

Separation of rare earths by split-anion extraction

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Abstract

Split-anion extraction is a new approach to the separation of mixtures of rare earths by solvent extraction. The rare-earth ions are extracted from a concentrated chloride aqueous phase to an organic phase, consisting of a water-immiscible thiocyanate or nitrate ionic liquid. This allows for efficient extraction of trivalent rare-earth ions from a chloride aqueous phase, without the need of using acidic extractants. The process is called split-anion extraction because the aqueous and organic phase contain different anions. Thiocyanate and nitrate anions have a strong affinity for the organic phase, while chloride anions have a strong affinity for the aqueous phase. In split-anion extraction, the source of complexing anions is the organic phase which allows for the use of chloride aqueous feed solutions and easy stripping of the rare earths from the loaded ionic liquid phase by water (instead of strong inorganic acids). The principle of the new extraction approach is described in detail for the extraction of rare earths from aqueous chloride solutions by the ionic liquids tricaprylmethylammonium thiocyanate and trihexyl(tetradecyl)phosphonium thiocyanate. Rare-earth and chloride concentrations can be varied to optimize the separation process. Separation factors between the end members of the lanthanide series (La-Lu) exceed the value of 200000.

Keywords:

Ionic Liquids, Solvent Extraction, Rare Earths, Lanthanides, Thiocyanate, Nitrate

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 earths 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 earths 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 (Cyanex 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 neighbouring 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, 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

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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., 1959; Peppard et al., 1957; Dziwinski and Szymanowski, 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 earths efficiently from aqueous nitrate or thiocyanate solutions, not from chloride solutions.

Basic extractants (anion exchangers) are a third class of extractants (Genov and Pamukschiewa, 1976; Bagreev and Popov, 1985; Gorski et al., 1991; Maeck et al., 1961). Typical examples of such extractants are quaternary ammonium salts, e.g. tricaprylmethylammonium 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 in-

terest in ionic liquids derived of the quaternary ammonium salt tricaprylmethylammonium chloride (Aliquat 336) or the trihexyl(tetradecyl)phosphonium cation for solvent extraction studies (Wellens 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 (Wellens 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 earths 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. The split-anion extraction can find applications in the field of recycling of rare earths (Binnemans et al., 2013).

2. Theory

Ionic liquids based on tricaprylmethylammonium 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: $\text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{ClO}_4^- < \text{SCN}^-$. 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. Due to the preferential binding of nitrates or thiocyanates over 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. During split-anion extraction there is only a limited transfer of the different anions from one phase to the other, due to that the anions coordinate to the extracted rare-earth ions and the much stronger affinity for the ionic liquid phase for the thiocyanate or nitrate ions compared to the chloride ions, with exception of the chloride ions that are extracted to maintain the charge balance.

The distribution ratio (D) of a single metal is defined in equation (1) as the ratio of the total concentration in the ionic liquid

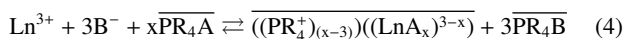
phase ($[M]_{IL}$) by the total concentration in the aqueous phase ($[M]_{aq}$) after extraction and phase separation. The phase ratios (Θ) were calculated by dividing the volume of the ionic liquid phase by the volume of the aqueous phase (equation (2)). Separation factors ($\alpha_{A,B}$) are defined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

$$D = \frac{[M]_{IL}}{[M]_{aq}} \quad (1)$$

$$\Theta = \frac{V_{IL}}{V_{aq}} \quad (2)$$

$$\alpha_{A,B} = \frac{D_A}{D_B} \quad (3)$$

In its most general form, the split-anion extraction separates rare-earth elements from an aqueous phase containing B^- anions to a water-immiscible organic phase (ionic liquid) with A^- anions. The interaction between rare-earth metal 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 equation (4) for a phosphonium ionic liquid (PR_4A). The bars in the equations mean that the species is in the organic phase and Ln represents any trivalent rare-earth ion.



It is also likely that a small amount of thiocyanate is available in the aqueous phase through an anion exchange reaction (equation 5).



