PAPER

Separation of rare earths and nickel by solvent extraction with two mutually immiscible ionic liquids

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It is shown that rare earths can be distributed between two immiscible ionic liquids, allowing the transfer of the rare earths from one ionic liquid phase to another. The ionic liquid 1-ethyl-3-methylimidazolium chloride was used as the initial feed phase and the ionic liquid trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) as the extracting phase. The rare earths could be recovered from the extracting phase by stripping with a 2 M HNO_3 solution. The ionic liquids could be regenerated for reuse in the next extraction step. This ionic liquid–ionic liquid extraction system can be used for the separation of rare earths from nickel, because nickel is not extracted under these experimental conditions. Such a separation process is relevant for the recycling of valuable metals from nickel metal hydride (NiMH) batteries. Direct dissolution of rare-earth oxides in 1-ethyl-3-methylimidazolium chloride was possible, provided that a small amount of concentrated hydrochloric acid was added to the ionic liquid.

Introduction

Ionic liquids (ILs) have been intensively investigated for use as the organic phase in solvent extraction systems. These solvents consist entirely of ions.[1–3] They have a negligible vapor pressure; as a consequence, ionic liquids are not volatile and do not form flammable solvent–air mixtures. Many researchers have used ionic liquids as a replacement for volatile organic diluents in the organic phase in solvent extraction systems.[4–10] Often, conventional extractants are used, dissolved in the ionic liquid phase. Most of the ionic liquids used for solvent extraction contain fluorinated anions, such as the hexafluorophosphate and the bis(trifluoromethylsulfonyl)imide anion, because these ionic liquids form immiscible phases with water, even in combination with small cations.[4,11–17] However, the use of fluorinated ionic liquids is not recommended from an economical (high price) and environmental point of view (persistence). Ionic liquids with simple anions such as chloride or nitrate are only immiscible with water in combination with large hydrophobic cations. Until recently, it was assumed that these ionic liquids were too viscous for use in solvent extraction systems, unless molecular diluents such as toluene or chloroform were used.[18–23] Of course, many of the advantages of ionic liquids are lost when such diluents are used. Recent investigations have shown that certain ionic liquids can be used with great success in their undiluted form for solvent extraction.[24–27] Moreover, several of these ionic liquids can act both as diluent

and extractant, so that no additional extractants are needed. Non-fluorinated ionic liquids can also be used as diluents for molecular extractants.[28]

Much less information is available on the use of two immiscible ionic liquids for solvent extraction studies. Although it has been known for some time that immiscible ionic liquid systems exist,[29,30] they had only been tested for the extraction of organic compounds.[31] In a recent paper, our research group has reported on a solvent extraction system consisting of the two mutually immiscible ionic liquids 1-ethyl-3-methylimidazolium chloride (initial feed phase) and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)-phosphinate (extracting phase) for the separation of cobalt from nickel.[32] Cobalt was efficiently extracted to the second ionic liquid phase, whereas nickel was not. However, this solvent extraction system has not yet been used for the separation of rare earths. A solvent extraction system in which the rare earths are extracted, but the nickel is not, is of interest for the recycling of rare earths and nickel from end-of-life nickel metal hydride (NiMH) batteries.[33] Nickel is the main component of the electrodes in such batteries, along with light lanthanides. Hydrometallurgical routes have been developed for the recovery of valuable metals from these batteries, but none of these have made use of ionic liquids.[34–37]

In this paper, we show that rare earths are strongly extracted from 1-ethyl-3-methylimidazolium chloride to trihexyl-(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate. It is also shown that rare-earth oxides can be dissolved in 1-ethyl-3-methylimidazolium chloride, provided that a small amount of concentrated hydrochloric acid solution is added to

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the ionic liquid phase. The solvent extraction system allows the separation of nickel and rare earths.

