

Manuscript for: *Green Chemistry* (revision 1)

Manuscript ID GC-ART-01-2013-040198

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Green Chemistry 15, 919–927 (2013).

**Removal of Transition Metals from Rare Earths by Solvent
Extraction with an Undiluted Phosponium Ionic Liquid:
Separations Relevant to Rare-Earth Magnet Recycling**

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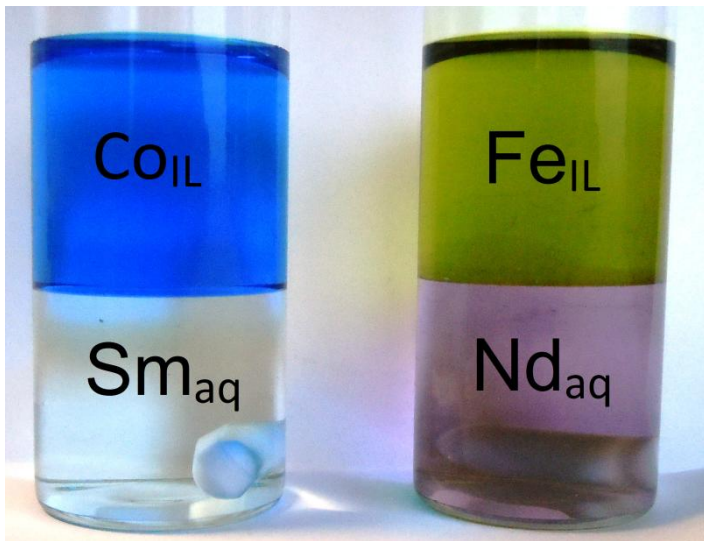
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Abstract

An environmentally friendly process for the separation of rare earths from the transition metals copper, cobalt, iron, manganese and zinc by solvent extraction with the ionic liquid trihexyl(tetradecyl)phosphonium chloride has been developed. The solvent extraction process is carried without the use of organic diluents or extra extraction agents and it can be applied as a sustainable hydrometallurgic method for removing transition metals from neodymium-iron-boron or samarium-cobalt permanent magnets. The recycling of rare earths is of high importance because of the possible supply risk of these elements in the near future. The method was tested for the removal of cobalt and iron from samarium and neodymium, respectively. The highest distribution ratios for cobalt and iron were found with 8.5 and 9 M HCl. At the tested conditions, the concentration of neodymium and samarium in the ionic liquid were below 0.5 mg L^{-1} (0.5 ppm), even for feed concentrations of 45 g L^{-1} . The separation factors of Nd/Fe and Sm/Co are $5.0 \cdot 10^6$ and $8.0 \cdot 10^5$ and, respectively. The percentage extraction of iron is still higher than 99.98% at loadings of the ionic liquids with 70 g L^{-1} of iron. The viscosity of the ionic liquid containing the tetrachloroferrate(III) complex $[\text{FeCl}_4]^-$ is lower, and less depending on the feed concentration, than in the case with a tetracobaltate(II) anion $[\text{CoCl}_4]^{2-}$. After extraction, cobalt can be stripped very easily from the ionic liquid phase with water. However, due to the very high distribution ratio, iron could only be stripped by forming a water-soluble iron complex with ethylenediaminetetraacetic acid (EDTA). Also the possibility to extract chromium, nickel, aluminium, calcium and magnesium with trihexyl(tetradecyl)phosphonium chloride has been investigated, but the distribution ratios of these elements are very low in the tested conditions.

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An environmentally friendly hydrometallurgic method for the separation of the transition metals iron, cobalt, copper, manganese and zinc from the rare earths neodymium and samarium with the undiluted ionic liquid trihexyl(tetradecyl)phosphonium chloride has been developed.

Keywords: ionic liquids; hydrometallurgy; lanthanides; rare earths; recycling

Introduction

Liquid-liquid extraction (solvent extraction) is the most commonly applied technique for the separation of metal ions. In this technique, the aqueous phase containing a metal salt, is mixed with an organic phase containing an extraction agent (extractant).¹⁻³ The metal ion forms a hydrophobic complex with the extraction agent and migrates to the organic phase. The separation of metals is based on differences in the affinity of complexes for different metals in the organic phase, as well as on the relative solubilities of the complexes in the aqueous and organic phase. The simplicity with which the parameters controlling extraction such as the organic phase, pH or extractant can be changed is a major advantage of solvent extraction. The water-immiscible organic phase often consists of a volatile and flammable solvent, such as kerosene, toluene, dichloromethane or diethyl ether. Ionic liquids (ILs) are greener and safer alternative for these molecular solvents,⁴⁻⁷ and have already successfully been applied for the extraction of metal ions.⁸⁻¹⁷ Ionic liquid solvents are organic salts which consist entirely of ions and typically have a melting point below 100 °C.¹⁸⁻²⁰ Their negligible vapour pressure and non-flammability make this class of solvents safer and more environmentally friendly than molecular solvents that are commonly applied in biphasic extraction systems.²¹ In many cases, metal extractions with ionic liquids occur via an ion-exchange process,²²⁻²⁵ in which a neutral extractant (e.g. crown ether, amine) extracts the positively charged metal ion to the ionic liquid phase. In order to obtain charge neutrality, the cation of the ionic liquid has to dissolve into the aqueous phase where it forms a new ionic liquid with the anions of the metal. This loss of ionic liquid can be alleviated by introducing long alkyl chains on the cation or by using fluorinated anions such as bis(trifluoromethylsulfonyl)imide (Tf_2N^-) or hexafluorophosphate (PF_6^-), which make the product produced by the ion exchange more hydrophobic.²⁶⁻²⁸ Moreover, introduction of these structural variations decreases the solubility of the ionic liquid in the aqueous phase, and significantly reduces losses of the ionic liquid

into the aqueous phase. Besides the persistency of fluorinated compounds, also their high prices and, in some cases, their hydrolysis to dangerous hydrofluoric acid are disadvantages.²⁹ From an economical point of view, it is therefore better to increase the hydrophobicity the ionic liquid by introducing longer alkyl chains instead of using fluorinated anions.²⁷ Although several non-fluorinated hydrophobic ionic liquids such as Aliquat 336,³⁰⁻³⁴ Cyphos[®] IL 101,³⁵⁻⁴⁴ and Cyphos[®] IL 104,³⁷ have already been used for extraction of metal ions, they are in general diluted in molecular solvents such as toluene, kerosene or chloroform. Diluents are added to decrease the viscosity of the ionic liquids, which is often high, especially for ionic liquids having longer or bulky alkyl chains. A decrease of viscosity results in an increase in mass transfer and faster kinetics. Unfortunately, the advantages of pure ionic liquids for extraction are lost by addition of diluents. Recently, it was shown that the problem of viscosity can be overcome in some cases by saturating the ionic liquid with water, by working slightly elevated temperatures and by using intermediate metal feed concentrations.⁴⁵ The toxicity of ionic liquids needs to be addressed when ionic liquids are proposed for use in solvent extraction. Since the vapour pressure of ionic liquids is negligible, toxicity of ionic liquid vapours is not an issue. However, there is still the possibility of toxic effects upon contact with the skin and problems related to aquatic toxicity and potential for bioaccumulation.⁴⁶⁻⁴⁹ The toxicity of hydrophobic ionic liquids (of the type considered in this paper), is mainly determined by the cation. Fortunately, the solubility of these ionic liquids in water is very low, so that it is often difficult to reach toxic concentrations in aqueous solutions. For the toxicity of trihexyl(tetradecyl)phosphonium bromide, a log LC₅₀ value of 0.41±0.02 for the marine bacterium *Vibrio fischeri* has been reported.⁴⁹ This value is very favourable in comparison with the values of other ionic liquids with long alkyl chains. A similar value is expected for the corresponding chloride salt.

