Separation of rare earths by split-anion extraction

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1. Introduction

Solvent extraction is the most important separation technique for rare earths on an industrial scale (Gupta and Krishnamurthy, 1992; Krishnamurthy and Gupta, 2004; Xie et al., 2014; Thakur, 2000; Kronholm et al., 2013; Brown and Sherrington, 1979; Preston and du Preez, 1990). The separation of rare-earth ions by solvent extraction depends upon the preferential distribution of the rare earths between two immiscible phases, typically an aqueous phase and an organic phase that are in contact with each other. The transfer of rare-earth ions from the aqueous to the organic phase is facilitated by extractants. The most often used extractants for the separation of rare-earth ions are the acidic phosphorus-containing extractants bis(2-ethylhexyl)phosphoric acid (HDEHP, D2EHPA or P204) (Peppard et al., 1957; Sato, 1989; Preston et al., 1996), (2-ethylhexyl)phosphonic acid, mono(2-ethylhexyl) ester (HEHEHP, or P507) (Sato, 1989; Zhou et al., 2007; Mishra et al., 2000; Fontana and Pietrelli, 2009), and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyaxen 272) (Kim et al., 2012; Banda et al., 2012; Li and Freiser, 1986). An advantage of these acidic extractants is that one single extractant can be used for the separation of a mixture containing all the rare earths, due to the relatively large separation factors for neighboring rare-earth ions. Another advantage is that they are widely applicable and that they can be used to extract rare-earth ions from aqueous feed solutions containing different types of anions (chloride, nitrate, sulfate), as long as the rare-earth ions are present in the aqueous feed solution as hydrated cations or cationic complexes. However, the acidic extractants have several disadvantages. The extraction process is pH-sensitive. Although selectivity can be achieved by pH control, the adjustment of the pH requires a careful process monitoring. Stripping of the rare-earth ions from the loaded organic phase can be very difficult, due to the strong affinity of the rare-earth ions for these extractants. For instance, concentrated sulfuric acid or even hydrogen fluoride solutions are required to strip the heavy rare earths from the organic phase after extraction with HDEHP. The pH control and back-extraction (stripping) consume considerable amounts of chemicals. Acids are required for pH control and back-extraction, and bases are required for pH control and for pre-neutralization (saponification) of the acidic extractants before extraction and for neutralization of the very acidic stripping solutions. As a consequence of the reactions between acids and bases, large volumes of waste water with high salt concentrations are produced (Wang et al., 2013). Another disadvantage of acidic extractants is the difficulty to work with very concentrated aqueous feed solutions. In general the concentrations of the aqueous feed solutions are between 30 and 50 g/L (total rare-earth oxide content). A high loading of the organic phase should be avoided, because otherwise a gel can form (Yurtov and Murashova, 2007). In the case of HDEHP, gel formation occurs at approximately 50% saturation of the extractant. The low rare-earth concentration in the aqueous feed solution results in low concentrations in the organic phase and in diluted aqueous solutions after back-extraction. The back-extraction solution is even further diluted...
by the large amounts of acids used for back-extraction. This leads to a low efficiency of the solvent extraction process.

**Neutral extractants (solvating extractants)** are a second type of extractants used for rare-earth separations. Examples of neutral extractants are tri-n-butylphosphate (TBP) and the phosphine oxide mixtures Cyanex 923 or Cyanex 925 (Majdan, 1994; Hesford et al., 1999; Peppard et al., 1957; Dziwinski and Szymanski, 1998). These extractants have several advantages compared to acidic extractants. First of all, they can be used to extract rare earths from very concentrated aqueous feed solutions, containing 100 to 500 g/L of dissolved rare-earth oxides. This results in concentrated organic phases after extraction. There are less issues with gel formation in the highly loaded organic phases compared to extraction with acidic extractants. Secondly, the extraction process shows little dependence on the pH, so that careful pH control is not required. Thirdly, back-extraction can simply be achieved with neutral or slightly acidified water. The aqueous solution after back-extraction has a high rare-earth concentration and contains very few contaminants. A disadvantage of neutral extractants is that they only extract rare-earth ions efficiently from aqueous nitrate or thiocyanate solutions, not from chloride solutions.

