 mmol kg^{-1} , 16 wt % NaCl solution, $pH_{eq} = -0.15$, room temperature, 2500 rpm).

which the phases were allowed to settle by centrifuging. Billard and co-workers reported on quantitative NMR studies for the determination of the quantity of both IL cations and anions transferred in the upper phase of biphasic systems.⁸⁰ Here, the solubility of the IL cation in the water-rich phase was investigated via quantitative 1H NMR. So far, little research has been performed on the effect of pH on ABS. Generally, an ABS is more easily formed under alkaline conditions than under acidic or neutral conditions.^{51,81} When a citrate salt is used as a salting-out agent, it is observed that a decrease of the pH of the aqueous solution leads to an increase of the homogeneous area of the phase diagram.^{82,83} Different surface charges and degree of protonation form the basis of the differences in the ABS formation. This is also visualized in Figure 5: at lower pH, there is a higher solubility of the IL cation in the water-rich phase.

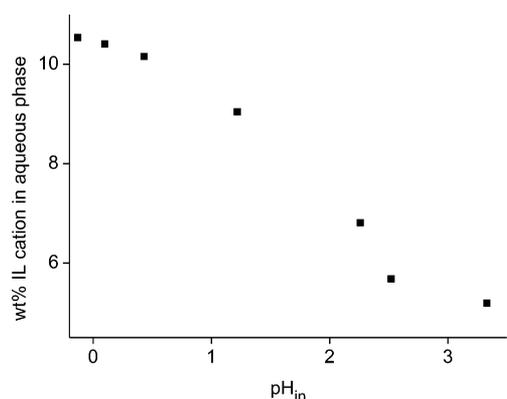


Figure 5. Solubility of the IL cation $[P_{444}C_1COOH]^+$ in the water-rich-phase is higher with lower pH.

It should be remarked the pH of scandium(III) solution should always be kept below pH 4 to avoid hydrolysis of the scandium(III) ions, and prevent precipitation of $Sc(OH)_3$ ($K_{sp} \approx 10^{-32}$).⁷⁹ The solubility of IL cation into the water-rich-phase was also determined for the presaturated solution (without $ScCl_3$), this amounted in 5.79 wt %, with an aqueous solution having a pH of 6.8. This is comparable to the solubility of IL cation contacted with a Sc(III) feed solution of pH 2.5, again showing the favorable salting-out effect of the Sc^{3+} .

In this study, the pH dependence is based on the acid–base equilibrium in the water-rich-phase (eq 6).



Via titration of the monoprotic acid cation, a complete fractional composition diagram was determined (see Figure S2 in the Supporting Information). It can be seen that, for given pH values, there will be a different ratio of zwitterion to protonated cation. In addition, quantitative ^{13}C NMR experiments show a steady increase in the amount of zwitterions with higher pH (Figure 6). The zwitterionic form is more hydrophobic; thus, a lower solubility is observed at higher pH values.

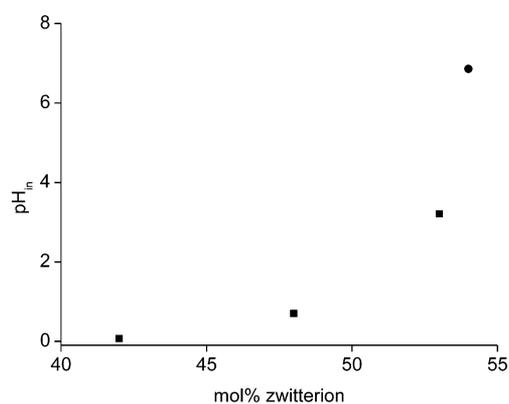


Figure 6. Amount of zwitterion (mol %), as a function of initial pH the IL-rich phase is contacted with: (■) IL-rich phase in contact with Sc feed solution of 5 mmol/kg and 16 wt % NaCl, and (●) IL-rich phase in contact with an aqueous solution of 16 wt % NaCl.

The influence of the initial metal feed concentration on the percentage extraction also was investigated. As expected, the percentage extraction lowers with increasing metal concentration, since the distribution of scandium is now influenced by the loading effect. To ensure full equilibrium with the higher metal concentrations, 30 min was taken as the shaking time. Until an initial scandium(III) loading of $\sim 10 \text{ mmol kg}^{-1}$, 100% extraction efficiency is found. Then, a sharp decrease in extraction efficiency is seen, reaching only 60% extraction for an initial feed of 130 mmol kg^{-1} . For higher initial feed concentrations, the slope of the decrease is lower. At $\sim 1.4 \text{ mol kg}^{-1}$, only 30% extraction is reached (Figure 7). Note that the pH_{eq} is fairly low at -0.3 , caused by the protons that are set free during the extraction.