3. Experimental

3.1. Chemicals

Tricaprylmethylammonium chloride (Aliquat 336, [A336][Cl]), is a mixed ammonium salt of mainly tri-octylmethylammonium 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 of the solvents. Using the molecular mass and density of the pure compounds with the average purity gives for [C101][Cl] (519.31 g/mol, 882 g/L) approximately 1.66 M and for [A336][Cl] (approximately 430 g/mol, 884 g/L) approximately 1.8 M.

To prepare thiocyanate forms of the ionic liquids, they were pre-equilibrated two times with a 3 M NH_4SCN solution to exchange the chloride ions for thiocyanate ions. This

gave water-saturated trihexyl(tetradecyl)phosphonium thiocyanate ([C101][SCN]) and tricaprylmethylammonium thiocyanate ([A336][SCN]). To obtain the nitrate forms of the ionic liquids, [A336][Cl] and [C101][Cl] were pre-equilibrated three times respectively with a 2.5 M KNO_3 solution. The chloride concentration after the equilibrations in these ionic liquid phases were under the instrumental detection limits (Vander Hoogerstraete et al., 2014). The ionic liquids were used both directly after pre-equilibrations and after washing with pure water. When used directly they were pre-saturated with a small excess of anions and this excess could be removed by washing with pure water. To obtain trihexyl(tetradecyl)phosphonium perchlorate ([C101][ClO₄]), [C101][Cl] was pre-equilibrated three times with a 2 M $NaClO_4$ solution and washed with pure water. All dilutions were made using pure water (MilliQ, Millipore, >18 M Ω /cm).

The following salts were used: $MgCl_2$ (Sigma-Aldrich, >98%), NH_4SCN (Sigma-Aldrich, >99%), $NaClO_4 \cdot H_2O$ (Fluka, $\geq 99\%$), KNO_3 (Chem-lab, >99%), $(NH_4)_2SO_4$ (Chem-lab, >99%), $Fe(NO_3)_3 \cdot 9H_2O$ (J. T. Baker Chemicals, >98%). The following rare earth chlorides were supplied as 99.9% pure reagent: $LaCl_3 \cdot 7H_2O$, $CeCl_3 \cdot 7H_2O$, $NdCl_3 \cdot 6H_2O$, $GdCl_3 \cdot 6H_2O$, $TbCl_3 \cdot 6H_2O$, $HoCl_3 \cdot 6H_2O$ (Alfa Aesar); $PrCl_3 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$ (Acros Organics); $SmCl_3 \cdot 6H_2O$, $ErCl_3 \cdot 6H_2O$ (Strem Chemicals); $DyCl_3 \cdot 6H_2O$, $LuCl_3 \cdot 6H_2O$ (Sigma-Aldrich); $TmCl_3 \cdot xH_2O$ (Reacton); $YbCl_3 \cdot 6H_2O$ (ABCR); $YCl_3 \cdot 6H_2O$ (Heraeus).

3.2. Analysis techniques

A Bruker S2 Picofox total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal content in both aqueous and organic phases. Thiocyanate concentrations in the aqueous phase after extraction were determined using UV-VIS absorption spectroscopy with a Varian Cary 5000 spectrophotometer. A small sample of the aqueous phase (10–100 μ L) was diluted to 2 mL together with an iron(III) solution (0.05 M), which was added in order to create the strongly coloured hexathiocyanatoferrate(III) complex and subsequently the absorbance was measured at 474 nm.

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 elements varies in the relevant systems, experiments were performed using both individual rare-earth element 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, Tm, Lu, Y; solution 2: Ce, Nd, Gd, Dy,

Er, Yb). The two solutions were of roughly equimolar concentrations, approximately 0.02 M for each individual metal, with an 8 M chloride matrix (4 M MgCl₂). The extractions were carried out with thiocyanate or nitrate ionic liquid phases at 50 °C with a phase ratio of 1:1 and mixture was shaken for 2 h.

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.