**Basic extractants (anion exchangers)** are a third class of extractants (Genov and Pamuktschiowa, 1976; Bagreev and Popov, 1985; Gorski et al., 1991; Maeck et al., 1961). Typical examples of such extractants are quaternary ammonium salts, e.g., triacylphosphonium chloride (Aliquat 336). The performance of basic extractants is somewhat similar to that of neutral extractants, in the sense that they have been used to extract rare earths from nitrate and thiocyanate media (not from a pure chloride medium), and that the rare earths can easily be stripped from the loaded organic phase (Bauer and Lindstrom, 1971) (Gaudernack et al., 1974). However, the possibility to extract rare earths from chloride solutions by basic extractants is very useful for the development of new industrial separation processes, because hydrochloric acid is much cheaper and more readily available than nitric acid. Hydrochloric acid is easier to recycle and to use in a closed-loop process than nitric acid. Waste water treatment of chloride-containing waste streams is easier than treatment of nitrate-containing waste streams.

**Ionic liquids** (ILs) are solvents that consist entirely of cations and anions (Welton, 1999; Seddon, 1997; Plechkova and Seddon, 2008). Basic extractants with a low melting point (<100 °C) are ionic liquids. Ionic liquids are not volatile, have a very low flammability and are good solvents for many classes of metal complexes. Water-immiscible ionic liquids have been used as an alternative for conventional organic solvents in solvent extraction processes (Stojanovic and Keppler, 2012; Billard, 2013; Billard et al., 2011; Visser et al., 2001; Liu et al., 2012; Kolarik, 2013; Nakashima et al., 2003; Sun et al., 2012; Kubota et al., 2012; Dietz, 2006). Ionic liquids can be used as undiluted extractants or as diluents for other extractants. From an industrial point of view, ionic liquids with non-fluorinated anions are of special interest, because these ionic liquids are much cheaper and environmentally friendlier than their fluorinated counterparts. Presently, there is a strong research interest in ionic liquids derived of the quaternary ammonium salt triacrylphosphonium chloride (Aliquat 336) or the trihexyl(tetradecyl)phosphonium cation for solvent extraction studies (Wells et al., 2012; Vander Hoogerstraete et al., 2013; Vander Hoogerstraete and Binnemans, 2014; Sun et al., 2011; Rout and Binnemans, 2013). These ionic liquids are most often used in the chloride or nitrate form, but many other anions are possible. It has been shown that undiluted ionic liquids are compatible with continuous solvent extraction processes (Wells et al., 2013).

In this paper, we describe a new approach to the extraction of rare-earth ions from a concentrated chloride aqueous phase to an organic phase, consisting of a water-immiscible nitrate or thiocyanate ionic liquid. The largest benefits of this new approach is that anions such as thiocyanate or nitrate can be used for extraction and separation of rare-earth ions from chloride aqueous media and that the thiocyanate-based systems show significant separation factors. When comparing with the traditionally used basic extractants this can lead to reduced operational costs and more environmentally friendly processes (waste water will contain chloride instead of nitrate ions). The term split-anion extraction is introduced to describe this new solvent extraction process, since different anions are present in the aqueous phase and in the organic phase and the distribution of the ionic liquid anions strongly favors the ionic liquid phase. Split-anion extraction is unusual in the sense that it is performed with basic extractants, but the extraction mechanism is not an anion exchange.

2. Theory

Ionic liquids based on triacrylphosphonium or trihexyl(tetradecyl)phosphonium cations with thiocyanate or nitrate anions can be used in combination with aqueous feed phases containing chloride ions because the order of preference for the ions with regard to the organic phase is in ascending order: $SO_4^{–} < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < SCN^-$. This order reflects the hydration numbers of the different anions, with the sulfate ion being the most hydrated one, and corresponds to the Hofmeister series or lyotropic series (Larsen and Magid, 1974; Kunz et al., 2004). Depending on the cation of the ionic liquid, there can be a reversal in the order of some of the anions. Since nitrates and thiocyanates have a higher affinity for the organic phase than chlorides, hydrophobic quaternary ammonium chlorides such as $[A336][Cl]$ can be transformed into their nitrate or thiocyanate forms by contacting the chloride salt with a concentrated aqueous solution of a water-soluble nitrate or thiocyanate salt, respectively. During split-anion extraction there is only a limited transfer of the different anions from one phase to the other, because the extraction does not occur via an anion exchange mechanism but rather by extraction of the rare-earth ions together with the chloride ions that are required to maintain electrical neutrality. Moreover, due to the much stronger affinity of the nitrate and thiocyanate ions for the ionic liquids phase compared to the aqueous phase, these ions remain in the ionic liquid phase.