The low extraction efficiencies at high initial feed stocks, together with the high solubility of the IL cation in the water layer at these low pH values made further increases in the loading in the IL-rich-phase not economical. Yet, another technique to load the IL was performed: the cumulative loading. In this experiment, the IL is repeatedly brought into contact with a novel Sc(III) feed. The IL-rich phase (500 mg) was contacted with 500 mg of a Sc(III) feed of 0.80 mol kg^{-1} (also containing 16 wt % NaCl). After the first extraction, 0.42 mol kg^{-1} scandium was taken up in the IL. The IL-rich-phase was isolated and after two repeated contacts with the Sc(III) feed, the IL was loaded with 0.95 mol kg^{-1} Sc(III). ATR-FTIR spectra of the IL-rich phase of the extraction, loaded with increasing amounts of scandium (0 – 0.95 mol kg^{-1}), showed that the scandium ion is coordinated to the IL via the carboxylic acid function on the cation (Figure 8). Taking in account the deprotonation of the carboxylic group in $[P_{444}C_1COOH]Cl$ and its affinity to Sc^{3+} , a complex of the form

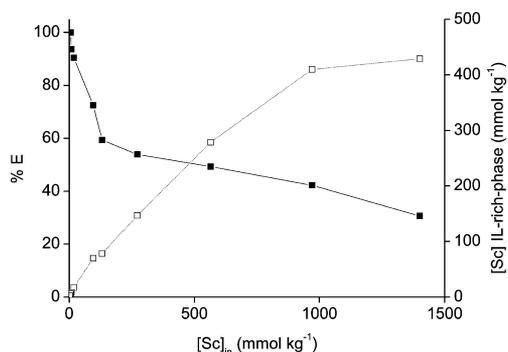


Figure 7. Loading of the IL-rich-phase: (■) percentage extraction and (□) scandium concentration in the IL-rich-phase after extraction, as a function of the initial scandium concentration. ([P₄₄₄C₁COOH]Cl (presaturated with 16 wt % NaCl), pH_{eq} = -0.3, 16 wt % NaCl feed solution with varying scandium concentration, room temperature, 2500 rpm, 30 min.)

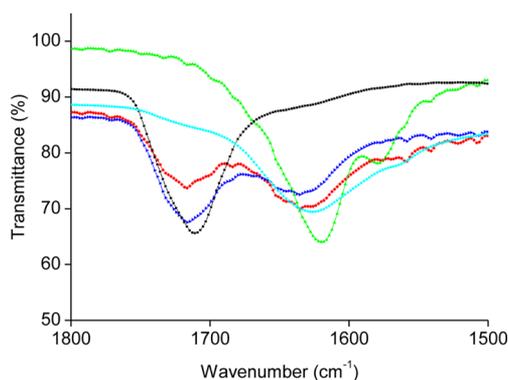
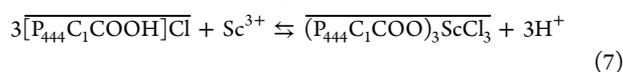


Figure 8. ATR-FTIR spectra of the carboxyl peak of [P₄₄₄C₁COOH]Cl. (Legend: black symbols, dry IL; blue symbols, IL-rich-phase ABS; red symbols, IL-rich-phase ABS loaded with Sc (0.2 mol kg⁻¹); light blue, IL-rich-phase ABS maximum loading of Sc (0.95 mol kg⁻¹); green symbols, P₄₄₄C₁COO⁻ zwitterion.)

[(P₄₄₄C₁COO)_nSc]³⁺ must take part in the extraction. The maximum loading was confirmed by ATR-FTIR and is consistent with a ligand-to-metal ratio of 3:1, proposing that the extraction mechanism is occurring via a complex with three IL-zwitterionic molecules.