The influence of the chloride concentration in the aqueous phase was significant for the extraction and was studied for thiocyanate ionic liquid phases using magnesium chloride. The rare-earths were divided in the same groups as solution 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 earths were split into four separate groups: Solutions 3 (La, Pr, Sm, Gd), 4 (Y, Dy, Er, Yb), 5 (Ce, Nd, Eu) and 6 (Tb, Ho, Tm, 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.

The most significant effect on the experiments was given by the metal ion loading in the ionic liquid phase. The loading was studied using both individual elements, thereby determining free loading curves and by using mixtures of metal ions and modifying concentrations to study the loading behavior in the presence of multiple elements and preferential extraction.

To study the effect of the aqueous matrix of chloride, perchlorate and sulfate, solutions of 2 M, 3 M, 4 M, 6 M and 8 M of MgCl₂ and NaClO₄ were prepared. To have more comparable solutions, since the charge of the sulfate is double that of chloride or perchlorate, normality concentrations were used. The sulfate solutions were prepared with (NH₄)₂SO₄ and the data represented using normality with an equivalence factor of 0.5 for sulfate. The aqueous solutions were spiked with 50 mM of dysprosium chloride and mixed with [C101][SCN] for 1 h at 30 °C.

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 Figure 1. The separation factors obtained using the distribution ratios are listed in Table 1

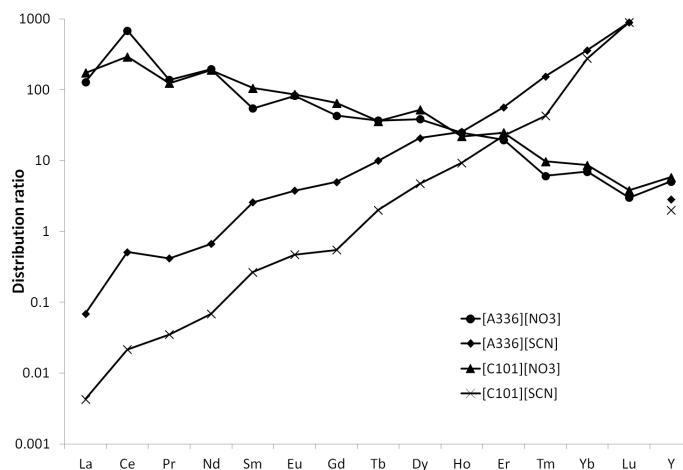


Figure 1: Distribution ratios for split-anion extraction of rare-earth ions from chloride solutions by thiocyanate or nitrate ionic liquids. Use was made of two separate aqueous mixtures, containing rare-earth ions at concentrations of approximately 0.02 M each in a 4 M MgCl₂ matrix. The aqueous phase was contacted at 50 °C with the organic phases [A336][SCN], [A336][NO₃], [C101][SCN] and [C101][NO₃], in a phase ratio of 1:1.

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 elements, 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 (Figure 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

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

	Yb	Tm	Er	Ho	Dy	Y	Tb	Gd	Eu	Sm	Nd	Pr	Ce	La
Lu	3.2	20	40	100	190	450	450	1600	1900	3300	13000	26000	42000	210000
	Yb	6.5	12	30	59	140	140	500	590	1000	4000	7900	13000	65000
		Tm	1.9	4.6	9	21	21	78	91	160	630	1200	2000	10000
			Er	2.4	5	11	11	41	48	84	330	640	1000	5200
				Ho	2.0	4.6	4.6	17	20	35	140	270	430	2200
					Dy	2.4	2.4	8.6	10	18	69	140	220	1100
						Y	1.0	3.7	4.3	7.5	29	57	93	470
							Tb	3.7	4.3	7.5	29	57	93	470
								Gd	1.2	2.0	8.0	16	25	130
									Eu	1.8	6.9	14	22	110
										Sm	3.9	7.6	12	62
											Nd	1.9	3.2	8.2
												Pr	1.6	8.2
													Ce	5.0

¹ The separation factors were determined by measuring the distribution ratios in two individual solutions (La, Pr, Sm, Eu, Tb, Ho, Tm, 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 Figure 1.