Experimental

The ionic liquids 1-ethyl-3-methylimidazolium chloride, [C_2mim][Cl] and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate ([P_{66614}][R_2POO], Cyphos® IL 104) were purchased from IoLiTec (Heilbronn, Germany). All the hydrated rare-earth chlorides (99.9%) and the oxides (99.9%) used in this study were obtained from ACROS Organics (Geel, Belgium) or from Sigma-Aldrich (Diegem, Belgium). NiCl$_2$ (>98%) was purchased from Sigma-Aldrich. A 1000 ppm gallium standard was purchased from Merck (Overijse, Belgium). Hydrochloric acid and nitric acid were purchased from Sigma Aldrich. Ammonia solution (Analar Normapur, min. 25 wt%) was obtained from VWR (Leuven, Belgium). All chemicals were used as received, without further purification. The rare-earth chlorides LaCl$_3 \cdot$7H$_2$O, NdCl$_3 \cdot$6H$_2$O, EuCl$_3 \cdot$6H$_2$O, HoCl$_3 \cdot$6H$_2$O, DyCl$_3 \cdot$6H$_2$O, YbCl$_3 \cdot$6H$_2$O and YCl$_3 \cdot$6H$_2$O (all with a metal concentration of 5 g L^{-1}) were dissolved in [C_2mim][Cl], (5.55 g, 5 mL) at 95 °C and [P_{66614}][R_2POO] (5 mL) was used as the extracting phase. For individual metal extraction tests, a similar procedure was used. A mixture of the two ionic liquids was stirred for 15 minutes at 95 °C and the metal content in both phases was analyzed after centrifugation (3000 rpm, 5 min) using a Heraeus Megafuge 1.0 centrifuge. The viscosity of the ionic liquid phase before and after extraction was measured using an automatic Brookfield plate cone viscometer, Model LVDV-II+P CP (Brookfield Engineering Laboratories, USA). To quantify the metal content, a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker) was used. For quantification of the metal, about 0.2 g of the ionic liquid solution was diluted in 20 mL of ethanol (for analysis of [P_{66614}][R_2POO] phase) or 20 mL of water (for analysis of [C_2mim][Cl] phase). Then, a gallium solution (1000 mg L^{-1} in HNO$_3$) was added as an internal standard to the solution. An aliquot of 10 μL of this solution was put on a quartz glass carrier, dried in a hot-air-oven at 60 °C, and then measured with a measurement time of 200 seconds. UV-visible absorption spectra were recorded with a Varian Cary 5000 spectrophotometer, with a cuvette holder, which was heated to 80 °C by a circulating water bath. A quartz cuvette with an optical path length of 0.1 mm was used to record the spectra of the highly absorbing solutions. For the metal oxide dissolution tests, the rare-earth oxides (0.029 g of Nd$_2$O$_3$ or 0.028 g of Ho$_2$O$_3$) were added in 5.5 g of [C_2mim][Cl]. The dissolution experiments of Nd$_2$O$_3$ were performed at 95 °C, in the presence of concentrated HCl (1 wt% related to the mass of ionic liquid), while the dissolution experiments of Ho$_2$O$_3$ were done at 145 °C, in the presence of concentrated HCl (5 wt% related to the mass of ionic liquid).

Results and discussions

The structures of the two immiscible ionic liquids 1-ethyl-3-methylimidazolium chloride [C_2mim][Cl] and trihexyl(tetradecyl)-phosphonium bis(2,4,4-trimethylpentyl)phosphinate [P_{66614}] [R_2POO] (R = 2,4,4-trimethylpentyl) are shown in Fig. 1. The latter ionic liquid is also known as Cyphos® IL 104. [C_2mim][Cl] has a negligible solubility in [P_{66614}][R_2POO].[32] The extractant [P_{66614}] [R_2POO] was used without adding any diluents. Extraction experiments were carried out at 95 °C, which is above the melting point of [C_2mim][Cl] (mp = 77–79 °C). The initial metal loading in [C_2mim][Cl] was 5 g L^{-1}.

The *distribution ratio* (D) was determined using the following equation:

$$D = \frac{[M]_{IL2}}{[M]_{IL1}} = \frac{C_i - C_f}{C_f} \times \frac{\text{volume of } [C_2\text{mim}][\text{Cl}]}{\text{volume of } [P_{66614}][R_2\text{POO}]} \quad (1)$$