The development of sustainable energy resources (wind turbines) and the tendency for miniaturisation of electronic devices have led to an increasing interest in permanent rare-earth magnets. This class of magnets has a much higher energy density than the traditional ferrite magnets, resulting in smaller and lighter magnets for similar magnetic strengths.⁵⁰ Neodymium-iron-boron magnets (NdFeB magnets) are currently the most often used rare-earth permanent magnet (98% market share) and can be found in several applications such as computer hard disk drives, wind turbines, electric vehicles or motors of air conditioners. To increase the temperature stability and depending on the application, dysprosium can be up to 8% of the total rare-earth content in NdFeB magnets.⁵¹ Samarium-cobalt magnets (SmCo magnets) are very useful for high temperature applications and for applications where corrosion resistance is important due to their higher coercive force.⁵⁰ In 2010, the European Commission published a list of critical raw materials at EU level.⁵² Besides the rare-earth elements, having the highest supply risk of all reported elements, also cobalt can be found on this list. Furthermore the U.S. department of Energy has recently published its own list of critical elements, where neodymium and dysprosium have been put, as the only two elements, in the highest supply risk class.⁵³ Both reports stress the importance of finding new rare-earth resources as soon as possible. Substitution of critical elements or reopening old mines such as the Mountain Pass Mine in California can solve part of the problem in the USA, but Europe has only limited amounts of primary ores available on its continent, so it has to invest in technospheric mining, which is the recycling of End-of-Life products or rare-earth scrap produced throughout production processes.⁵⁴ Moreover, primary mining of rare-earth ores for neodymium leads to an over-production of lanthanum and cerium. This is the so-called “balance problem”.⁵⁵

In 2008, about 38% of the rare-earth market was taken by rare-earth magnets in terms of value, so it is no surprise that magnet recycling can solve a large part of the supply problem.⁵²

In the light of the attention that rare-earth elements have attracted recently, some reviews appeared summarizing the scarce work on the recycling of rare-earths.^{51,56} After preprocessing End-of-Life rare-earth magnets, mainly pyrometallurgic or hydrometallurgic methods have already been applied in lab-scale experiments for the separation of the main elements from rare earths in rare-earth magnets.⁵⁷⁻⁶¹ The separation based on hydrometallurgic methods has several advantages such as applicable to different types of magnet compositions, applicable to (partly) oxidized alloys, low energy consuming and same processing steps as necessary when processing rare-earths from their primary ores.⁵¹

Trihexyl(tetradecyl)phosphonium chloride (Cyphos[®] IL 101) is an effective extractant for cobalt(II) and iron(III) from strongly acidic hydrochloric acid conditions, because these metal ions form stable anionic chloro complexes^{43, 45, 62-64} On the other hand, the trivalent rare-earth ions cannot be extracted as anionic chloro complexes under the same conditions. The differences in affinity of metal ions for Cyphos[®] IL 101 can be applied to separate cobalt or iron from rare earths. Moreover, Cyphos[®] IL 101 can be used in undiluted form.⁴⁵ Although strongly acidic conditions are less environmentally friendly, they are anyway necessary to dissolve the magnets in case of recycling of magnets via a hydrometallurgical process. In addition to iron or cobalt, also copper, nickel, manganese, zinc, aluminium, calcium, magnesium, zirconium and some non metals can be expected in SmCo and NdFeB magnets.^{50, 56, 65, 66}

In this paper, we present an efficient and environmentally friendly method to separate Fe(III) from Nd(III) and Co(II) from Sm(III) by solvent extraction with the undiluted non-fluorinated ionic liquid trihexyl(tetradecyl)phosphonium chloride from aqueous hydrochloric acid solutions. The metals could be stripped efficiently from the ionic liquid phase. Moreover, the extraction behavior of the transition metals copper, nickel, manganese and zinc were tested at the optimal extraction conditions. The composition of the synthetic solutions loaded

with metals ions reflect the composition that would be obtained by actual dissolution of NdFeB and SmCo magnets in hydrochloric acid.

Experimental

Chemicals

Trihexyl(tetradecyl)phosphonium chloride (>97%) (Cyphos[®] IL 101) was purchased from Iolitec (Heilbronn, Germany). NdCl₃·xH₂O (>99.9%) and SmCl₃·xH₂O (>98%) were obtained from Alfa Aesar. CrCl₃·6H₂O (>98%), AlCl₃·6H₂O (>99%), CuCl₂·xH₂O and disodium ethylenediaminetetraacetate dihydrate (Na₂EDTA·2H₂O, >99%) from ACROS Organics (Geel, Belgium) and FeCl₃ (>99%) from Honeywell Riedel-de Haën (Seelze, Germany). CoCl₂·6H₂O (>97 %), MnCl₂·4H₂O (>99%), MgCl₂·6H₂O (>99%), and the 1000 ppm gallium standard were purchased from Merck (Overijse, Belgium). NiCl₂·6H₂O (>99%), CaCl₂·2H₂O (>98%) and HCl (36%) were purchased from VWR (Leuven, Belgium). An ammonia solution (25 wt.%) was purchased from Chem-Lab NV (Zedelgem, Belgium). The silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). All chemicals were used as received, without further purification.

Instrumentation and analysis methods

Metal concentrations were determined with a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). After extraction, part of the aqueous phase was removed and a gallium internal standard was added until a total volume of 1 mL was obtained. The quartz glass sample carriers were first treated with 20 µL of silicone solution in isopropanol. Afterwards, the sample carriers were dried for 5 minutes in a hot air oven at 60

°C, followed by the addition of 5 μL of the sample and a drying process of 20 minutes at the same temperature. The metal concentrations were measured for 100 seconds, although for the lighter metals aluminium and magnesium, a measuring time of 500 seconds has been applied. For the organic phase, the gallium internal standard was added to a small amount of the organic phase (0.05 g) and was further diluted with dioxane until 1 mL. Pretreatment of the sample carrier, sampling volume, drying procedure and measuring time have been performed in the same way for the organic phase as described for the aqueous phase. All samples were diluted with MilliQ50 water if necessary. The viscosity of the organic phase was measured using a falling-ball type viscosimeter (Gilmont Instruments), densities were measured with a 10 mL pycnometer and pH measurement were performed with a S220 SevenCompact™ pH/Ion meter (Mettler–Toledo) and a Slimtrode (Hamilton) electrode. ^1H NMR has been recorded on a Bruker Avance 300 MHz NMR spectrometer and analysed with the SPINWORKS software package. NMR spectra of trihexyl(tetradecyl)phosphonium chloride were recorded in deuterated methanol. Absorption spectra were measured with a Varian Cary 5000 spectrophotometer and a quartz cuvette with an optical path length of 0.1 mm.

Extraction experiments

All extraction experiments were performed with chloride salts and undiluted trihexyl(tetradecyl)phosphonium chloride as the organic phase. Extractions were performed with intensive stirring at 600 rpm for 10 minutes at 60°C. Hydrochloric acid was used as the chloride source. After the extraction, separation of the phases was assisted by centrifugation for 10 minutes at 2800 rpm.