For the carboxyl-functionalized IL [Hbet][Tf₂N], the extraction mechanism has been thoroughly investigated.⁸⁴ It has been shown that scandium(III) was extracted as a complex with the zwitterionic betaine in a 1:3 stoichiometry, with three bistriflimide counterions. Proton exchange occurs upon extraction of scandium(III), and three protons are transferred to the aqueous phase. Since (i) the [P₄₄₄C₁COOH]Cl IL has a structure similar to that of the IL [Hbet][Tf₂N] and (ii) from the maximum loading, the ligand-to-metal ratio of 3:1 was also confirmed, the suggested expression for the extraction mechanism of this system is given as eq 7:



Stripping Experiments. After the extraction, it is important to remove the metal ions from the IL-rich phase. This is done during the stripping process, which is usually achieved by the addition of an acid to the IL-rich phase. However, the system is already working at very low pH values and the addition of HCl to the system is troublesome, since it

induces phase changes. Therefore, a more appropriate technique for removing the metals from the IL is precipitation stripping. This can be easily done via the addition of solid oxalic acid to the IL-rich phase. For the stripping of scandium, a larger extraction experiment was performed. First, the IL-rich phase was loaded with 65 mmol kg⁻¹ of scandium. The effect of the molar ratios of oxalic acid over scandium of the same loaded IL was then investigated. The stripping efficiency is expressed by the percentage stripping (S; recall eqs 4 and 5). The stripping efficiency, as a function of the oxalic acid/scandium molar ratio in the IL-rich phase, is given in Figure 9. In the first instance,

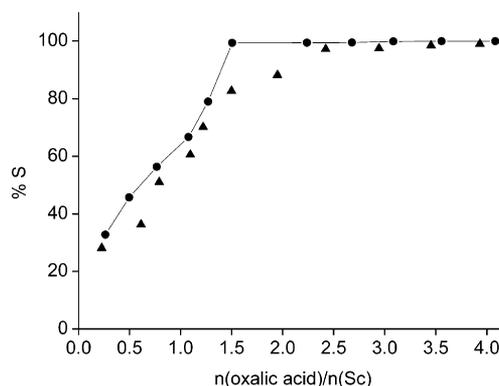
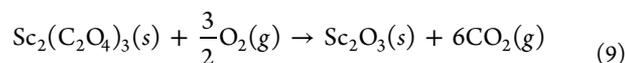
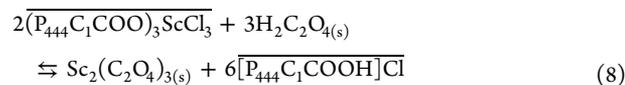


Figure 9. Precipitation stripping of the IL-rich-phase, where the percentage stripping is a function of the molar ratio of oxalic acid to Sc(III): (▲) pure IL-rich-phase, 70 °C, 30 min, and (●) 16 wt % NaCl solution added to isolate HCl, 30 °C, 1 h. (IL-rich-phase loaded with 65 mmol kg⁻¹ Sc, 16 wt % NaCl solution, 2500 rpm).

oxalic acid was added to the scandium-loaded IL-rich phase and the mixture was shaken at 70 °C for 30 min for kinetic reasons. The expected 100% stripping at a molar ratio of 1.5 is not observed. Most likely, this is caused by the presence of HCl in the IL-rich phase after the extraction. In this way, oxalate is present in the protonated form, so the precipitation equilibrium is pushed to the left (eq 8). With the addition of a 16 wt % NaCl solution, HCl gets isolated from the IL-rich phase and full stripping is obtained. The molar ratios of oxalic acid over scandium $n(\text{oxalic acid})/n(\text{Sc})$ is 1.5 when a stripping efficiency of 100% is reached (Figure 9); thus, three oxalic acid molecules surround two scandium(III) metal centers (eq 8). The big advantage of precipitation stripping is that the scandium(III) oxalate precipitate can be converted to scandium(III) oxide by calcination (eq 9).



After a calcination step at 950 °C for 2 h, Sc₂O₃ with a purity of 99.45% was obtained. Also, the fact that the IL can be recycled is a major benefit for the system. An extraction efficiency of >95% was reached with the recycled IL.

4. CONCLUSIONS

The use of a nonfluorinated, functionalized ionic liquid (IL) in an aqueous biphasic system for the extraction of metal ions is shown. With the [P₄₄₄C₁COOH]Cl–16 wt % NaCl–water system, an environmentally friendly solvent extraction process

for the extraction of scandium(III) was investigated in detail. The viscosity of the carboxyl-functionalized IL was drastically lowered by contacting it with the 16 wt % NaCl solution. The ternary phase diagram for the system was constructed to determine the suitable working conditions. Fast kinetics, the possibility to extract from a fairly low pH, and a reasonable metal loading are advantageous in this system. A plausible extraction mechanism is proposed where three IL cations are involved in the extraction of scandium. The metal ions can be stripped from the IL-rich phase via the addition of oxalic acid and 16 wt % NaCl solution, regenerating the IL that can be used again in an efficient extraction cycle.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b01910.