IL1 is the ionic liquid feed phase [C_2mim][Cl] and IL2 is the ionic liquid extraction phase [P_{66614}][R_2POO]. C_i and C_f are the concentration of the metal ions in the aqueous phase before and after extraction, respectively. M is a metal ion. The *extraction efficiency* (%E) was determined by using the following equation:

$$\%E = \frac{D}{D + \frac{V_{IL2}}{V_{IL1}}} \times 100 \quad (2)$$

The separation factor ($\alpha_{M1,M2}$) was calculated as follows:

$$\alpha_{M1,M2} = \frac{D_{M1}}{D_{M2}} \quad (3)$$

D_{M1} and D_{M2} are the distribution ratios of the metal ions M$_1$ and M$_2$, respectively. The distribution ratios D of the rare-earth ions Y(III), La(III), Nd(III), Eu(III), Dy(III), Ho(III) and Yb(III) after 15 minutes of equilibration are quite high (Fig. 2). The high D values are attributed to the strong complex-forming ability of the [R_2POO]$^-$ anion. The D values for the rare-earth ions in the mixture of different rare earths are almost identical to the values observed for the extraction of individual rare-earth ions from an ionic liquid solution containing only one single rare-earth ion (Fig. 2). This confirms that there is no decrease in the extent of metal complex formation due to competition of the different rare-earth ions for coordination to the [R_2POO]$^-$ anion. This indicates also that the present ionic liquid–ionic
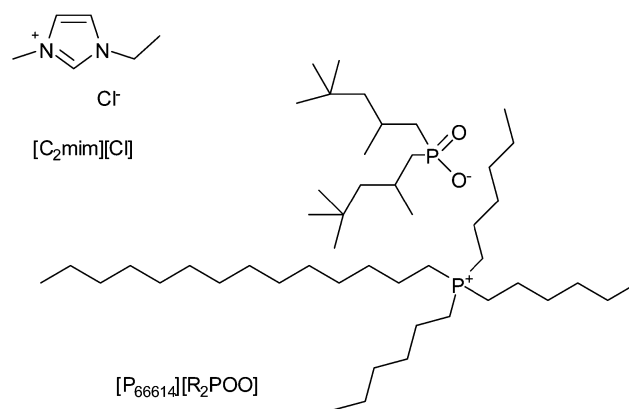

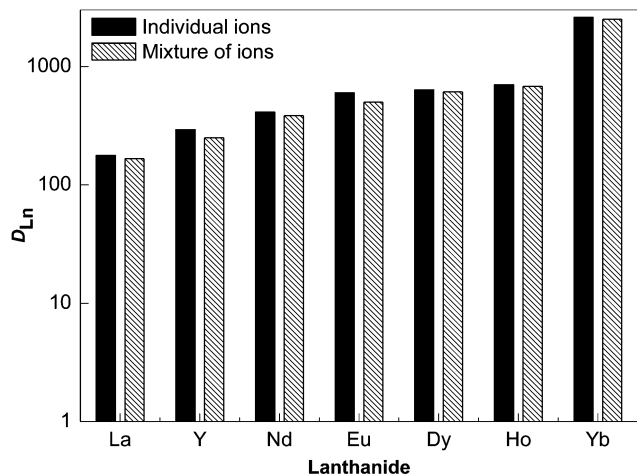Fig. 1 Structures of the ionic liquids [C_2mim][Cl] and [P_{66614}][R_2POO].

Fig. 2 Distribution ratios D of rare-earth ions for extraction studies with individual Ln(III) ions (striped bar) or with mixtures of Ln(III) ions (black bar). Equilibration time: 15 minutes, temperature: 95 °C. Metal feed phase: $[C_2mim][Cl]$ and a single Ln(III) ion (5 g L^{-1} of), or a mixture of all the Ln(III) ions (5 g L^{-1} each, 35 g L^{-1} of lanthanide ions in total).

liquid extraction system can be used to co-extract chemically similar metal ions from a solution containing bulk concentrations. The general trend is that the distribution ratios for the heavy rare earths are larger than for the light rare earths, so that the heavy rare earths are extracted preferentially to the $[P_{66614}][R_2POO]$ phase. This can be explained by a stronger interaction of the $[R_2POO]^-$ anion with the heavy rare earths compared to the light ones. Fig. 2 also shows that the extraction behaviour of yttrium is in between that of lanthanum and neodymium. It is known that the apparent position of yttrium in the lanthanide series differs from one extraction system to the other. Whereas, yttrium is situated between erbium and holmium for extraction by phosphoric acid dialkyl esters, as expected on the basis of its ion radius, yttrium is situated between neodymium and samarium for extraction with tetra-alkylammonium thiocyanates, and between thulium and ytterbium for extraction with tetraalkylammonium nitrates.[38,39] This is the so-called "itinerant" behaviour of yttrium. Some authors have tried to attribute the itinerant behaviour of yttrium to the absence of 4f-orbitals in yttrium, while other authors have tried to correlate the position of yttrium with different thermodynamic parameters such as steric hindrance of ligands, or with the hardness and softness of the ligands (HSAB theory).[40,41] It must be mentioned that in the ionic liquid–ionic liquid extraction system that solvation in the feed phase is totally different from that for extraction from an aqueous chloride medium, wherein the rare-earth ions occur as fully hydrated ions. It can be expected that the rare-earth ions occur as hexachloro or similar complexes in $[C_2mim][Cl]$.[42] However, the coordination of one of more water molecules to the rare-earth ion cannot be excluded, even at high extraction temperatures, because no special efforts were made to rigorously exclude water from the ionic liquid extraction system. It was challenging to obtain reproducible