The distribution ratio ($D$) of a single metal is defined in Eq. (1) as the ratio of the total concentration in the ionic liquid phase ([M]$_{IL}$) by the total concentration in the aqueous phase ([M]$_{aq}$) after extraction and phase separation. The phase ratios ($\Theta$) were calculated by dividing the volume of the ionic liquid phase by the volume of the aqueous phase (Eq. (2)). Separation factors ($\alpha_{A,B}$) are defined in Eq. (3), where the metals A and B are chosen so that $\alpha > 1$ by convention.

\[
D = \frac{[M]_{IL}}{[M]_{aq}} \tag{1}
\]

\[
\Theta = \frac{V_{IL}}{V_{aq}} \tag{2}
\]

\[
\alpha_{A,B} = \frac{D_A}{D_B} \tag{3}
\]

In its most general form, the split-anion extraction separates rare-earth ions from an aqueous phase containing $B^+$ anions to a water-immiscible organic phase (ionic liquid) with $A^+$ anions. The interaction between rare-earth ions (Ln$^{3+}$) and anions from the IL (A$^+$) is much stronger than with the anion from the rare-earth or background salt ($B^+$). The $A^+$ anions can be for example nitrates or thiocyanates. The $B^+$ anions have to form more weakly extracted complexes with rare-earth ions and can be for example chlorides. The $B^+$ anions also need to have a lower affinity for the ionic liquid cations than $A^+$. A general form of the reaction is described in Eq. (4) for a phosphonium ionic
liquid (PR4A). The bars in the equations mean that the species is in the organic phase and Ln represents any trivalent rare-earth ion.

\[ \text{Ln}^{3+} + 3B^- + x PR4A_{\text{org}} \rightarrow (PR4_4)_{(x-3)} \left( (\text{Ln}A_{\text{org}})^{3-x} \right) + 3PR4B \]  

(4)

It is also likely that a small amount of A^- ions is available in the aqueous phase through an anion exchange reaction (Eq. (5)).

\[ B^- + PR4A_{\text{org}} \rightarrow A^- + PR4B \]  

(5)

3. Experimental

3.1. Chemicals

Tricaprylmethylammonium chloride (Aliquat 336, [A336][Cl]), is a mixed ammonium salt of mainly trioctylmethylammonium and tridecylmethylammonium chloride (Sigma-Aldrich, 88.2–90.6% quaternary). Cyphos IL 101 ([C101][Cl]) is an ionic liquid containing trihexyl(tetradecyl)phosphonium chloride (Cytec, 97.7%). The molar concentration of the extractants is important for the loading capacity and a high mixing speed (3000 rpm). Samples were centrifuged for 30 s and immediately afterwards the phases were separated.

The influence of the chloride concentration in the aqueous phase was significant for the extraction and was studied for thiocyanate and nitrate. The rare earths were divided in the same groups as solutions 1 and 2 for each chloride ion concentration, resulting in eight solutions for four chloride concentrations (2 M, 4 M, 6 M and 8 M). Each solution had a concentration of approximately 0.005–0.01 M for each metal. The extractions were carried out at 30 °C with a phase ratio of 1:1 and mixture was shaken for 2 h.

To attain a sufficiently high (within TXRF detection limits) metal concentration to study the stripping the rare-earth ions were split into four separate groups: solutions 3 [La, Pr, Sm, Eu], 4 [Y, Dy, Er, Yb], 5 (Ce, Nd, Gd, Dy, Er, Yb), and 6 (Th, Ho, Tb, Lu). These groups were chosen because the heavier lanthanides were preferentially extracted and having non-adjacent rare earths improves TXRF detection limits. The aqueous solutions used to prepare the loaded organic solutions had a 4 M MgCl2 matrix. Pre-saturated ionic liquids were used and the loaded organic phases had approximately 5–10 g/L of total metal ion content.

3.3. Extraction protocols

Batch solvent extraction experiments were performed using approximately 1 mL of each phase, unless other phase ratios were tested, in which case the ionic liquid volume was increased. Samples were shaken at constant temperature (30 °C or 50 °C) using a TMS-200 turbo thermoshaker (Hangzhou Allsheng Instruments Co., Ltd.). A Heraeus Labofuge 200 at 3000 rpm was used for centrifugation.

In order to show how the distribution ratios of individual rare-earth ions varies in the relevant systems, experiments were performed using both individual rare-earth ion solutions and mixed solutions with low concentrations where the rare earths were split into groups with equimolar concentrations. Two solutions were used to improve TXRF detection and to limit the loading of the metal in the ionic liquids (solution 1: La, Pr, Sm, Eu, Tb, Ho, Tb, Mn, Y; solution 2: Ce, Nd, Gd, Dy, Er, Yb). The two solutions were of approximately equimolar concentrations (~0.02 M for each metal ion), with an 8 M chloride matrix (4 M MgCl2). The extractions were carried out with thiocyanate or nitrate. The extraction kinetics of the [A336][SCN] and [C101][SCN] systems were studied using an aqueous solution with a chloride matrix (4 M MgCl2), spiked with ytterbium(III) chloride to approximately 30 g/L. The experiments were carried out at 30 °C with a phase ratio of 1:1 and a high mixing speed (3000 rpm). Samples were centrifuged for 30 s and immediately afterwards the phases were separated.