Table 2: Separation factors between individual rare-earth elements for the quaternary ammonium ionic liquid [A336][SCN].¹

	Yb	Tm	Er	Ho	Dy	Tb	Gd	Eu	Y	Sm	Nd	Pr	Ce	La
Lu	2.5	6	16	35	43	90	180	240	310	350	1300	2100	1800	13000
	Yb	2.3	6	14	17	36	73	96	130	140	540	860	700	5200
		Tm	2.7	6	7	15	31	41	54	60	230	370	300	2200
			Er	2.2	3	6	11	15	20	22	85	140	110	820
				Ho	1.2	2.6	5.1	7	9	10	38	61	50	370
					Dy	2.1	4.2	5.5	7	8	31	50	41	300
						Tb	2.0	2.7	3.5	4	15	24	20	150
							Gd	1.3	1.7	1.9	7	12	10	72
								Eu	1.3	1.5	5.7	9	7	55
									Y	1.1	4.3	7	6	41
										Sm	3.9	6.1	5	37
											Nd	1.6	1.3	6.0
												Pr	1.2 ²	6.0
													Ce	7.4

¹ The separation factors were determined by measuring the distribution ratios in two individual solutions (La, Pr, Sm, Eu, Tb, Ho, Tm, 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 Figure 1.

² The separation factor of praseodymium versus cerium is inverted since the distribution ratio for cerium was higher.

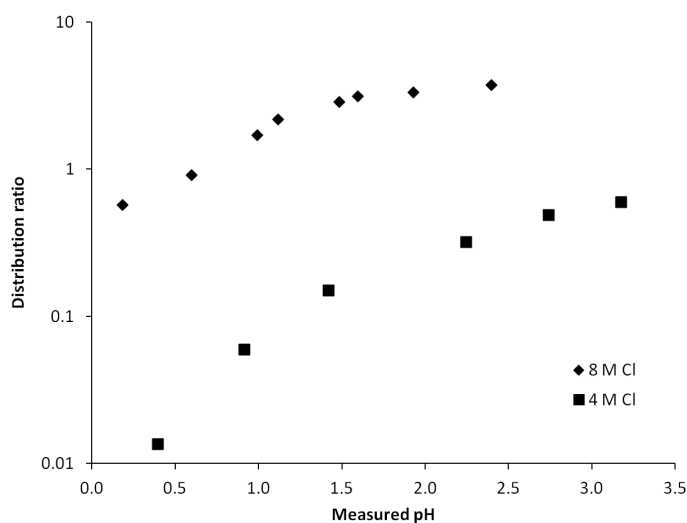


Figure 2: Variation of the distribution ratios of ytterbium(III) as a function of pH, for extraction with [C101][SCN] at 30 °C.

to 12 min (Figure 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] (Figure 4) is similar to that of pre-saturated [A336][SCN] (Figure

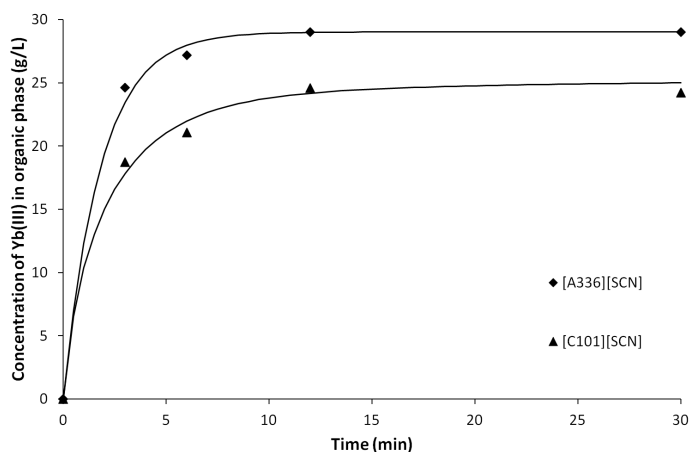


Figure 3: Influence of the equilibration time on the loading of the [A336][SCN] or [C101][SCN] phase with ytterbium(III) at 30 °C.