results for the distribution ratios for the extraction of rare earths from an ionic liquid phase containing a mixture of more rare earths than shown in Fig. 2, since the extracting ionic liquid phase became very viscous (gel formation) within few minutes of contact, probably due to the very high metal loading.

The fine structure of the absorption bands in the optical absorption spectra of Nd(III) in $[C_2mim][Cl]$ and $[P_{66614}][R_2POO]$ was quite different (Fig. 3), indicating that the coordination environment of Nd(III) in the two ionic liquids is different as well. The differences are very pronounced for the hypersensitive transition $(^4G_{5/2}, ^2G_{7/2}) \leftarrow {}^4I_{9/2}$ at about 580 nm. Although it is impossible to identify the extracted species on the basis of these absorption spectra, it can be stated that no simple anion exchange of an anionic neodymium(III) species takes place between the two ionic liquid phases and that is very likely due to the R_2POO^- anions being coordinated to Nd(III) in the $[P_{66614}][R_2POO]$ phase.

The extraction kinetics was studied for the extraction of neodymium(III) by varying the equilibration time from 15 minutes to 1.5 hours. It was observed that D_{Nd} did not change with the equilibration time, indicating that 15 minutes is sufficient to achieve close to 100% extraction. In our earlier work, it was observed that D_{Co} decreased with an increase in temperature.[32] This was attributed to the increase in the solubility of the $[R_2POO]^-$ anion in the $[C_2mim][Cl]$ phase. In the present study, we found a similar trend for the extraction of neodymium, i.e., D_{Nd} varied from 412 to 277, when the temperature was increased from 95 to 145 °C. This decrease in extraction efficiency with increasing temperature suggests that the extraction of Nd(III) is exothermic in nature. Also the increase in solubility of the $[R_2POO]^-$ anion in $[C_2mim][Cl]$
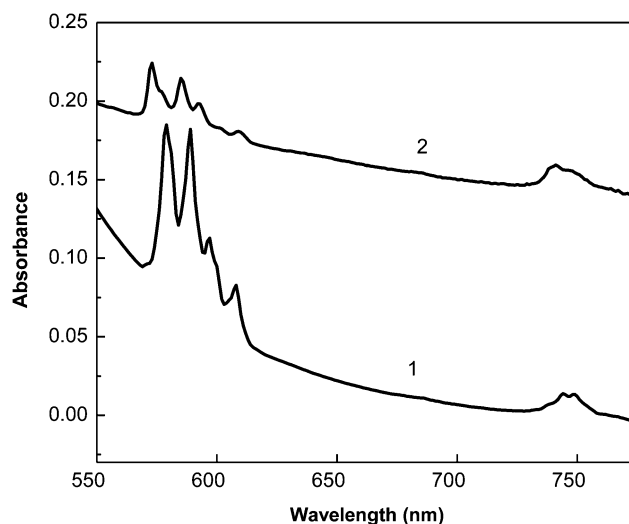

Fig. 3 Absorption spectra of Nd(III) dissolved in the $[C_2mim][Cl]$ phase before extraction (lower curve, 1) and in the $[P_{66614}][R_2POO]$ phase after extraction (upper curve, 2). The displayed part of the absorption spectrum shows the transition $(^4F_{7/2}, ^4S_{3/2}) \leftarrow {}^4I_{9/2}$ at about 740 nm and the hypersensitive transition $(^4G_{5/2}, ^2G_{7/2}) \leftarrow {}^4I_{9/2}$ at about 580 nm.