Distribution ratio studies

The distribution ratios of copper(II), cobalt(II), zinc(II) and manganese(II) at different HCl concentrations were performed with equal volumes of ionic liquid and an acidified water phase containing 5 g L^{-1} of the metal. For Fe(III), the metal concentration was increased to 10 g L^{-1} , in order to have a sufficiently high concentration after the extraction in the aqueous phase to get reliable analysis results. The same procedure was performed for nickel(II) and aluminium(III), although the concentration in the organic phase was measured here in order to calculate the distribution coefficients. The distribution coefficient of 5 g L^{-1} of calcium(II) and 5 g L^{-1} of magnesium(II) were determined within an extraction mixture containing also manganese(II), cobalt(II) and nickel(II), as described elsewhere.⁴⁵ The distribution ratios of iron(III) as function of the feed concentration were studied at the optimal hydrochloric concentration of 9 M HCl and with feed solution concentrations ranging from 5 to 70 g L^{-1} . The metal content of the aqueous phase was measured after the extraction with equal volumes of ionic liquid. The effect of the cobalt feed concentration on the distribution coefficient has been described elsewhere.⁴⁵

Separation experiments. For the separation experiments, 4 mL of the aqueous phase was mixed with 1 mL of ionic liquid. The elemental concentration for a samarium cobalt mixture is approximately the ratio found in $\text{Sm}_2\text{Co}_{17}$ magnets (0.8 g L^{-1} of samarium(III) and 2.6 g L^{-1} of cobalt(II)). For the neodymium/iron separation, the relative concentration of neodymium is higher than found in $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets due to practical issues (1.5 g L^{-1} neodymium(III) and 2.7 g L^{-1} of iron(III)). Measuring iron concentrations in the aqueous phase with TXRF was impossible closer to the optimal hydrochloric concentration of 9 M because the iron K_α peak, caused by trace amounts of non extracted iron, disappears because of overlap with the intense L_β peak of non extracted neodymium. By using a higher iron concentration, some extra data points could be obtained.

Stripping experiments. The ionic liquid phase was first presaturated with 9 M HCl after which it was mixed with a 9 M HCl aqueous phase containing 30 g L⁻¹ of iron(III). After extraction, the ionic liquid phase was washed three times with equal volumes of water to remove as much chloride anions as possible. 1.5 equivalents of Na₂EDTA were added to the iron(III)-loaded organic phase, further diluted with water and the pH of the solution was adjusted to the desired value by a 25 wt.% ammonia solution. The mixture was stirred for 10 minutes at 60 °C and subsequently, the separation of the two phases was facilitated by centrifugation at 2800 rpm for 10 minutes. Stripping of cobalt from the ionic liquid can be performed by washing the organic phase five times with equal amounts of water. The efficiency of the stripping procedure has been described already elsewhere.⁴⁵

Distribution ratio and separation factor

The distribution ratio D of a metal M is defined as:

$$D_M = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \quad (1)$$

For metals which are strongly extracted to the ionic liquid phase, the remaining metal concentration in the aqueous phase was measured after extraction and equation (1) can be rewritten as:

$$D_M = \frac{V_{\text{aq}} \cdot ([M]_0 - [M]_{\text{aq}})}{V_{\text{org}} \cdot [M]_{\text{aq}}}, \quad (2)$$

where $[M]_0$ is the initial metal concentration in the aqueous phase, $[M]_{\text{aq}}$ is the metal concentration in the aqueous phase after extraction, and V_{org} and V_{aq} are the volumes of the organic (ionic liquid) and aqueous phase assuming constant volumes. In most cases, equal

volumes of organic and aqueous phase have been used. In that case, equation (2) can be simplified to:

$$D_M = \frac{[M]_o - [M]_{aq}}{[M]_{aq}} \quad (3)$$

For metals extracted which are poorly extracted, the metal concentration of the organic phase was measured and equation (1) becomes:

$$D_M = \frac{V_{aq} \cdot [M]_{org}}{V_{aq} \cdot [M]_o - V_{org} \cdot [M]_{org}}, \quad (4)$$

where $[M]_{org}$ is the metal concentration in the organic phase. In case of equal volumes, equation (4) can be simplified to

$$D_M = \frac{[M]_{org}}{[M]_o - [M]_{org}} \quad (5)$$

The *percentage extraction* (%*E*) is defined as the amount of metal extracted to the organic phase over the total amount of metal in both phases. It can be defined as:

$$\%E = \frac{V_{org} \cdot [M]_{org}}{V_{aq} \cdot [M]_o} \times 100 = \frac{[M]_o - [M]_{aq}}{[M]_o} \times 100 \quad (6)$$

The efficiency of a separation between two metals can be described with the *separation factor* α :

$$\alpha_{M_1, M_2} = \frac{D_{M_1}}{D_{M_2}}, \quad (7)$$

where D_{M_1} and D_{M_2} are the distribution ratios D of metal M_1 and M_2 , respectively

After extraction, metals are removed from the organic phase by a stripping agent. The percentage recovery (%*R*) in the stripping phase can be defined as the amount of metal

stripped from the organic phase to the total amount of metal in the organic phase before stripping:

$$\%R = \frac{V_{\text{aq}} \cdot [M]_{\text{aq}}}{V_{\text{org}} \cdot [M]_{\text{org},0}} \times 100 , \quad (8)$$

where $[M]_{\text{org},0}$ is the metal concentration in the organic phase after extraction or before stripping.

Results and Discussion

In the first series of experiments, the distribution ratios between the IL phase and the aqueous phase of copper(II), iron(III), zinc(II), manganese(II) and cobalt(II) were determined as a function of the hydrochloric acid concentration (Figure 1). For cobalt(II) and manganese(II), the maximum distribution ratio was found at a HCl concentration of approximately 8 M and the distribution ratios were found to be 460 for cobalt(II) and 31 for manganese(II). For iron(III), the maximum distribution ratio was found at a slightly higher HCl concentration of 9 M. Moreover, the distribution ratios of iron(III) were significant higher than those of manganese(II) and cobalt(II) over the whole HCl concentration range. The maximum value of the distribution ratio of iron(III) is 7000. For copper(II) and zinc(II) the behavior was distinctly different than that of cobalt(II), manganese(II) and iron(III). Here the distribution ratios were high at low HCl concentrations and decreased with increasing HCl concentration. The distribution ratios at concentrations between 0.5 and 2 M HCl are above 10000. In this concentration range, the remaining copper and zinc concentration in the aqueous phase was below 0.5 mg L^{-1} (0.5 ppm) after extraction. The strong affinity of both metals for the

trihexyl(tetradecyl)phosphonium chloride phase at lower HCl concentrations can be used for separating them from manganese or cobalt.

[Insert Figure 1]

In the second series of experiments, the separation of iron(III) from neodymium(III) and cobalt(II) from samarium(III) was tested (Figure 2). The loading of the organic phase after extraction has been increased compared to previous experiments, to obtain a concentration in the organic phase after extraction over 10 g L^{-1} for both iron(III) and cobalt(II). For cobalt, the distribution factor reached a maximum at 8.5 M HCl, with a value of 450 (Figure 3). This value is also slightly higher than the distribution ratio found in our earlier work for an organic phase loaded with 10 g L^{-1} of cobalt, but this is probably due to the difference in experimental conditions.⁴⁵ It was not possible to determine the maximum value for the distribution ratio for iron(III) with TXRF as the analysis method, because of spectral interferences between the L lines of neodymium with K lines of iron. However it is expected that the distribution ratio reaches again a maximum around 9 M HCl, just as is the case without adding neodymium(III). The distribution ratio at a concentration of 0.1 M HCl was still 10.

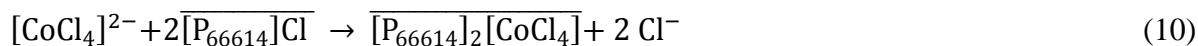
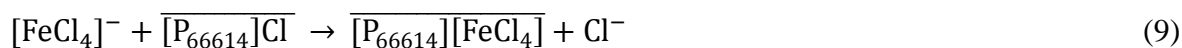
[Insert Figure 2]

[Insert Figure 3]

Although it is possible to measure concentrations as low as 0.1 mg L^{-1} (100 ppb) for all the elements of the whole lanthanide series by the TXRF technique, no lanthanides could be detected in the organic phase. Even for a very small and undiluted droplet, no TXRF signal could be observed at the expected energy for a given lanthanide ion. Even for a single element extraction of 45 g L^{-1} of neodymium, no peaks were detected in an undiluted ionic liquid droplet. If an arbitrary value of 0.5 mg L^{-1} was chosen as the concentration of neodymium or samarium in the organic phase, the separation factors for the couples Fe/Nd and Co/Sm are $5.0 \cdot 10^6$ at 6 M HCl and $8.0 \cdot 10^5$ at 9 M HCl, respectively.