3.4. Results and discussion

4.1. Extraction with nitrates and thiocyanates

The distribution ratios across the lanthanide series using thiocyanate and nitrate ionic liquids on chloride aqueous phases (solutions 1 and 2) are shown in Fig. 1. The separation factors obtained using the
distribution ratios are listed in Table 1 for [C101][SCN] and Table 2 for [A336][SCN]. These experimental data show that thiocyanate-based ILs had larger separation factors than the nitrate-based ILs. The thiocyanate-based ILs are therefore more suitable for further research into the separation of rare earths and the split-anion extraction was studied in detail for the chloride-thiocyanate systems. The ammonium-based ILs extract the light rare earths more strongly than the phosphonium-based ILs, giving lower separation factors. Part of the difference in distribution ratios can be related to the loading capacity of the ionic liquids. The ammonium-based ionic liquid has a higher loading capacity, related to its lower molecular mass.

4.2. pH dependence

The trend of the pH dependence of the solvent extraction process is similar over the different rare-earth ions, but varies with the chloride concentration. In order to easily describe the pH dependence low (4 M) and high (8 M) chloride concentration solutions were used in combination with a single element, ytterbium, and with [C101][SCN] as the ionic liquid. The pH measurements have not been corrected to compensate for the high ionic strength of the solutions. The pH dependence is such that at above 1.5–2.0 the distribution ratios are fairly constant for the 8 M chloride solution and in more acidic conditions (pH < 1.5) the distribution ratios fall rapidly (Fig. 2). For the solution with the lower chloride concentration (4 M) the distribution ratios are small at low pH but increase linearly with increasing pH values beyond pH 1.5. The solutions referred to throughout the article had pH values above 1.5, which have stable distribution ratios in solutions with high chloride concentrations.

4.3. Influence of equilibration time

The time required to reach equilibrium for both the [A336][SCN] and [C101][SCN] systems was approximately 10 to 12 min (Fig. 3). The equilibration time can be influenced by changing the mixing speed or the temperature. The reason for the lower ytterbium(III) concentration in the organic phase at equilibrium for the [C101][SCN] system is explained by the loading capacity of the ionic liquid which was higher for the [A336][SCN] system. The concentrations of ytterbium(III) in the organic phase were determined using aqueous phase concentrations and a mass balance. The time to reach equilibrium is quite short so one can conclude that using the ionic liquid system is feasible from a kinetic point of view.

4.4. Chloride concentration

The chloride concentration has a major impact on the distribution ratios and can be used to fine-tune the desired extraction properties and this can be utilized during the scrub and strip steps. The dependence of the extraction efficiency on the chloride concentration for pre-saturated [C101][SCN] (Fig. 4) is similar to that of pre-saturated [A336][SCN] (Fig. 5). The greater difference in distribution ratio across the lanthanide series for [C101][SCN] gave larger separation factors than [A336][SCN]. Yttrium was similar in behavior to terbium in these experiments. The slopes remain fairly constant with varying chloride concentrations.

4.5. Loading

To achieve the desired separations, the phase ratio should be optimized, dependent on the feed concentrations, to such an extent that the organic phase loads the desired heavier rare earths. The heavier rare earths have a crowding effect on the extraction of lighter rare earths (the rare earths with a higher D displaces the ones with a lower D at high loading). The crowding occurs significantly when the organic phase reaches its loading capacity, which is limited primarily by the availability of complexing anions (nitrates or thiocyanates). The loading capacity for individual metal ions in the thiocyanate ionic liquid phases varied in the range 0.14–0.26 mol/L, depending on the type of rare-earth ion. The loading capacity of [A336][SCN] (0.26 mol/L or 46 g/L for ytterbium) was higher than for [C101][SCN], but was of the same order of magnitude. This is probably due to the anion concentration in the organic phase.

![Fig. 1. Distribution ratios for split-anion extraction of rare-earth ions from chloride solutions by thiocyanate or nitrate ionic liquids. Two separate aqueous mixtures, containing approximately 0.02 M of each individual rare-earth ion in a 4 M MgCl₂ matrix when contacted at 50 °C with a phase ratio of 1:1. Distribution ratios are graphically represented in Fig. 1.](image)

Table 1: Separation factors between individual rare earths for extraction with the phosphonium ionic liquid [C101][SCN].