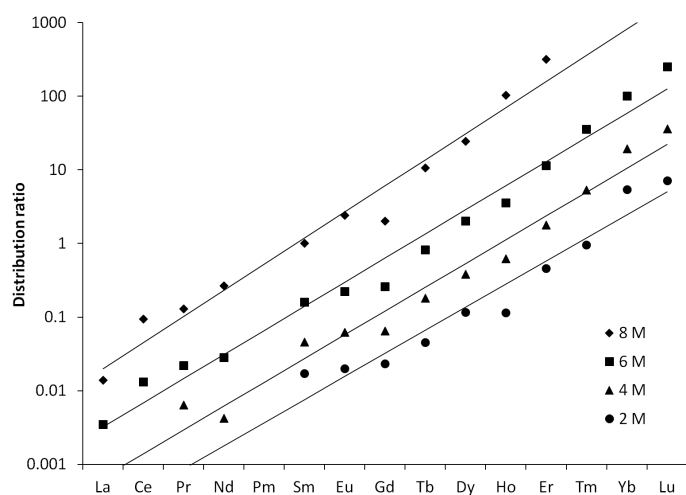


Figure 4: Distribution ratios across the lanthanide series for pre-saturated [C101][SCN] with varying chloride concentrations. Phase ratio 1:1.

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 organic phase loading capacity for individual metals in the thiocyanate ionic liquids was approximately 0.14–0.26 mol/L (depending on the individual metal). The loading capacity of [A336][SCN] (0.26 mol/L or 46 g/L for ytterbium) was higher than for [C101][SCN], but

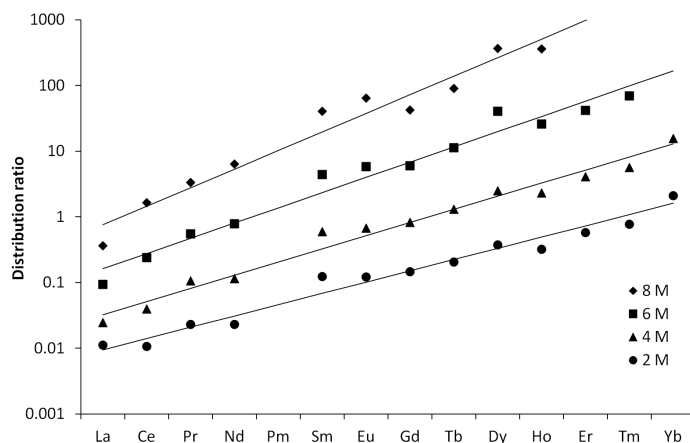


Figure 5: Distribution ratios across the lanthanide series for pre-saturated [A336][SCN] with varying chloride concentrations. Phase ratio 1:1.

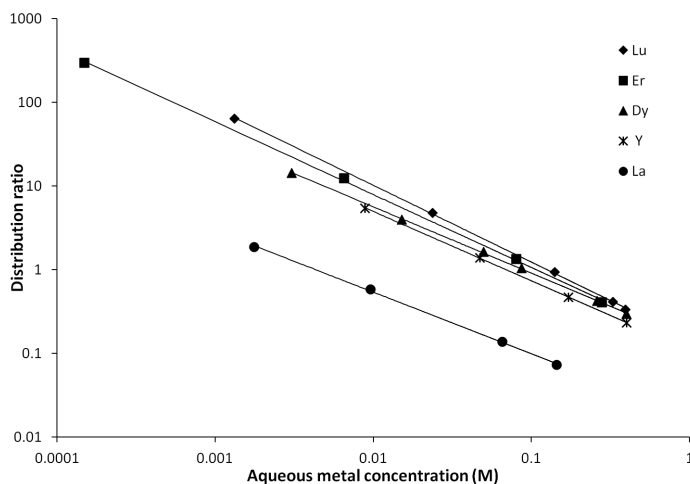


Figure 6: Log-log plots of the distribution ratios of lutetium, dysprosium, yttrium, erbium and lanthanum at different metal concentrations in the aqueous phase (at equilibrium) for extraction with [C101][SCN].