medium at higher temperature could hinder the extraction to some extent. However, this decreasing trend was much less pronounced when the extraction process was described in terms of extraction efficiency. The extraction efficiencies are almost similar at 95 °C and 145 °C: 99.7% and 99.6%, respectively. Thus it is confirmed that rare-earth ions can be efficiently extracted, even at higher temperatures. The viscosity of pure $[P_{66614}][R_2POO]$ is 203 cP at 60 °C which increases to 362 cP in contact with $[C_2mim][Cl]$. This could be attributed to the partial dissolution of $[C_2mim][Cl]$ (9 wt%) in $[P_{66614}][R_2POO]$. It should be noted that this dissolved amount of $[C_2mim][Cl]$ is recovered from the $[P_{66614}][R_2POO]$ phase during the recovery step (*vide infra*). The viscosity of the $[P_{66614}][R_2POO]$ phase further increases to 505 cP at 60 °C upon the loading of the Nd(III) ion (5 g L^{-1}). The viscosity at the temperature at which the extractions were performed (95 °C) could not be measured since it was about the upper operational temperature of our viscometer. Therefore the viscosity measurements have been carried out at 60 °C.

After the extraction into the $[P_{66614}][R_2POO]$ phase, it is necessary to strip the metal ion back into an aqueous phase and to recycle the ionic liquid phase for further use. The $[P_{66614}][R_2POO]$ phase was equilibrated with 2 M HNO_3 in order to get back all of the Nd(III) from the organic phase. It was observed that all of the Nd(III) could be recovered from the $[P_{66614}][R_2POO]$ phase after two contacts with the HNO_3 solution. Then, the $[P_{66614}][R_2POO]$ phase was washed with distilled water to remove the dissolved $[C_2mim][Cl]$. The $[C_2mim][Cl]$ phase was subsequently regenerated by removing water using a rotary evaporator under reduced pressure. In the next step, the $[P_{66614}][R_2POO]$ phase was scrubbed with a 2 M aqueous NH_3 solution to transform R_2POOH back into the anionic form. The $[P_{66614}][R_2POO]$ phase was then dried for re-use in the next cycle. The distribution ratios obtained with the recycled ionic liquids were within the error limits identical to the values observed for the first extraction experiments. In contrast to stripping with 2 M HNO_3, stripping with 2 M HCl was found to be difficult. Even though 60 to 70% of the metal content could be stripped from the $[P_{66614}][R_2POO]$ phase by HCl in the first stage, the remaining metals could not be removed from the $[P_{66614}][R_2POO]$ phase, even after several successive stripping stages. This observation shows that the bidentate nitrate ions have a stronger stripping power than the monodentate chloride ions.

Since this ionic liquid–ionic liquid extraction system favours efficient extraction of rare earths from their chloride feed, attempts were made to dissolve directly the rare-earth oxides in the $[C_2mim][Cl]$ phase and to carry out the extraction. Unfortunately, rare-earth oxides are not soluble in pure $[C_2mim]$ [Cl].[43] This can be understood by the fact that the Ln–O bond is much more stable than the Ln–Cl bond. However, dissolution is possible if a source of protons is added to the ionic liquid phase. Concentrated hydrogen chloride solution was used as the proton source in $[C_2mim][Cl]$, but the amount of acid added was minimized. Solid Nd_2O_3 (0.029 g) was added to $[C_2mim][Cl]$ and the suspension was stirred at 95 °C, and 1 wt% of conc. HCl (1 wt% related to the 5.5 g of $[C_2mim][Cl]$) was added to

complete the dissolution of the oxide. This small amount of acid was sufficient for complete dissolution of Nd_2O_3 in the $[C_2mim][Cl]$ phase and the time required for dissolution was about one hour. Then the extraction was carried out as described above. It was observed that 99.9% extraction of Nd(III) was possible. This value is very similar to that observed for extraction from $NdCl_3$ dissolution (99.75%). On the contrary, the oxides of the heavy rare earths were much more difficult to dissolve in $[C_2mim][Cl]$. The dissolution process was much slower: more than 4 hours at an elevated temperature (145 °C) were required to completely dissolve Ho_2O_3 in $[C_2mim][Cl]$. To compensate for evaporation of HCl at this high temperature, 5 wt% of HCl was required for dissolution (compared to the 1 wt % for dissolution of Nd_2O_3). Moreover, the larger amount of HCl also increased the reaction kinetics. The differences in reactivity of the lanthanide sesquioxides Ln_2O_3 towards acids can be explained by structural differences: the light lanthanides (La–Nd) have sesquioxides that are A-type (hexagonal), whereas those of the middle lanthanides (Sm–Gd) are either B-type (monoclinic) or C-type (cubic), and the heavy lanthanides (Tb–Lu) are of C-type.[44] C-type sesquioxides react very slowly with acids compared to A-type or B-type compounds. The possibility of dissolving rare-earth oxides rather than rare-earth salts in ionic liquids is of importance for the use of ionic liquids as leaching solutions to dissolve rare earths from ores or concentrates.[45,46] One should notice that in the case of the use of ionic liquids instead of an aqueous phase, it is advisable to speak about *ionometallurgy* rather than about hydrometallurgy.[47] A flow sheet can be proposed for the whole process, starting from dissolution of rare-earth oxides in $[C_2mim][Cl]$, followed by extraction to $[P_{66614}][R_2POO]$, stripping to an aqueous phase, and regeneration of the ionic liquid phases (Fig. 4).