⁴⁵Sc NMR spectra, fractional composition (α) diagram of monoprotic acid P₄₄₄C₁COOH with pK_a = 2.32, and ATR-FTIR spectrum of the carboxyl peak (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Koen.Binnemans@chem.kuleuven.be.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was financially supported by the FWO-Flanders (Research Project No. G.0900.13), IWT-Flanders (Ph.D. fellowship to D.D.), and KU Leuven (Research Project Nos. GOA 13/008 and IOF-KP RARE³). The authors also wish to thank Karel Duerinckx for NMR measurements and Dirk Henot for performing CHN analyses. Bieke Onghena and Tom Vander Hoogerstraete are thanked for useful scientific discussions.

■ REFERENCES

- (1) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2008.
- (2) Plechkova, N. V.; Seddon, K. R. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2008**, *37*, 123.
- (3) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071.
- (4) Davis, J. H., Jr. Task-Specific Ionic Liquids. *Chem. Lett.* **2004**, *33*, 1072.
- (5) Preston, J. S. Solvent Extraction of Metals by Carboxylic Acids. *Hydrometallurgy* **1985**, *14*, 171.
- (6) Flett, D. S.; Spink, D. R. Solvent Extraction of Non-Ferrous Metals: A Review 1972–1974. *Hydrometallurgy* **1976**, *1*, 207.
- (7) 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.
- (8) Shkrob, I. A.; Marin, T. W.; Jensen, M. P. Ionic Liquid Based Separations of Trivalent Lanthanide and Actinide Ions. *Ind. Eng. Chem. Res.* **2014**, *53*, 3641.
- (9) Chiappe, C.; Pomelli, C. S. Point-Functionalization of Ionic Liquids: An Overview of Synthesis and Applications. *Eur. J. Org. Chem.* **2014**, *2014*, 6120.
- (10) 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.
- (11) Sasaki, K.; Takao, K.; Suzuki, T.; Mori, T.; Arai, T.; Ikeda, Y. Extraction of Pd(II), Rh(III) and Ru(III) from HNO₃ Aqueous Solution to Betainium Bis(Trifluoromethanesulfonyl)imide Ionic Liquid. *Dalton Trans.* **2014**, *43*, 5648.
- (12) Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. Ionic Liquids Are Not Always Green: Hydrolysis of 1-Butyl-3-Methylimidazolium Hexafluorophosphate. *Green Chem.* **2003**, *5*, 361.
- (13) Aly, H. F.; El-Garhy, M.; El-Reefy, S. Extraction of Iron, Cobalt, and Manganese from Hydrochloric Acid with Quaternary Amine, Aliquat-336. *Microchem. J.* **1972**, *17*, 431.
- (14) Wassink, B.; Dreisinger, D.; Howard, J. Solvent Extraction Separation of Zinc and Cadmium from Nickel and Cobalt Using Aliquat 336, a Strong Base Anion Exchanger, in the Chloride and Thiocyanate Forms. *Hydrometallurgy* **2000**, *57*, 235.
- (15) Sato, H. F.; Shimomura, T.; Murakami, S.; Maeda, T.; Nakamura, T. Liquid-Liquid Extraction of Divalent Manganese, Cobalt, Copper, Zinc and Cadmium from Aqueous Chloride Solutions by Tricaprylmethylammonium Chloride. *Hydrometallurgy* **1984**, *12*, 245.