<table>
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<th>Tb</th>
<th>Gd</th>
<th>Eu</th>
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<td>13,000</td>
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<td>21</td>
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*a The separation factors were determined by measuring the distribution ratios in two individual solutions (La, Pr, Sm, Eu, Tb, Ho, Tn, Lu; Ce, Nd, Gd, Dy, Er, Yb) at approximately 0.02 M each in a 4 M MgCl₂ matrix when contacted at 50 °C with a phase ratio of 1:1. Distribution ratios are graphically represented in Fig. 1.*
the ionic liquid, which is higher for the ammonium-based ionic liquid since the molar mass for the quaternary ammonium cation is lower.

Loading curves for single elements were obtained at 30 °C with a 4 M MgCl₂ matrix for [C₁₀₁][SCN]. The results followed power-law behavior and is therefore shown as a log–log plot (Fig. 6). These data show that the distribution ratios change by a factor of approximately 10,000 when the rare-earth concentration in the aqueous phase is varied between 0.0001 M and 0.1 M. This means that optimization with respect to loading is very important for process development. The [A₃₃₆][SCN] displayed a very similar loading behavior for single elements but with slightly higher loading capacity.

The crowding by heavier lanthanides was demonstrated using solution 1 and successively loading it with lutetium (Fig. 7, only Y, La, Pr, Tb, Lu shown for clarity). This allowed for the study of lanthanides lighter than lutetium in an increasingly loaded environment using [A₃₃₆][SCN]. The distribution ratios of all the elements fall rapidly with the increasing total metal concentration in the organic phase. The phosphonium-based ionic liquid displayed similar behavior of decreasing distribution ratios.

4.6. Stripping

Stripping from four separate organic phases with approximately 5–10 g/L of total metal content was studied using water and 2 or 4 M MgCl₂ solutions. The results for [A₃₃₆][SCN] and [C₁₀₁][SCN] both indicate that efficient scrub (selective removal) and strip steps can be achieved using aqueous phases of optimized chloride concentrations (Tables 3 and 4). This is due to the large difference in distribution ratios between rare earths at the medium and high chloride concentrations combined with a close to total strip when using water. It is also noteworthy that a total strip is easily attainable using pure water even when the ionic liquids have additional thiocyanate (pre-saturated), since an excess of anions in the strip phase can lead to poor stripping.

4.7. Distribution of thiocyanate

The distribution of thiocyanate was studied at two chloride concentrations representing the strip (pure water) and scrub (4 M MgCl₂) in the system (Tables 5, 6). The scrub was also spiked with ytterbium(III) chloride (approximately 10 g/L) since the presence of lanthanides in the ionic liquid binds thiocyanates and reduces the amount of thiocyanate lost to the aqueous phase. This demonstrated that ~10 mM of thiocyanate will be lost to the aqueous phase from an ionic liquid that does not have an excess of thiocyanate (double washed). When there is an excess of thiocyanate (pre-saturated) the loss of the excess thiocyanate is significant in pure water but mitigated at high chloride concentrations and in the presence of rare-earth ions. It will be important to determine if excess thiocyanate is necessary in the extraction stages since this can lead to increased thiocyanate levels in a strip solution, but likely not in a scrub solution.

In order to study the extraction behavior without removing the ionic liquid character of the organic phase, an ionic liquid with anions not...
forming extractable complexes with rare-earth ions was required. Since perchlorate has a low tendency to form such complexes and a higher tendency to reside in the ionic liquid than chloride anions, trihexyl(tetradecyl)phosphonium perchlorate, [C101][ClO4], was found to be very suitable for this purpose.

Extraction of dysprosium(III) into pure [C101][ClO4] was investigated with varying amounts of thiocyanate added to the initial 6 M chloride aqueous phase (Fig. 8). The slope of the distribution ratios versus the thiocyanate concentration (log–log plot) is equivalent to the number of thiocyanate anions required to extract from the aqueous phase. The obtained slope was 3.2, which indicates that the distribution ratio of the rare earths varies with the thiocyanate concentration in the aqueous phase to the power of three.