Given the fact that the rare earths are well extracted from the $[C_2mim][Cl]$ phase to the $[P_{66614}][R_2POO]$ phase and the previous knowledge that nickel is not extracted, the ionic liquid–ionic liquid system was tested for the separation of rare earths from nickel. As explained in the introduction, such separations are relevant for the recycling of metal values from end-of-life nickel metal hydride batteries. Solvent extraction experiments were carried out with $[C_2mim][Cl]$ feed solutions containing 5 g L^{-1} of La(III) or Ni(II), and with mixtures containing both La(III) and Ni(II) (5 g L^{-1} each) (Table 1). Nickel is not extracted from the lanthanum–nickel mixture (D_{Ni} = 0.086), and this result is quite similar to the behaviour of Ni(II) when it is present alone in the feed ionic liquid (D_{Ni} = 0.06). On the contrary, lanthanum is extracted from the mixture also as well as for extraction from the solution in which only La(III) is present, giving a separation factor $\alpha_{La,Ni}$ of 1440. These results show that nickel can be separated from lanthanum using the two mutually immiscible ionic liquids. Based on the results shown in Fig. 2, it can be concluded that also separation of nickel from rare earths other than lanthanum should be possible, especially because the distribution factors of the rare earths increase over the lanthanide series. Fig. 5 shows the flow sheet for a process to separate lanthanum from nickel by this ionic liquid–ionic liquid extraction system.
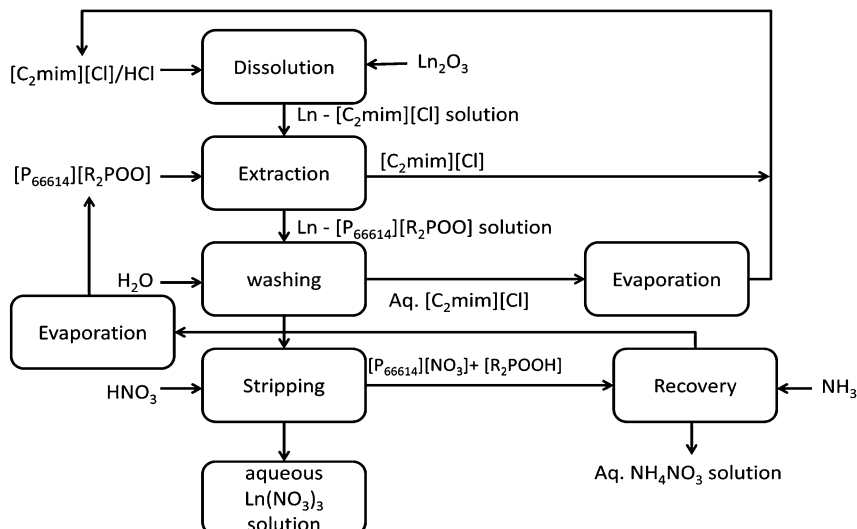
Fig. 4 Flow sheet for a process consisting of dissolution of rare-earth oxides in [C$_2$mim][Cl], followed by extraction to [P$_{66614}$][R$_2$POO], stripping to an aqueous phase, and regeneration of the ionic liquid phases.

Table 1 Distribution ratio and separation factors for the extraction of lanthanum and nickel with the ionic liquids [C$_2$mim][Cl] and [P$_{66614}$][R$_2$POO][a]

Extraction parameters[b]	Single-element solution	Mixed solution
D_{La}	175	124
D_{Ni}	0.06	0.086
$\alpha_{La,Ni}$	2916	1440

[a] Temperature: 95 °C; equilibration time: 15 minutes; metal feed phase: [C$_2$mim][Cl] and 5 g L^{-1} of La(III) and Ni(II) ions individually (single-element solution), or a mixture of La(III) and Ni(II), 5 g L^{-1} each (mixed solution). [b] D_{La} = distribution ratio of lanthanum(III); D_{Ni} = distribution ratio of nickel(II); α(La, Ni) = separation factor of lanthanum(III) over nickel(II).