[Insert Figure 4]

For industrial applications, it is much more interesting to work with more concentrated feed solutions. The effect of the feed solution concentration on the distribution ratio of cobalt has been described already elsewhere.⁴⁵ Due to strong affinity between trihexyl(tetradecyl)phosphonium chloride and iron(III), the organic phase can be loaded with higher amounts of iron(III), while it is still possible to obtain a high percentage extraction (Figure 4). Moreover, for the extraction of iron(III), only one mole of the ionic liquid is needed at 9 M HCl, because iron(III) is extracted as the singly negatively charged tetrachloroferrate(III) complex $[\text{FeCl}_4]^-$. Two equivalents of the ionic liquid are necessary to extract one cobalt(II) ion, because cobalt(II) is extracted as the doubly negatively charged tetracobaltate(II) complex, $[\text{CoCl}_4]^{2-}$. The extraction mechanism can be summarized as follows for the extraction of iron(III) and cobalt(II):



Here the upper bar represents the organic phase (ionic liquid phase). The formation of the tetrachlorocobaltate(II) ion was proven in an earlier study.⁴⁵ The formation of the tetrachloroferrate(III) anion was confirmed by UV-VIS spectroscopy (Figure 5). The spectrum was very similar to those reported in literature for this ion.⁶⁷ The percentage extraction of cobalt decreased drastically if equimolar ratios of ionic liquid over cobalt were approached. At a concentration of 40 g L⁻¹ of cobalt(II), the percentage of extraction dropped to 98%, whereas at a concentration of 50 g L⁻¹ it further decreased to 92%. In the case of iron(III), the percentage extraction is still higher than 99.98% at a iron(III) feed concentration of 70 g L⁻¹.

[Insert Figure 5]

The viscosity has a significant effect on the mass transfer and the kinetics of solvent extraction systems. Therefore, the viscosity of the undiluted and water saturated ionic liquid phase is an important experimental parameter. For extraction of cobalt(II), the viscosity of the ionic liquid phase increased significantly when the metal concentration in the organic phase was increased (Figure 6). The same effect was not observed for iron(III), and a nearly constant value (700 cP at 23 °C) was measured for the viscosity over a broad range of

iron(III) concentrations. This difference in behavior can be explained by the fact that cobalt forms a larger ionic liquid with two cations and an anion with a -2 electric charge, whereas the charge of the anion in the pure ionic liquid has a -1 charge (equation 10). A higher charge and thus stronger intermolecular interactions, combined with a larger ionic liquid, are both causing the increasing viscosity at higher cobalt loadings. The iron(III) complex in the ionic liquid phase contains only one cation and an anion with a -1 electric charge (equation 9). The viscosity of the presaturated ionic liquid at 23 °C and 60 °C is 830 cP and 95 cP, respectively. The difference in viscosity between these temperatures shows the importance of heating up the extraction system, in order to obtain faster kinetics. The viscosity of the ionic liquid loaded with cobalt was found to be higher than the viscosity of the unloaded presaturated ionic liquid at 60 °C. In the case of iron, the viscosity is lower than the pure presaturated ionic liquid at room temperature (23°C). After extraction of iron(III), the -1 charge of the chloride anion is distributed over the larger $[\text{FeCl}_4]^-$ anion which gives weaker intermolecular interactions and thus a lower viscosity. A similar trend of decreasing viscosity has been reported in dialkylimidazolium chloroaluminate melts.⁶⁸ Although the viscosity measurements for both metals has been performed at different temperatures, it can be concluded that the viscosity of the iron(III)-loaded ionic liquid is lower than that of the cobalt(II)-loaded ionic liquid and less dependent on the metal concentration in the ionic liquid phase. The densities at 23 °C are 0.97 g mL⁻¹ and 0.91 g mL⁻¹ for the ionic liquid loaded with 30 g L⁻¹ iron(III) and 5 g L⁻¹ cobalt (II), respectively.

[Insert Figure 6]

The percentage extraction of elements other than iron and cobalt has been investigated at the optimal pH range at 8 or 9 M HCl (Table 1). The percentage extractions of aluminium(III) is just below 10% respectively. For both nickel(II) and chromium(III), percentage extractions of only about 0.6% have been found. This means that nickel(II) and chromium(III) could be separated efficiently from iron(III), copper(II), cobalt(II), manganese(II) or zinc(II) with trihexyl(tetradecyl)phosphonium chloride, but not from samarium(III) or neodymium(III). Also calcium(II) and magnesium(II) were not extracted to the ionic liquid phase.

[Insert Table 1]

Due to the strong affinity of trihexyl(tetradecyl)phosphonium chloride for iron(III), the stripping of iron(III) from the ionic liquid phase after extraction is not straightforward. Although it was shown by other authors that the distribution ratio of iron(III) in the presence of 0.1 M HCl and toluene is low and a 0.1 M HCl solution could be used to strip iron(III) from trihexyl(tetradecyl)phosphonium chloride dissolved in toluene,³⁷ we found that it is not possible to strip iron(III) from the undiluted ionic liquid. This is probably due to the high solubility of HCl and water in the pure ionic liquid and the difficulty to remove it, so that the actual HCl concentration in the ionic liquid remains high.⁴⁵ Using acids other than HCl is also not recommended due to the metathesis reaction between the acid anion and ionic liquid chloride anion, so that the composition of the extraction system is changed and the ionic liquid is more difficult to re-use for a second extraction step.

Ethylenediaminetetraacetic acid (EDTA) forms a stable, highly water-soluble chelate complex with iron(III).⁶⁹ Therefore, it was tested to strip iron(III) from the ionic liquid with an aqueous solution of EDTA. A fully loaded organic phase is not suggested for the simultaneous

separation of iron(III) and other elements from neodymium(III). Especially metals with rather low distribution coefficients, such as cobalt(II) and manganese(II) are sensitive to the metal loading of the organic phase. Their distribution coefficients significantly decrease at high metal loadings of the organic phase and a second extraction step will be necessary to remove almost all metals from the aqueous phase. The organic phase was first loaded with 30 g L^{-1} of iron(III) and was washed three times with water to remove most of the chloride anions from the solution. After three scrubbing steps (i.e. washing steps), the iron(III) concentration in the organic phase could be lowered by 9% and the pH of the last washing phase was now increased above 1 (Table 2, Figure 7). Afterwards, 1.5 equivalent of Na_2EDTA was added to the organic phase and the pH was adjusted with an NH_3 solution to remove the remaining protons from Na_2EDTA .

[Insert Table 2]

At intermediate pH values (between pH 6 to 9.4), the stripping efficiency was low (about 50%) and a brown precipitate was found in the organic phase, which is contradictory to what has been published in earlier work on the speciation distribution of Fe(III) with EDTA.⁷⁰⁻⁷³ At pH values lower than 6, the percentage recovery was still low, but no precipitate was observed. At a pH value above 10, the stripping efficiency increased significantly to more than 80%. Most of the iron remained dissolved in the aqueous phase, although some small solid particles were observed. Higher pH values could not be used due to the formation of a large amount of precipitate. After washing the organic phase three times with water and a fourth stripping step with EDTA, the total percentage stripping obtained at a pH of 10.1 was 90.1%. The mechanism of stripping process with EDTA is not fully understood yet, because

the stripping efficiency is strongly dependent on different experimental parameters such as the pH and the concentrations of iron and EDTA, but will be investigated further in the future. Anion exchange of the ionic liquid with EDTA was tested with ^1H NMR and was determined to be as low as 1.6 mol%. After a washing step with 9 M of HCl, this value was further reduced to less than 0.1 mol%.