In a similar experiment using [C101][SCN] (washed) instead of [C101][ClO4], the slope of the log–log plot was 3.1, also indicating that three thiocyanate anions are required to extract one rare earth ion from the aqueous phase. The extracted complex is likely formed in the aqueous phase rather than in the ionic liquid, as indicated by the experiments with varying aqueous thiocyanate concentration. Eq. (4) can now be modified into Eq. (6), which assumes that a small amount of A anions is present in the aqueous phase (due to anion exchange between the aqueous and ionic liquid phase). It is reasonable to assume that the number of A anions complexed to the rare earth ion ≥ 3 when in the ionic liquid phase (x ≥ 3).

\[
\ln^{2+} + 3\text{SCN}^- + (x-3)\text{PR}_4\text{A} \rightarrow (\text{PR}_4^+)^{3-x} + (\text{Ln(SCN)}_x)^{-x} \quad (6)
\]

The reactions can now be expressed in terms specific to the thiocyanate extraction (Eq. (7)).

\[
\ln^{2+} + 3\text{SCN}^- + (x-3)\text{PR}_4\text{SCN} \rightarrow (\text{PR}_4^+)^{3-x} + (\text{Ln SCN})_x^{3-x} \quad (7)
\]

The information gained by varying the thiocyanate concentration with [C101][ClO4] showed that adding 0.295 M thiocyanate to the aqueous phase gave the same distribution ratio as pure [C101][SCN] (washed) for 50 mM dysprosium when in contact with 6 M chloride solutions. This is much lower than the approximately 1.6 M thiocyanate ions present in pure [C101][SCN] (depending on purity and water-saturation levels). This large difference indicates that a large part of the perchlorate anions remain in the ionic liquid, thereby increasing the free thiocyanate concentration available to complex with the rare-earth ions, when comparing how perchlorate and chloride ions distribute. This effect of the perchlorate could be utilized to reduce the total level of thiocyanate in the system while maintaining high distribution ratios.
creases the amount of thiocyanate available for complexation and of thiocyanate anions, an increased tendency to reside in the IL likely in-
this can be explained by the influence of the anions on the distribution of thiocyanate ions according to the order in the Hofmeister series (sulfate and perchlorate). The distribution ratios for the anions correspond to the non-linear behavior in a log–log plot. Two processes that can influence this are the salting-out effect and the displacement of the equilibrium of anion distribution (freeing up thiocyanate through anion exchange) between the ionic liquid and the aqueous phase. With increasing chloride or perchlorate concentrations, a large number of ionic liquid cations associate with these anions rather than thiocyanate ions, while the thiocyanate ions extract rare-earth ions. Since both sulfate and chloride have a very strong tendency to be highly hydrated, and since many anions are void of these anions. The distribution ratios can be increased by adding anions forming extractable complexes since the aqueous phase is deficient in these anions. The distribution ratios and the separation factors can be tuned by an appropriate choice of the chloride concentration. Separation schemes for mixtures of rare-earth ions can be designed based on these variations of the chloride concentration. The possibility of switching between different ionic liquids in a process is an advantage since the different ionic liquid anions (nitrate or thiocyanate) exhibit such different extraction behavior for rare-earth ions, without having to change the chloride-containing aqueous phase. Selectively stripping with an aqueous phase containing the same anions as the ionic liquid phase could give higher separation factors. The IL phase needs to have a relatively high concentration of metal ions.

<p>| Table 3 |
| Distribution ratios for stripping of rare earths from [A136][SCN]. |</p>
<table>
<thead>
<tr>
<th>4 M MgCl₂</th>
<th>2 M MgCl₂</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.5</td>
<td>0.03</td>
</tr>
<tr>
<td>Pr</td>
<td>5.4</td>
<td>0.17</td>
</tr>
<tr>
<td>Sm</td>
<td>61</td>
<td>0.95</td>
</tr>
<tr>
<td>Gd</td>
<td>79</td>
<td>1.4</td>
</tr>
<tr>
<td>Ce</td>
<td>1.9</td>
<td>0.06</td>
</tr>
<tr>
<td>Nd</td>
<td>8.5</td>
<td>0.19</td>
</tr>
<tr>
<td>Eu</td>
<td>91</td>
<td>1.1</td>
</tr>
<tr>
<td>Y</td>
<td>4</td>
<td>0.002</td>
</tr>
<tr>
<td>Dy</td>
<td>28</td>
<td>0.11</td>
</tr>
<tr>
<td>Er</td>
<td>64</td>
<td>0.17</td>
</tr>
<tr>
<td>Yb</td>
<td>460</td>
<td>0.66</td>
</tr>
<tr>
<td>Tb</td>
<td>90</td>
<td>0.61</td>
</tr>
<tr>
<td>Ho</td>
<td>210</td>
<td>1.0</td>
</tr>
<tr>
<td>Tm</td>
<td>960</td>
<td>2.6</td>
</tr>
<tr>
<td>Lu</td>
<td>&gt;1000</td>
<td>12</td>
</tr>
</tbody>
</table>