- (16) Fabrega, F. d. M.; Mansur, M. B. Liquid-Liquid Extraction of Mercury(II) from Hydrochloric Acid Solutions by Aliquat 336. *Hydrometallurgy* **2007**, *87*, 83.
- (17) Campos, K.; Vincent, T.; Bunio, P.; Trochimczuk, A.; Guibal, E. Gold Recovery from HCl Solutions Using Cyphos IL-101 (a Quaternary Phosphonium Ionic Liquid) Immobilized in Biopolymer Capsules. *Solvent Extr. Ion Exch.* **2008**, *26*, 570.
- (18) Campos, K.; Domingo, R.; Vincent, T.; Ruiz, M.; Sastre, A. M.; Guibal, E. Bismuth Recovery from Acidic Solutions Using Cyphos IL-101 Immobilized in a Composite Biopolymer Matrix. *Water Res.* **2008**, *42*, 4019.
- (19) Gallardo, V.; Navarro, R.; Saucedo, I.; Avila, M.; Guibal, E. Zinc(II) Extraction from Hydrochloric Acid Solutions Using Amberlite XAD-7 Impregnated with Cyphos IL 101 (Tetradecyl(Trihexyl)-Phosphonium Chloride. *Sep. Sci. Technol.* **2008**, *43*, 2434.
- (20) Regel-Rosocka, M. Extractive Removal of Zinc(II) from Chloride Liquors with Phosphonium Ionic Liquids/Toluene Mixtures as Novel Extractants. *Sep. Purif. Technol.* **2009**, *66*, 19.
- (21) Cieszyńska, A.; Wisniewski, M. Extraction of Palladium(II) from Chloride Solutions with Cyphos (R) IL 101/Toluene Mixtures as Novel Extractant. *Sep. Purif. Technol.* **2010**, *73*, 202.
- (22) Kogelnig, D.; Stojanovic, A.; Jirsa, F.; Körner, W.; Krachler, R.; Keppler, B. K. Transport and Separation of Iron(III) from Nickel(II) with the Ionic Liquid Trihexyl(Tetradecyl)Phosphonium Chloride. *Sep. Purif. Technol.* **2010**, *72*, 56.
- (23) Mishra, R. K.; Rout, P. C.; Sarangi, K.; Nathsarma, K. C. Solvent Extraction of Fe(III) from the Chloride Leach Liquor of Low Grade Iron Ore Tailings Using Aliquat 336. *Hydrometallurgy* **2011**, *108*, 93.
- (24) Comesana, A.; Rodriguez-Monsalve, J.; Cerpa, A.; Alguacil, F. J. Non-Dispersive Solvent Extraction with Strip Dispersion (NDSXSD) Pertraction of Cd(II) in HCl Medium Using Ionic Liquid CYPHOS IL101. *Chem. Eng. J.* **2011**, *175*, 228.
- (25) Regel-Rosocka, M.; Wisniewski, M. Selective Removal of Zinc(II) from Spent Pickling Solutions in the Presence of Iron Ions with Phosphonium Ionic Liquid Cyphos IL 101. *Hydrometallurgy* **2011**, *110*, 85.
- (26) Cieszyńska, A.; Wisniewski, M. Selective Extraction of Palladium(II) from Hydrochloric Acid Solutions with Phosphonium Extractants. *Sep. Purif. Technol.* **2011**, *80*, 385.
- (27) Regel-Rosocka, M.; Nowak, L.; Wisniewski, M. Removal of Zinc(II) and Iron Ions from Chloride Solutions with Phosphonium Ionic Liquids. *Sep. Purif. Technol.* **2012**, *97*, 158.
- (28) Vander Hoogerstraete, T.; Wellens, S.; Verachttert, 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.