[Insert Figure 7]

Conclusions

The transition metals iron, cobalt, copper, manganese and zinc can be removed from rare earths by using the ionic liquid trihexyl(tetradecyl)phosphonium chloride. The ionic liquid has been used in its undiluted form, and acts both as the organic phase and the extraction agent. The efficiencies of neodymium/iron and samarium/cobalt separations were tested, because of the relevance of these separations for the design of efficient hydrometallurgical routes for the recycling of rare earths from permanent magnets. The separation factors were $5.0 \cdot 10^6$ for Nd/Fe and $8.0 \cdot 10^5$ for Sm/Co. Cobalt can easily be stripped from the ionic liquid phase with water. The high affinity of iron(III) for the ionic liquid results in very high distribution ratios. The percentage extractions of iron(III) is still above 99.98% when the ionic liquid phase is loaded with 70 g L^{-1} of iron(III). The viscosity of iron(III)-containing ionic liquid is lower and less dependent on the feed concentration than that of the cobalt(II)-containing ionic liquid. Stripping of iron(III) from the ionic liquid phase could not be performed with water or with a diluted HCl solution, but the stripping was possible with an aqueous EDTA solution. After

three sequential scrubbing steps with water and a stripping step with EDTA, the recovery rate of iron(III) was 90%. The extraction behavior of aluminium, magnesium, nickel, calcium and chromium has been tested as well, but the percentage extraction was found to be very low. This work illustrates the potential of hydrophobic non-fluorinated ionic liquids for the design of environmentally friendly solvent extraction processes, i.e. solvent extraction processes without volatile organic solvents and added extraction agents.

Acknowledgements

The authors thank the KU Leuven for financial support (GOA/13/008 and IOF-KP RARE³). SW thanks the IWT-Flanders and Umicore Research for a PhD fellowship. Support by IoLiTec (Heilbronn, Germany) and Cytec (Canada) is also gratefully acknowledged.

Table 1. Percentage extraction (%*E*) of different metal chlorides at 8 or 9 M HCl.

	HCl conc. (M)	% <i>E</i>
Aluminium(III)	9	9.4
Chromium(III)	9	0.6
Nickel(II)	8	0.6
Magnesium(II)	8	0.1
Calcium(II)	8	0.6

Table 2. Percentage recovery (%*R*) of iron(III) from trihexyl(tetradecyl)phosphonium chloride in each stripping step. The volume ratio of the aqueous to the organic phase is 1:1 for stripping step 1, 2 and 3 with water and 5:1 for stripping step 4 with EDTA and pH = 10.1.

Stripping step	% <i>R</i>
1	0.7
2	5.7
3	2.7
4	81.0
Total	90.1

Figure captions

Figure 1. A plot of the distribution ratio for 5 g L⁻¹ of copper(II) (▲), 5 g L⁻¹ of manganese(II) (▼), 5 g L⁻¹ of cobalt(II) (■), 5 g L⁻¹ zinc(II) (◆) and 10 g L⁻¹ of iron(III) (●) solution, as a function of the hydrochloric acid concentration. The volume ratio of the aqueous to the organic phase is 1:1.

Figure 2. Left: separation of cobalt(II) (5 g L⁻¹, blue) from samarium(III) (2.5 g L⁻¹, colourless). Right: iron(III) (30 g L⁻¹, yellow or brown) from neodymium(III) (60 g L⁻¹, purple). Top: before extraction and bottom: after mixing and extraction.

Figure 3. A plot of the distribution ratio of 2.6 g L⁻¹ cobalt(II) (■) in a mixture with 0.8 g L⁻¹ samarium(III) and the distribution ratio of 2.7 g L⁻¹ iron(III) (●) in a mixture with 1.5 g L⁻¹ neodymium(III). The volume ratio of the aqueous to the organic phase is 4:1.

Figure 4. Graph showing the influence of the relative feed solution concentration $n(\text{IL})/n(\text{M})$ on the percentage extraction (%E) by decreasing the ratio $n(\text{IL})/n(\text{M})$. The HCl concentrations were 8 M for cobalt(II) (■) and 9 M HCl for iron(III) (●). The volume ratio of the aqueous to the organic phase is 1:1.

Figure 5. Absorption spectrum of the ionic liquid phase after extraction of iron(III), which is typical for the $[\text{FeCl}_4]^-$ anion.

Figure 6. Graph showing the influence of the metal concentration of iron(III) (●) (23°C) and cobalt(II) (■) (60°C) on the viscosity of the water saturated ionic liquid.

Figure 7. Graph showing the dependence of the pH on the percentage recovery (%R) of iron(III) with EDTA. $[\text{M}]_{\text{org},0} = 30 \text{ g L}^{-1}$. The volume ratio of the aqueous to the organic phase is 5:1.

Figure1.

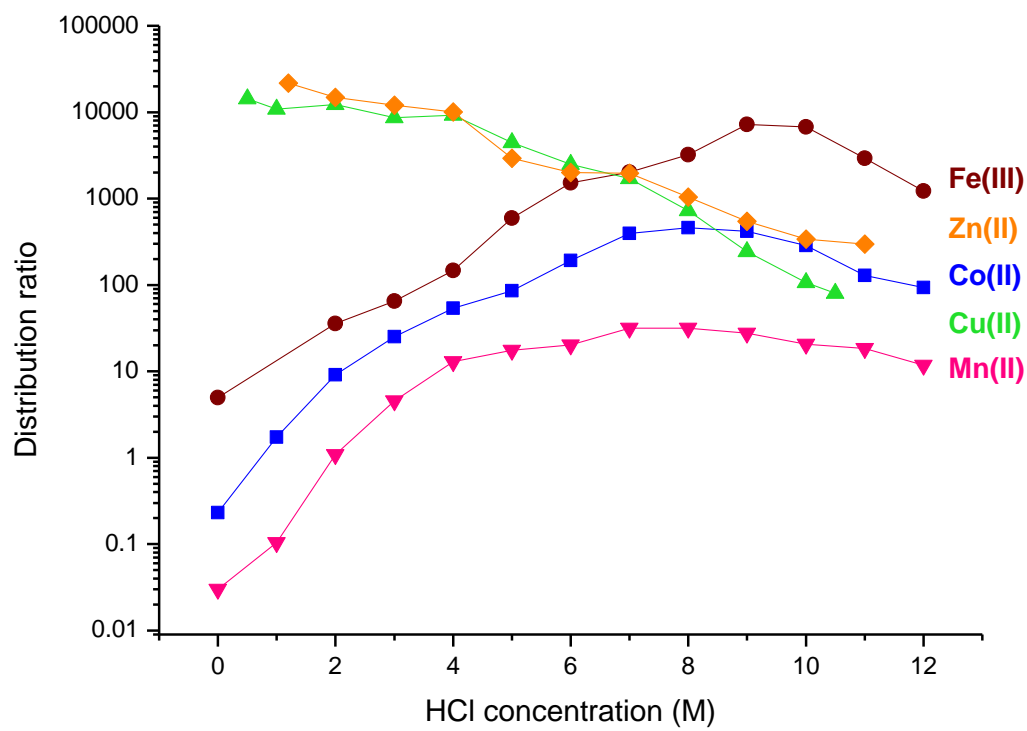


Figure 2.