<p>| Table 4 |
| Distribution ratios for stripping of rare earths from [C101][SCN]. |</p>
<table>
<thead>
<tr>
<th>4 M MgCl₂</th>
<th>2 M MgCl₂</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.03</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Pr</td>
<td>0.5</td>
<td>0.06</td>
</tr>
<tr>
<td>Sm</td>
<td>3.0</td>
<td>0.28</td>
</tr>
<tr>
<td>Gd</td>
<td>5.9</td>
<td>0.39</td>
</tr>
<tr>
<td>Ce</td>
<td>0.2</td>
<td>0.02</td>
</tr>
<tr>
<td>Nd</td>
<td>0.6</td>
<td>0.06</td>
</tr>
<tr>
<td>Eu</td>
<td>5.0</td>
<td>0.29</td>
</tr>
<tr>
<td>Y</td>
<td>0.6</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Dy</td>
<td>2.0</td>
<td>0.03</td>
</tr>
<tr>
<td>Er</td>
<td>7.5</td>
<td>0.07</td>
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<tr>
<td>Yb</td>
<td>65</td>
<td>0.66</td>
</tr>
<tr>
<td>Tb</td>
<td>3.5</td>
<td>0.04</td>
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<tr>
<td>Ho</td>
<td>17</td>
<td>0.12</td>
</tr>
<tr>
<td>Tm</td>
<td>140</td>
<td>1.0</td>
</tr>
<tr>
<td>Lu</td>
<td>1000</td>
<td>6.9</td>
</tr>
</tbody>
</table>

<p>| Table 5 |
| Thiocyanate concentrations (mol/L) in the aqueous phase before and after washing [A136][SCN] with pure water, and subsequent equilibration with three different aqueous solutions. |</p>
<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>4 M MgCl₂</th>
<th>4 M MgCl₂ + Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-saturated</td>
<td>0.17</td>
<td>0.038</td>
<td>0.020</td>
</tr>
<tr>
<td>Wash step</td>
<td>0.0081</td>
<td>0.017</td>
<td>0.0070</td>
</tr>
<tr>
<td>Wash steps</td>
<td>0.0036</td>
<td>0.010</td>
<td>0.0062</td>
</tr>
</tbody>
</table>

<p>| Table 6 |
| Thiocyanate concentrations (mol/L) in the aqueous phase before and after washing [C101][SCN] with pure water, and subsequent equilibration with three different aqueous solutions. |</p>
<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>4 M MgCl₂</th>
<th>4 M MgCl₂ + Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-saturated</td>
<td>0.10</td>
<td>0.035</td>
<td>0.0056</td>
</tr>
<tr>
<td>Wash step</td>
<td>0.0018</td>
<td>0.011</td>
<td>0.0029</td>
</tr>
<tr>
<td>Wash steps</td>
<td>0.0009</td>
<td>0.005</td>
<td>0.0024</td>
</tr>
</tbody>
</table>

* The Yb spike concentration was approximately 10 g/L.

4.9. Matrix effects

The effect of the aqueous phase matrix on the distribution ratios of dysprosium, extracting with the ionic liquid [C101][SCN], was investigated by varying concentrations of chloride, sulfate and perchlorate ions in the aqueous phase (Fig. 10). The distribution ratios in the sulfate matrix were fairly low, while chloride and perchlorate matrices had a non-linear behavior in a log–log plot. Two processes that can influence this are the salting-out effect and the displacement of the equilibrium of anion distribution (freeing up thiocyanate through anion exchange) between the ionic liquid and the aqueous phase. The IL phase needs to have a relatively high concentration of metal ions. Typically extract metal salts (metal cations + their anions) rather than metal ions.

In a split-anion extraction process, rare-earth ions are coordinated by thiocyanate or nitrate ions in the ionic liquid phase, because the rare-earth ions form more easily extracted complexes with nitrate and thiocyanate ions than with chloride ions. The chloride ions remain dissolved in the organic phase, as counter anions for the ionic liquid cations that are not involved as counter cations for the anionic rare-earth ion complexes. The IL phase needs to have a relatively high concentration of anions forming extractable complexes since the aqueous phase is devoid of these anions. The distribution ratios can be increased by adding salts to the aqueous phase with the same type of anions as present in the IL. The distribution ratios and the separation factors can be tuned by an appropriate choice of the chloride concentration. Separation schemes for mixtures of rare-earth ions can be designed based on these variations of the chloride concentration. The possibility of switching between different ionic liquids in a process is an advantage since the different ionic liquid anions (nitrate or thiocyanate) exhibit such different extraction behavior for rare-earth ions, without having to change the chloride-containing aqueous phase. Selectively stripping with an aqueous phase containing the same anions as the ionic liquid phase could give higher separations but could make a complete strip more difficult.
aqueous feed solution, the phase volume ratios (feed solution, the concentration of potential complexing agents in the need to be optimized are the ionic strength (salt concentration) of the