- (29) Wellens, S.; Goovaerts, R.; Moller, C.; Luyten, J.; Thijs, B.; Binnemans, K. A Continuous Ionic Liquid Extraction Process for the Separation of Cobalt From Nickel. *Green Chem.* **2013**, *15*, 3160.
- (30) Sato, T.; Yamamoto, M.; Sato, K. Effect of Anions on the Extraction of Nickel(II) from Aqueous Solutions by Long-Chain Alkyl Quaternary Ammonium Carboxylates. *Solvent Extr. Res. Dev. Jpn.* **2005**, *12*, 101.
- (31) Sato, T.; Yamamoto, M.; Adachi, K. Liquid-Liquid Extraction of Bivalent Zinc and Cadmium from Aqueous Solutions by Long-Chain Alkyl Quaternary Ammonium Carboxylates. *Shigen to Sozai* **2005**, *121*, 603.
- (32) Sato, T.; Yamamoto, M. The Extraction of Bivalent Transition Metals from Aqueous Chloride Solutions by Long-Chain Alkyl Quaternary Ammonium Carboxylates. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 90.
- (33) 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.
- (34) Vander Hoogerstraete, T.; Onghena, B.; Binnemans, K. Homogeneous Liquid-Liquid Extraction of Metal Ions with a Functionalized Ionic Liquid. *J. Phys. Chem. Lett.* **2013**, *4*, 1659.
- (35) Vander Hoogerstraete, T.; Onghena, B.; Binnemans, K. Homogeneous Liquid-Liquid Extraction of Rare Earths with the Betaine-Betainium Bis(Trifluoromethylsulfonyl)Imide Ionic Liquid System. *Int. J. Mol. Sci.* **2013**, *14*, 21353.
- (36) Onghena, B.; Jacobs, J.; Van Meervelt, L.; Binnemans, K. Homogeneous Liquid-Liquid Extraction of Neodymium(III) by Choline Hexafluoroacetylacetonate in the Ionic Liquid Choline Bis(Trifluoromethylsulfonyl)Imide. *Dalton Trans.* **2014**, *43*, 11566.
- (37) Hoogenboom, R. Temperature-Responsive Polymers: Properties, Synthesis and Applications. In *Smart Polymers and Their Applications*; Aguilar, M. R., Román, J. S., Eds.; Woodhead Publishing: Cambridge, U.K., 2014; Chapter 2.
- (38) Albertsson, P. A. *Partitioning of Cell Particles and Macromolecules*; Wiley: New York, 1986.
- (39) Zaslavsky, B. Y. *Aqueous Two-Phase Partitioning*; Marcel Dekker: New York, 1994.
- (40) Watanabe, H.; Tanaka, H. A Non-Ionic Surfactant as a New Solvent for Liquid-Liquid Extraction of Zinc(II) with 1-(2-Pyridylazo)-2-Naphthol. *Talanta* **1978**, *25*, 585.
- (41) Igarashi, S.; Yotsuyanagi, T. Homogeneous Liquid-Liquid Extraction by pH Dependent Phase Separation with a Fluorocarbon Ionic Surfactant and Its Application to the Preconcentration of Porphyrin Compounds. *Microchim. Acta* **1992**, *106*, 37.
- (42) Rogers, R. D.; Eiteman, M. A. *Aqueous Biphasic Separations: Biomolecules to Metal Ions*; Plenum Press: New York, 1995.
- (43) Rogers, R. D.; Bond, A. H.; Bauer, C. B.; Zhang, J.; Griffin, S. T. Metal Ion Separations in Polyethylene Glycol-Based Aqueous Biphasic Systems: Correlation of Partitioning Behavior with Available Thermodynamic Hydration Data. *J. Chromatogr., Biomed. Appl.* **1996**, *680*, 221.
- (44) Lahiri, S.; Roy, K. A Green Approach for Sequential Extraction of Heavy Metals from Li Irradiated Au Target. *J. Radioanal. Nucl. Chem.* **2009**, *281*, 531.
- (45) Silva, M. d. C. H.; Silva, L. H. M.; Paggioli, F. J.; Coimbra, J. S. R.; Minim, L. A. Aqueous Biphasic Systems: An Efficient Alternative for Extractions of Ions. *Quim. Nova* **2006**, *29*, 1332.
- (46) Rogers, R. D.; Bond, A. H.; Bauer, C. B. Metal Ion Separations in Polyethylene Glycol-Based Aqueous Biphasic Systems. *Sep. Sci. Technol.* **1993**, *28*, 1091.
- (47) Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddleston, J. G.; Swatoski, R. P.; Holbrey, J. D.; Rogers, R. D. Controlling the Aqueous Miscibility of Ionic Liquids: Aqueous Biphasic Systems of Water-Miscible Ionic Liquids and Water-Structuring Salts for Recycle, Metathesis, and Separations. *J. Am. Chem. Soc.* **2003**, *125*, 6632.
- (48) Abraham, M. H.; Zissimos, A. M.; Huddleston, J. G.; Willauer, H. D.; Rogers, R. D.; Acree, W. E. Some Novel Liquid Partitioning Systems: Water-Ionic Liquids and Aqueous Biphasic Systems. *Ind. Eng. Chem. Res.* **2003**, *42*, 413.