Conclusions

In this paper, the proof-of-principle is given for the extraction of trivalent rare-earth ions from the ionic liquid 1-ethyl-3-methyl-imidazolium chloride to the ionic liquid trihexyl(tetradecyl)-phosphonium bis(2,4,4-trimethylpentyl)phosphinate. This work extends our earlier findings that two mutually immiscible ionic liquid phases can be used as solvent extraction systems for metals.[32] The two phases contain non-fluorinated ionic liquids, which is an advantage both from an economical and environmental point of view. The extraction phase does not contain any other components than the ionic liquid, so that the ionic liquid acts both as diluent and extractant. The solvent extraction system can be used for the separation of rare earths from nickel, because nickel is extracted to a very limited degree. Therefore,
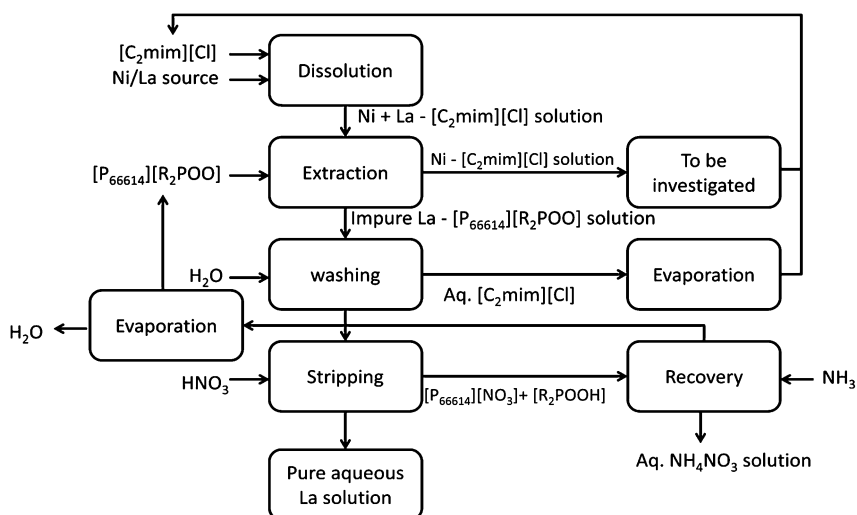

Fig. 5 Flow sheet for the separation of lanthanum from nickel with the ionic liquid–ionic liquid extraction system [C$_2$mim][Cl]/[P$_{66614}$][R$_2$POO].

such an extraction system is useful for the recovery of nickel and rare earths from end-of-life nickel metal hydride batteries. This paper also shows that rare-earth oxides can be dissolved in 1-ethyl-3-methylimidazolium chloride, provided that a small amount of concentrated hydrochloric acid is added. Different reactivities were observed depending on the type of rare-earth sesquioxide. This opens up the possibility for using ionic liquids as leaching solutions of rare-earth ores or concentrates.

Acknowledgements

References

1 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.

2 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.

3 J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.

4 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766.

5 I. Billard, A. Ouadi and C. Gaillard, *Anal. Bioanal. Chem.*, 2011, **400**, 1555–1566.

6 I. Billard, A. Ouadi and C. Gaillard, *Dalton Trans.*, 2013, **42**, 6203–6212.

7 Z. Kolarik, *Solvent Extr. Ion Exch.*, 2013, **31**, 24–60.

8 P. R. Vasudeva Rao, K. A. Venkatesan, A. Rout, T. G. Srinivasan and K. Nagarajan, *Sep. Sci. Technol.*, 2012, **47**, 204–222.

9 X. Q. Sun, H. M. Luo and S. Dai, *Chem. Rev.*, 2012, **112**, 2100–2128.

10 Y. Baba, F. Kubota, N. Kamiya and M. Goto, *J. Chem. Eng. Jpn.*, 2011, **44**, 679–685.

11 M. P. Jensen, J. Neuefeind, J. V. Beitz, S. Skanthakumar and L. Soderholm, *J. Am. Chem. Soc.*, 2003, **125**, 15466–15473.