ionic liquid. The loading capacity is determined by the availability of traction is determined by the stability of the rare-earth complex in the

vent extraction of lighter rare earths. The preferential order of this ex-

rameter in split-anion extraction. The separation factors are raised due

rare-earth resources and the loading of the organic phase is a crucial pa-

ers need to be optimized for each different aqueous feed solution.

To develop an efficient separation process, the extraction parameters need to be optimized for each different aqueous feed solution. This is due to the fact that the concentrations are different in most rare-earth resources and the loading of the organic phase is a crucial pa-

parameter in split-anion extraction. The separation factors are raised due to the crowding generated by the extracted heavier rare earths that pre-

vention of lighter rare earths. The preferential order of this ex-

traction is determined by the stability of the rare-earth complex in the

ionic liquid. The loading capacity is determined by the availability of thiocyanate or nitrate anions and is thereby fixed by the anion concen-

tration in the ionic liquid. In an efficient process the organic phase is likely to be loaded close to maximum capacity and is thereby strongly affected by the phase ratio (flow rates). Other process parameters that need to be optimized are the ionic strength (salt concentration) of the

feed solution, the concentration of potential complexing agents in the

aqueous feed solution, the phase volume ratios (flow rates), the compo-

sition of the organic phase and optimal temperatures for the different stages.

This study focused on thiocyanate ionic liquids, because of the more

efficient extraction of trivalent rare-earth ions from chloride feed solution,

without the need of using acidic extractants. The rare-earth ions are ex-

tracted from a concentrated chloride aqueous phase to an organic

phase, consisting of a water-immiscible thiocyanate (or nitrate) ionic

liquid. The new extraction process is called split-anion extraction

major advantage of split-anion extraction is that the source of the

complexing anion is the organic phase. Another advantage is the easy

stripping of the rare earths from the ionic liquid phase by water (instead

of strong inorganic acids). The phosphonium ionic liquid [C101][SCN] gives higher separation factors for pairs of neighboring rare-earth ions

compared to the quaternary ammonium ionic liquid [A336][SCN]. How-

ever, [A336][SCN] gives higher separation factors for pairs of neighboring rare-earth ions

across the lanthanide series (positive extraction sequence).

A remark on the stability of the thiocyanate ionic liquids is that

Hofmeister series. However, there is a fundamental difference between extractions with thiocyanate ions compared to that with nitrate ions

due to the trends in distribution ratios across the lanthanide series

(Preston and du Preez, 1990). For the extraction of rare earths with nitrate

ionic liquids, a negative sequence is observed, i.e., the distribution ratios decrease from lanthanum to lutetium. For extraction of rare

earths with thiocyanate ionic liquids, the distribution ratios increase across the lanthanide series (positive extraction sequence).

5. Conclusions

This paper describes a fundamentally new approach to the separa-

tion of mixtures of rare earths by solvent extraction, which enables effi-

cient extraction of trivalent rare-earth ions from chloride feed solution,

without the need of using acidic extractants. The rare-earth ions are ex-

tracted from a concentrated chloride aqueous phase to an organic

phase, consisting of a water-immiscible thiocyanate (or nitrate) ionic

liquid. The new extraction process is called split-anion extraction

because the aqueous and organic phases comprise different anions. Thio-

cyanate and nitrate anions have a strong affinity for the organic phase,

while chloride anions have a strong affinity for the aqueous phase. The

major advantage of split-anion extraction is that the source of the

complexing anion is the organic phase. Another advantage is the easy

stripping of the rare earths from the ionic liquid phase by water (instead

of strong inorganic acids). The phosphonium ionic liquid [C101][SCN] gives higher separation factors for pairs of neighboring rare-earth ions

compared to the quaternary ammonium ionic liquid [A336][SCN]. How-

ever, [A336][SCN] gives higher distribution ratios for the light and middle

rare earths. Also the loading capacity and distribution ratios during

scrubbing with chloride solutions are higher for [A336][SCN].

Acknowledgments

The research leading to these results has received funding from the European Community’s Seventh Framework Programme (FP7/2007-

2013), EURARE) under grant agreement n°309373. This publication reflects only the authors’ view, exempting the Community from any liability.
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