- (49) Kurnia, K. A.; Freire, M. G.; Coutinho, J. A. P. Effect of Polyvalent Ions in the Formation of Ionic-Liquid-Based Aqueous Biphasic Systems. *J. Phys. Chem. B* **2014**, *118*, 297.
- (50) Bridges, N. J.; Gutowski, K. E.; Rogers, R. D. Investigation of Aqueous Biphasic Systems Formed from Solutions of Chaotropic Salts with Kosmotropic Salts (Salt-Salt ABS). *Green Chem.* **2007**, *9*, 177.
- (51) Freire, M. G.; Claudio, A. F.; Araujo, J. M. M.; Coutinho, J. A. P.; Marrucho, I. M.; Lopes, J. N. C.; Rebelo, L. P. Aqueous Biphasic Systems: A Boost Brought about by Using Ionic Liquids. *Chem. Soc. Rev.* **2012**, *41*, 4966.
- (52) Pei, Y.; Wang, J.; Liu, L.; Wu, K.; Zhao, Y. Liquid-Liquid Equilibria of Aqueous Biphasic Systems Containing Selected Imidazolium Ionic Liquids and Salts. *J. Chem. Eng. Data* **2007**, *52*, 2026.
- (53) Li, Z.; Pei, Y.; Wang, H.; Fan, J.; Wang, J. Ionic Liquid-Based Aqueous Two-Phase Systems and Their Applications in Green Separation Processes. *TrAC, Trends Anal. Chem.* **2010**, *29*, 1336.
- (54) Pereira, J. F. B.; Rebelo, L. P.; Rogers, R. D.; Coutinho, J. A. P.; Freire, M. G. Combining Ionic Liquids and Polyethylene Glycols to Boost the Hydrophobic-Hydrophilic Range of Aqueous Biphasic Systems. *Phys. Chem. Chem. Phys.* **2013**, *15*, 19580.
- (55) Pereira, J. F. B.; Kurnia, K. A.; Cojocar, O. A.; Gurau, G.; Rebelo, L. P.; Rogers, R. D.; Freire, M. G.; Coutinho, J. A. P. Molecular Interactions in Aqueous Biphasic Systems Composed of Polyethylene Glycol and Crystalline vs. Liquid Cholinium-Based Salts. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5723.
- (56) Tome, L. I. N.; Pereira, J. F. B.; Rogers, R. D.; Freire, M. G.; Gomes, J. R. B.; Coutinho, J. A. P. "Washing-Out" Ionic Liquids from Polyethylene Glycol To Form Aqueous Biphasic Systems. *Phys. Chem. Chem. Phys.* **2014**, *16*, 2271.
- (57) Rodriguez, H.; Francisco, M.; Rahman, M.; Sun, N.; Rogers, R. D. Biphasic Liquid Mixtures of Ionic Liquids and Polyethylene Glycols. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10916.
- (58) Louros, C.; Cláudio, A.; Neves, C.; Freire, M.; Marrucho, I.; Pauly, J.; Coutinho, J. Extraction of Biomolecules Using Phosphonium-Based Ionic Liquids + K₃PO₄ Aqueous Biphasic Systems. *Int. J. Mol. Sci.* **2010**, *11*, 1777.
- (59) Deive, F. J.; Rodriguez, A.; Pereiro, A. B.; Araujo, J. M. M.; Longo, M. A.; Coelho, M. A. Z.; Lopes, J. N. C.; Esperanca, J. M. S. S.; Rebelo, L. P. N.; Marrucho, I. M. Ionic Liquid-Based Aqueous Biphasic System for Lipase Extraction. *Green Chem.* **2011**, *13*, 390.
- (60) Dreyer, S.; Kragl, U. Ionic Liquids for Aqueous Two-Phase Extraction and Stabilization of Enzymes. *Biotechnol. Bioeng.* **2008**, *99*, 1416.
- (61) 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.
- (62) 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.
- (63) Royset, J.; Ryum, N. Scandium in Aluminium Alloys. *Int. Mater. Rev.* **2005**, *50*, 19.
- (64) Badwal, S. P. S.; Ciacchi, F. T.; Milosevic, D. Scandia-Zirconia Electrolytes for Intermediate Temperature Solid Oxide Fuel Cell Operation. *Solid State Ionics* **2000**, *136-137*, 91.
- (65) Kobayashi, S. Scandium Triflate in Organic Synthesis. *Eur. J. Org. Chem.* **1999**, *1999*, 15.
- (66) Wang, W.; Pranolo, Y.; Cheng, C. Y. Metallurgical Processes for Scandium Recovery From Various Resources: A Review. *Hydrometallurgy* **2011**, *108*, 100.
- (67) Wang, W.; Cheng, C. Y. Separation and Purification of Scandium by Solvent Extraction and Related Technologies: A Review. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 1237.
- (68) Zhao, Z.; Baba, Y.; Kubota, F.; Kamiya, N.; Goto, M. Synergistic Extraction of Rare-Earth Metals and Separation of Scandium Using 2-Thenoyltrifluoroacetone and Tri-*n*-Octylphosphine Oxide in an Ionic Liquid System. *J. Chem. Eng. Jpn.* **2014**, *47*, 656.