12 I. Billard, A. Ouadi, E. Jobin, J. Champion, C. Gaillard and S. Georg, *Solvent Extr. Ion Exch.*, 2011, **29**, 577–601.

13 A. Rout, S. Karmakar, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *Sep. Purif. Technol.*, 2011, **81**, 109–115.

14 A. Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *J. Hazard. Mater.*, 2012, **221**, 62–67.

15 J. M. Lee, *Fluid Phase Equilib.*, 2012, **319**, 30–36.

16 X. Q. Sun, H. M. Luo and S. Dai, *Dalton Trans.*, 2013, **42**, 8270–8275.

17 M. L. Dietz and D. C. Stepinski, *Green Chem.*, 2005, **7**, 747–750.

18 A. Stojanovic, C. Morgenbesser, D. Kogelnig, R. Krachler and B. K. Keppler, Quaternary Ammonium and Phosphonium Ionic Liquids in Chemical and Environmental Engineering, in *Ionic Liquids: Theory, Properties, New Approaches*, ed. A. Kokorin, InTech, New York, 2011, pp. 657–680.

19 A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, 2010, **73**, 202–207.

20 A. Cieszynska and M. Wisniewski, *Hydrometallurgy*, 2012, **113**, 79–85.

21 A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, 2011, **80**, 385–389.

22 P. Rybka and M. Regel-Rosocka, *Sep. Sci. Technol.*, 2012, **47**, 1296–1302.

23 D. Kogelnig, A. Stojanovic, F. Jirsa, W. Korner, R. Krachler and B. K. Keppler, *Sep. Purif. Technol.*, 2010, **72**, 56–60.

24 S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, **14**, 1657–1665.

25 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.

26 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, **15**, 205–209.

27 S. Wellens, R. Goovaerts, C. Möller, J. Luyten, B. Thijs and K. Binnemans, *Green Chem.*, 2013, **15**, 3160–3164.

28 X. Q. Sun, Y. Ji, L. Guo, J. Chen and D. Q. Li, *Sep. Purif. Technol.*, 2011, **81**, 25–30.

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

30 A. Arce, M. J. Earle, S. P. Katdare, H. Rodriguez and K. R. Seddon, *Fluid Phase Equilib.*, 2007, **261**, 427–433.

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

32 S. Wellens, B. Thijs, C. Möller and K. Binnemans, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9663–9669.

33 K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton and M. Buchert, *J. Clean. Prod.*, 2013, **51**, 1–22.

34 K. Larsson, C. Ekberg and A. Odegaard-Jensen, *Hydrometallurgy*, 2012, **129**, 35–42.

35 K. Larsson, C. Ekberg and A. Odegaard-Jensen, *Waste Manage.*, 2013, **33**, 689–698.

36 K. Larsson, C. Ekberg and A. Odegaard-Jensen, *Hydrometallurgy*, 2013, **133**, 168–175.

37 P. W. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T. M. Suzuki and K. Inoue, *Hydrometallurgy*, 1998, **50**, 61–75.

38 Z. S. Yu and M. B. Chen, *Rare Earth Elements and their Applications*, Metallurgical Industry Press, Beijing (P.R. China), 1995.

39 M. Borkowski and S. Siekierski, *Radiochim. Acta*, 1992, **56**, 31–35.

40 S. Siekierski, *J. Solid State Chem.*, 1981, **37**, 279–283.

41 S. Siekierski, *Radiochem. Radioanal. Lett.*, 1981, **48**, 201–208.

42 K. Matsumoto, T. Tsuda, T. Nohira, R. Hagiwara, Y. Ito and O. Tamada, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2002, **58**, m186–m187.

43 K. Binnemans, *Chem. Rev.*, 2007, **107**, 2592–2614.

44 G. Adachi and N. Imanaka, *Chem. Rev.*, 1998, **98**, 1479–1514.

45 J. A. Whitehead, J. Zhang, N. Pereira, A. McCluskey and G. A. Lawrance, *Hydrometallurgy*, 2007, **88**, 109–120.

46 J. A. Whitehead, J. Zhang, A. McCluskey and G. A. Lawrance, *Hydrometallurgy*, 2009, **98**, 276–280.

47 A. P. Abbott, G. Frisch, S. J. Gurman, A. R. Hillman, J. Hartley, F. Holyoak and K. S. Ryder, *Chem. Commun.*, 2011, **47**, 10031–10033.