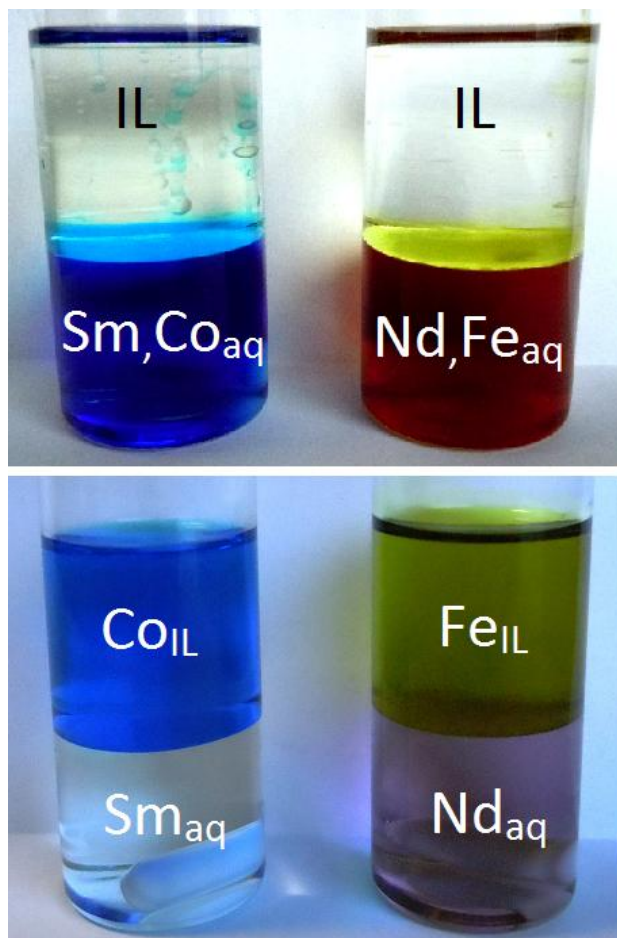


Figure 3.

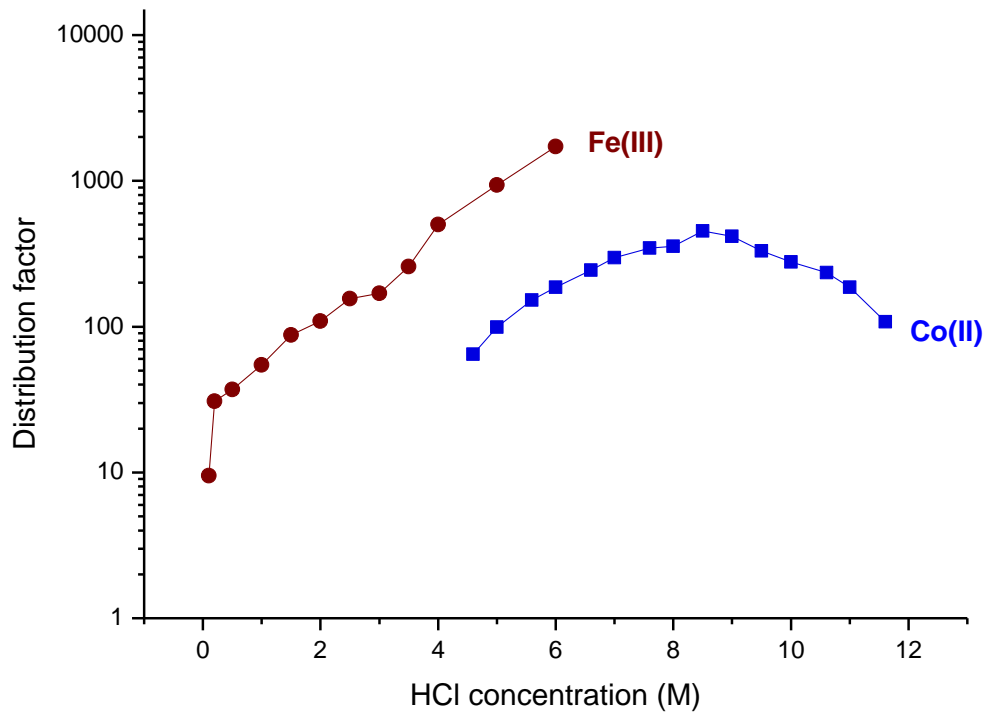


Figure 4

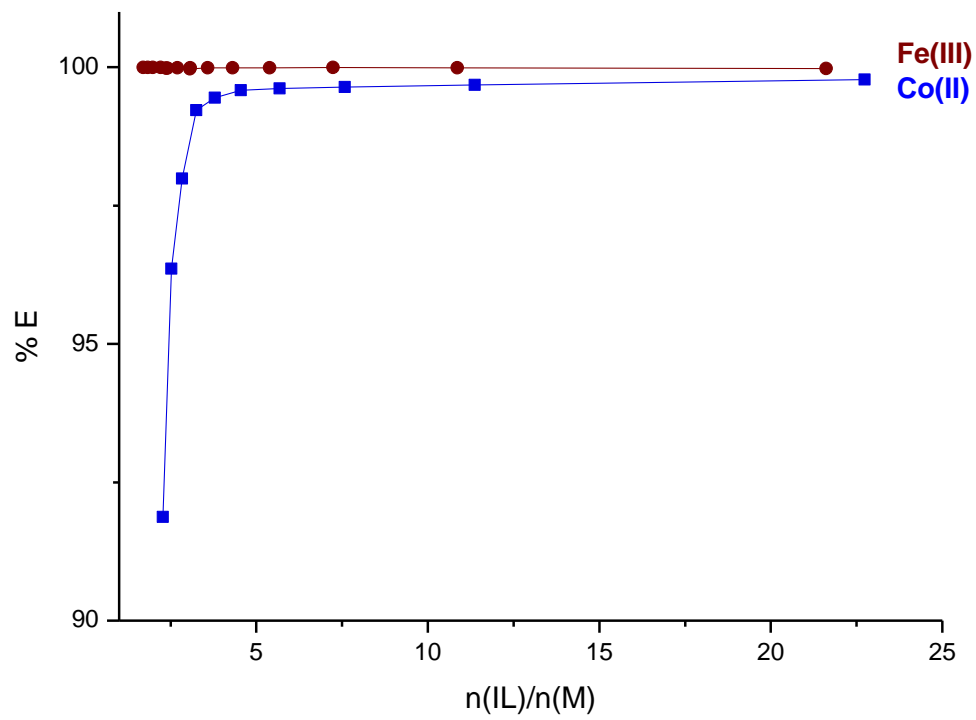


Figure 5.

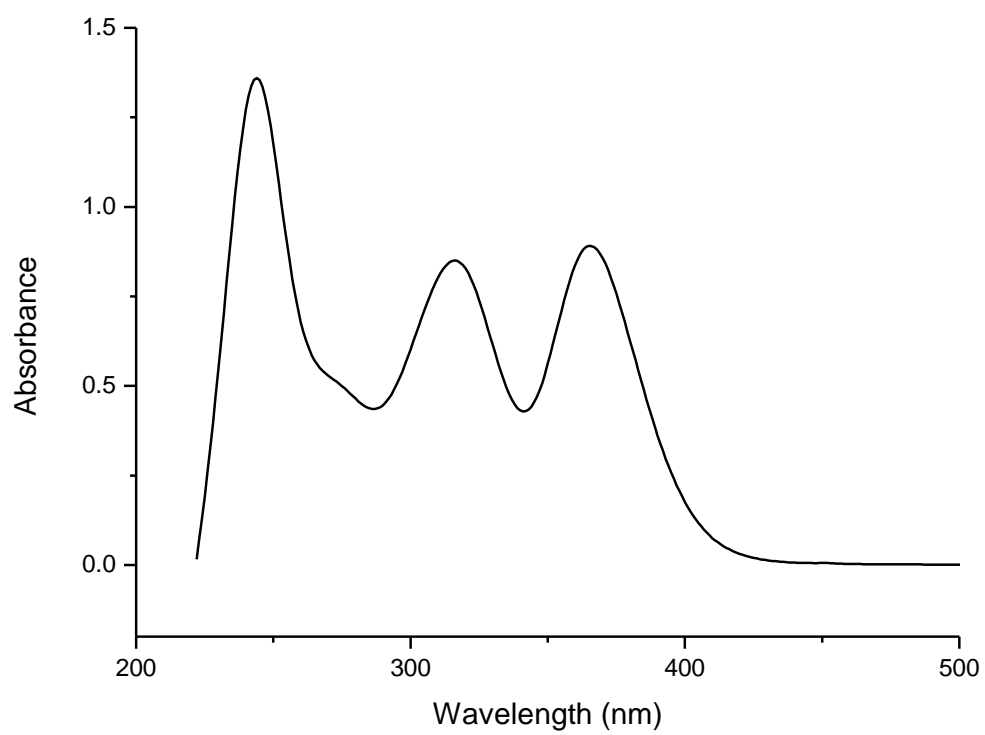


Figure 6.