- (69) Bo, Q.; Lu, J.; Li, D.; Zhang, X.; Ye, W. Extraction Separation and Mechanism of Scandium by sec-Octylphenoxy Acetic Acid from Other Rare Earth Elements. *Chin. J. Anal. Chem.* **2001**, *28*, 45.
- (70) Gorski, B.; Gorski, N.; Beer, M. Extraction of Se, Y, and Lanthanides by Quaternary Ammonium Salts. *Solvent Extr. Ion Exch.* **1991**, *9*, 623.
- (71) Karve, M.; Vaidya, B. Selective Separation of Scandium(III) and Yttrium(III) from Other Rare Earth Elements Using Cyanex302 as an Extractant. *Sep. Sci. Technol.* **2008**, *43*, 1111.
- (72) Li, D.; Wang, C. Solvent Extraction of Scandium(III) by Cyanex 923 and Cyanex 925. *Hydrometallurgy* **1998**, *48*, 301.
- (73) Peppard, D. F.; Mason, G. W.; Maier, J. L. Interrelationships in the Solvent Extraction Behaviour of Scandium, Thorium, and Zirconium in Certain Tributyl Phosphate-Mineral Acid Systems. *J. Inorg. Nucl. Chem.* **1956**, *3*, 215.
- (74) Sun, X.; Wu, D.; Chen, J.; Li, D. Separation of Scandium(III) From Lanthanides(III) With Room Temperature Ionic Liquid Based Extraction Containing Cyanex 925. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 267.
- (75) Sun, X.; Ji, Y.; Guo, L.; Chen, J.; Li, D. A Novel Ammonium Ionic Liquid Based Extraction Strategy for Separating Scandium From Yttrium and Lanthanides. *Sep. Purif. Technol.* **2011**, *81*, 25.
- (76) Chevalier, Y.; Le Perche, P. Intercharge Distance of Flexible Zwitterionic Molecules in Solution. *J. Phys. Chem.* **1990**, *94*, 1768.
- (77) Koumoto, K.; Ochiai, H.; Sugimoto, N. Structural Effect of Synthetic Zwitterionic Cosolutes on the Stability of DNA Duplexes. *Tetrahedron* **2008**, *64*, 168.
- (78) Willauer, H. D.; Huddleston, J. G.; Rogers, R. D. Solvent Properties of Aqueous Biphasic Systems Composed of Polyethylene Glycol and Salt Characterized by the Free Energy of Transfer of a Methylene Group Between the Phases and by a Linear Solvation Energy Relationship. *Ind. Eng. Chem. Res.* **2002**, *41*, 2591.
- (79) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 85th Edition; CRC Press: Boca Raton, FL, 2005.
- (80) Atanassova, M.; Mazan, V.; Billard, I. Modulating the Solubilities of Ionic Liquid Components in Aqueous-Ionic Liquid Biphasic Systems: A Q-NMR Investigation. *ChemPhysChem* **2015**, *16*, 1703.
- (81) Mourao, T.; Claudio, A. F.; Boal-Palheiros, I.; Freire, M. G.; Coutinho, J. A. P. Evaluation of the Impact of Phosphate Salts on the Formation of Ionic-Liquid-Based Aqueous Biphasic Systems. *J. Chem. Thermodyn.* **2012**, *54*, 398.
- (82) Zafarani-Moattar, M. T.; Hamzehzadeh, S. Effect of PH on the Phase Separation in the Ternary Aqueous System Containing the Hydrophilic Ionic Liquid 1-Butyl-3-Methylimidazolium Bromide and the Kosmotropic Salt Potassium Citrate at T = 298.15K. *Fluid Phase Equilib.* **2011**, *304*, 110.
- (83) Sintra, T. E.; Cruz, R.; Ventura, S. n. P. M.; Coutinho, J. A. P. Phase Diagrams of Ionic Liquids-Based Aqueous Biphasic Systems as a Platform for Extraction Processes. *J. Chem. Thermodyn.* **2014**, *77*, 206.
- (84) Onghena, B.; Binnemans, K. Recovery of Scandium(III) From Aqueous Solutions by Solvent Extraction with the Functionalized Ionic Liquid Betainium Bis(Trifluoromethylsulfonyl)Imide. *Ind. Eng. Chem. Res.* **2015**, *54*, 1887.