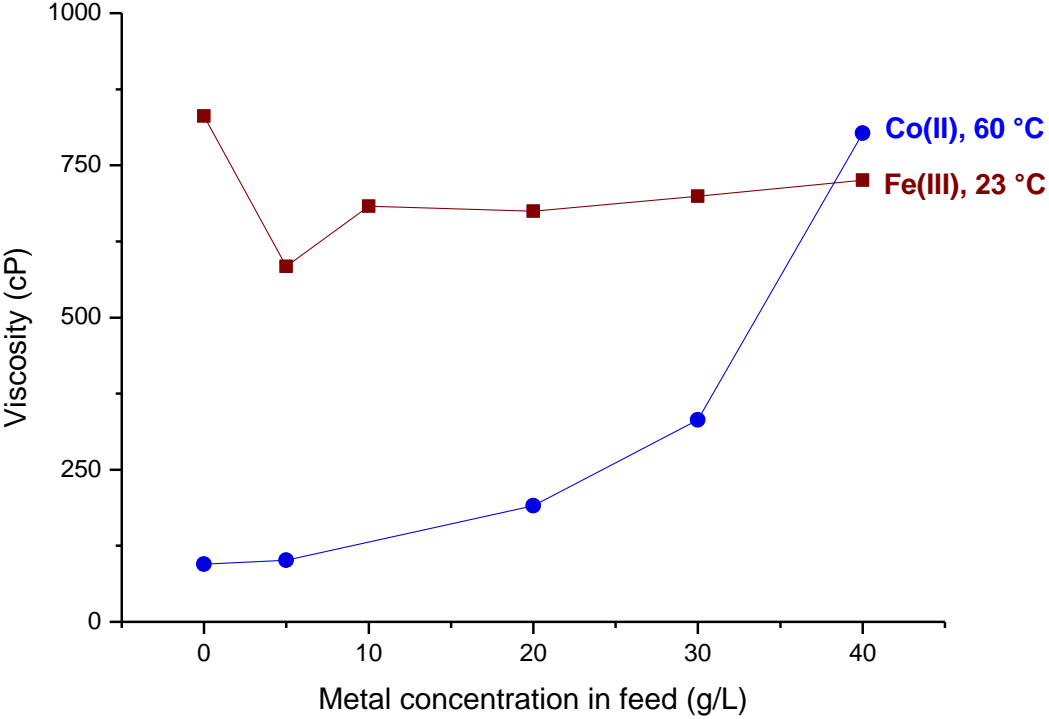
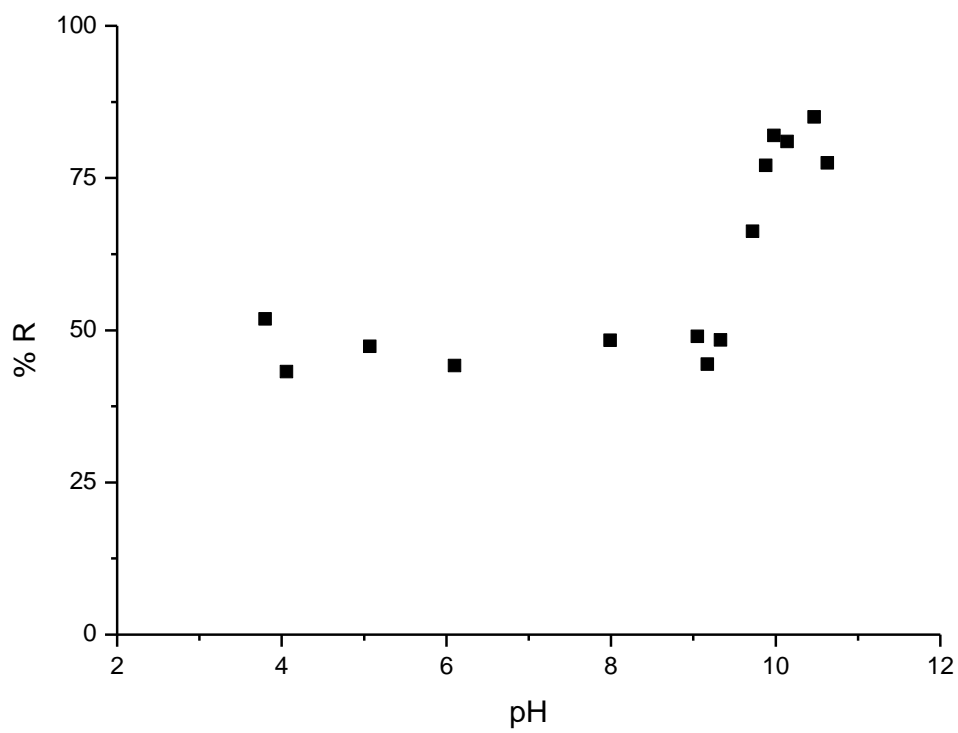


Figure 7.



Notes and References

1. J. Stary, *The solvent extraction of metal chelates*, Pergamon Press, New York, 1964.
2. V. Kislik, *Solvent Extraction, Classical and Novel Approaches*, Elsevier, Amsterdam, 2011.
3. J. C. Rydberg, M. Cox, C. Musikas and G. R. Choppin, *Solvent Extraction: Principles and Practice*, Marcel Decker, New York, 2004.
4. T. Welton, *Chem. Rev.*, 1999, **99**, 2071-2084.
5. K. R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 351-356.
6. P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772-3789.
7. P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, WILEY-VCH Verlag GmbH, Weinheim, 2008.
8. D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, **15**, 205-209.
9. M. Bonnaffe-Moity, A. Ouadi, V. Mazan, S. Miroshnichenko, D. Ternova, S. Georg, M. Sypula, C. Gaillard and I. Billard, *Dalton Trans.*, 2012, **41**, 7526-7536.
10. N. Papaiconomou, G. Vite, N. Goujon, J. M. Leveque and I. Billard, *Green Chem.*, 2012, **14**, 2050-2056.
11. A. Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *Sep. Purif. Technol.*, 2012, **95**, 26-31.
12. M. L. Dietz, *Sep. Sci. Technol.*, 2006, **41**, 2047-2063.
13. I. Billard, A. Ouadi and C. Gaillard, *Anal. Bioanal. Chem.*, 2011, **400**, 1555-1566.
14. F. Kubota, Y. Shimobori, Y. Baba, Y. Koyanagi, K. Shimojo, N. Kamiya and M. Goto, *J. Chem. Eng. Jpn.*, 2011, **44**, 307-312.
15. N. Hirayama, *Solvent Extr. Res. Dev., Jpn.*, 2011, **18**, 1-14.
16. P. R. Vasudeva Rao, K. A. Venkatesan, A. Rout, T. G. Srinivasan and K. Nagarajan, *Sep. Sci. Technol.*, 2011, **47**, 204-222.
17. A. P. Abbott, G. Frisch, J. Hartley and K. S. Ryder, *Green Chem.*, 2011, **13**, 471-481.
18. N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123-150.
19. X. Han and D. W. Armstrong, *Acc. Chem. Res.*, 2007, **40**, 1079-1086.
20. H. Zhao, S. Xia and P. Ma, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 1089-1096.
21. R. D. Rogers and K. R. Seddon, *Science*, 2003, **302**, 792-793.
22. M. Jensen, S. Skanthakumar, L. Soderholm, J. Neuefeind and J. Beitz, *J. Am. Chem. Soc.*, 2003, **125**, 15466-15473.
23. M. L. Dietz and J. A. Dzielawa, *Chem. Commun.*, 2001, 2124-2125.
24. M. P. Jensen, J. A. Dzielawa, P. Rickert and M. L. Dietz, *J. Am. Chem. Soc.*, 2002, **124**, 10664-10665.
25. M. L. Dietz, J. A. Dzielawa, I. Laszak, B. A. Young and M. P. Jensen, *Green Chem.*, 2003, **5**, 682-685.
26. P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168-1178.
27. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156-164.
28. P. G. Rickert, D. C. Stepinski, D. J. Rausch, R. M. Bergeron, S. Jakob and M. L. Dietz, *Talanta*, 2007, **72**, 315-320.
29. R. P. Swatloski, J. D. Holbrey and R. D. Rogers, *Green Chem.*, 2003, **5**, 361-363.
30. R. K. Mishra, P. C. Rout, K. Sarangi and K. C. Nathsarma, *Hydrometallurgy*, 2011, **108**, 93-99.
31. F. d. M. Fábrega and M. B. Mansur, *Hydrometallurgy*, 2007, **87**, 83-90.
32. B. Wassink, D. Dreisinger and J. Howard, *Hydrometallurgy*, 2000, **57**, 235-252.
33. H. F. Aly, M. El-Garhy and S. El-Reefy, *Microchem. J.*, 1972, **17**, 431-435.
34. T. Sato, T. Shimomura, S. Murakami, T. Maeda and T. Nakamura, *Hydrometallurgy*, 1984, **12**, 245-254.
35. A. Comesaña, J. Rodriguez-Monsalve, A. Cerpa and F. J. Alguacil, *Chem. Eng. J.*, 2011, **175**, 228-232.

36. M. Regel-Rosocka, Ł. Nowak and M. Wiśniewski, *Sep. Purif. Technol.*, 2012, **97**, 158-163.
37. A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, 2011, **80**, 385-389.
38. A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, 2010, **73**, 202-207.
39. M. Regel-Rosocka, *Sep. Purif. Technol.*, 2009, **66**, 19-24.
40. M. Regel-Rosocka and M. Wisniewski, *Hydrometallurgy*, 2011, **110**, 85-90.
41. K. Campos, T. Vincent, P. Bunio, A. Trochimczuk and E. Guibal, *Solvent Extr. Ion Exch.*, 2008, **26**, 570-601.
42. V. Gallardo, R. Navarro, I. Saucedo, M. Ávila and E. Guibal, *Sep. Sci. Technol.*, 2008, **43**, 2434-2459.
43. D. Kogelnig, A. Stojanovic, F. Jirsa, W. Körner, R. Krachler and B. K. Keppler, *Sep. Purif. Technol.*, 2010, **72**, 56-60.
44. K. Campos, R. Domingo, T. Vincent, M. Ruiz, A. M. Sastre and E. Guibal, *Water Res.*, 2008, **42**, 4019-4031.
45. S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, **14**, 1657-1665.
46. J. Ranke, A. Müller, U. Bottin-Weber, F. Stock, S. Stolte, J. Arning, R. Störmann and B. Jastorff, *Ecotoxicol. Environ. Saf.*, 2007, **67**, 430-438.
47. J. Ranke, S. Stolte, R. Stormann, J. Arning and B. Jastorff, *Chem Rev*, 2007, **107**, 2183-2206.
48. R. J. Cornmell, C. L. Winder, G. J. T. Tiddy, R. Goodacre and G. Stephens, *Green Chem.*, 2008, **10**, 836-841.
49. D.J. Couling, R.J. Bernot, K.M. Docherty, J.K. Dixon and E.J. Maginn, *Green Chem.*, 2006, **6**, 82-90.
50. O. Gutfleisch, M. A. Willard, E. Brück, C. H. Chen, S. G. Sankar and J. P. Liu, *Adv. Mater.*, 2011, **23**, 821-842.
51. K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton and M. Buchert, *J. Clean. Prod.*, 2013, in press, DOI <http://dx.doi.org/10.1016/j.jclepro.2012.12.037>
52. European Commission, *Critical raw materials for the EU, Report of the Ad-hoc Working Group on defining critical raw materials*, 2010.
53. U. S. Department of Energy, *2011 Critical Materials Strategy*, 2011.
54. D. Schüler, M. Buchert, R. Liu, S. Dittrich and C. Merz, *Study on Rare Earths and Their Recycling*, 2011, Oeko-Institut e.V. (Darmstadt, Germany).
55. P. Falconnet, *J. Less-Common Met.*, 1985, **111**, 9-15.
56. M. Tanaka, T. Oki, K. Koyama, H. Narita and T. Oishi, in *Handbook on the Physics and Chemistry of Rare Earths*, eds. J. C. G. Bünzli and V. K. Pecharsky, Elsevier, 2013, vol. Vol. 43, ch. 225, pp. 159-211.
57. M. Itoh, K. Miura and K.-i. Machida, *J. Alloys Compd.*, 2009, **477**, 484-487.
58. K. Koyama, A. Kitajima and M. Tanaka, *Kidorui*, 2009, **54**, 36-37.
59. Y. Baba, F. Kubota and N. Kamiya, *Solvent Extr. Res. Dev., Jpn.*, 2011, **18**, 193-198.
60. J. Rabatho, W. Tongamp, Y. Takasaki, K. Haga and A. Shibayama, *J. Mater. Cycles Waste Manage.*, 2012, in press, DOI: 10.1007/s10163-012-0105-6.
61. K. Miura, M. Roh and K. I. Machida, *J. Alloys Compd.*, 2008, **466**, 228-232.
62. B. Marszałkowska, M. Regel-Rosocka, Ł. Nowak and M. Wiśniewski, *Pol. J. Chem. Technol.*, 2010, **12**, 1-5.
63. *South Australia Pat.*, WO/2012/079130, 2012.
64. R. E. Del Sesto, T. M. McCleskey, A. K. Burrell, G. A. Baker, J. D. Thompson, B. L. Scott, J. S. Wilkes and P. Williams, *Chem. Commun.*, 2008, 447-449.
65. C.O. Bounds, in: Liddell, K.C., Bautista, R.G., and Orth, R.J. (Eds.), *Symposium on Metals and Materials Waste Reduction, Recovery and Remediation*, at the 1994 Materials Week Meeting Location: Rosemont, IL, October 03-06, 1994 The Minerals, Metals & Materials Society, Warrendale, Pennsylvania, pp. 173-186.
66. Z. S. Yu and M. B. Chen, *Rare Earth Elements and their Applications*, Metallurgical Industry Press, Beijing, 1995.

67. G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1953, 1435-1443.
68. J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263-1264.
69. J. R. Hart, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
70. G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, 1951, **34**, 576-591.
71. O. García de Alvarez and L. Gierst, *J. Electroanal. Chem. Interfac. Electrochem.*, 1979, **100**, 819-829.
72. I. González, J. G. Ibañez, M. A. Cárdenas and A. Rojas-Hernández, *Electrochim. Acta*, 1990, **35**, 1325-1329.
73. K. Shimizu, R. Hutcheson, M. D. Engelmann and I. Francis Cheng, *J. Electroanal. Chem.*, 2007, **603**, 44-50.