was of the same order of magnitude. This is probably due to the anion concentration in 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 $MgCl_2$ matrix for [C101][SCN]. The results followed power-law behavior and is therefore shown as a log-log plot (Figure 6). These data show that the distribution ratios change by a factor of approximately 10000 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 (Figure 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

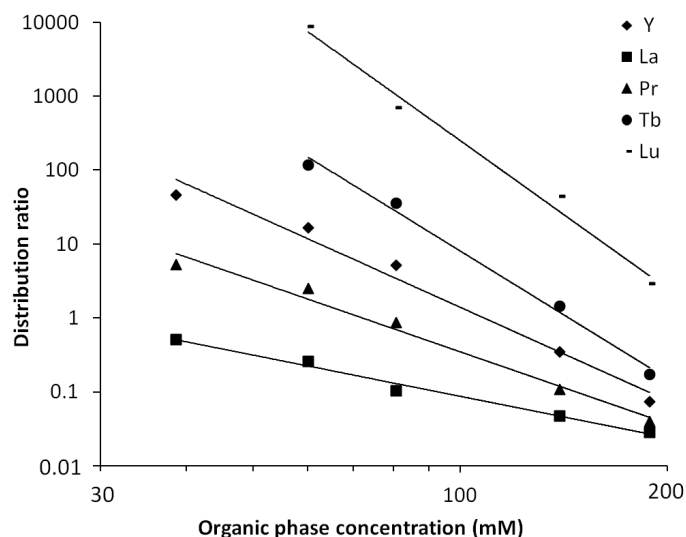


Figure 7: Distribution ratios for yttrium, lanthanum, praseodymium and terbium with varying loading in the organic phase (total metal concentration) by increasing lutetium concentration, using [A336][SCN] as organic phase.

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 (Table 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

Table 3: Distribution ratios for stripping of rare earths from [A336][SCN].¹

	4 M MgCl ₂	2 M MgCl ₂	Water
La	0.5	0.03	0.003
Pr	5.4	0.17	0.007
Sm	61	0.95	0.03
Gd	79	1.4	0.04
Ce	1.9	0.06	0.003
Nd	8.5	0.19	0.01
Eu	91	1.1	0.04
Y	4	0.002	<0.001 ²
Dy	28	0.11	0.001
Er	64	0.17	0.0004
Yb	460	0.66	0.0009
Tb	90	0.61	0.04
Ho	210	1.0	0.06
Tm	960	2.6	0.15
Lu	>1000	12	0.61

¹ Four groups of rare earths were contacted with three aqueous solutions with different chloride concentrations.

² Below the detection limit in the organic phase.

Table 4: Distribution ratios for stripping of rare earths from [C101][SCN].¹

	4 M MgCl ₂	2 M MgCl ₂	Water
La	0.03	<0.01 ²	<0.01 ²
Pr	0.5	0.06	0.01
Sm	3.0	0.28	0.06
Gd	5.9	0.39	0.07
Ce	0.2	0.02	<0.01 ²
Nd	0.6	0.06	0.01
Eu	5.0	0.29	0.07
Y	0.6	<0.01 ²	<0.01 ²
Dy	2.0	0.03	0.01
Er	7.5	0.07	0.002
Yb	65	0.66	0.01
Tb	3.5	0.04	0.01
Ho	17	0.12	0.03
Tm	140	1.0	0.22
Lu	1000	6.9	1.6

¹ Four groups of rare earths were contacted with three aqueous solutions with different chloride concentrations.

² Below the detection limit in the organic phase.

thiocyanate levels in a strip solution, but likely not in a scrub solution.

Table 5: Thiocyanate concentrations (mol/L) in the aqueous phase before and after washing [A336][SCN] with pure water, and subsequent equilibration with three different aqueous solutions.^{1,2}

	Water	4 M MgCl ₂	4 M MgCl ₂ + Yb
pre-saturated	0.17	0.038	0.020
1 wash step	0.0081	0.017	0.0070
2 wash steps	0.0036	0.010	0.0062

¹ Thiocyanate concentrations were measured with UV-VIS absorption spectroscopy.

² The Yb spike concentration was approximately 10 g/L.

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.^{1,2}

	Water	4 M MgCl ₂	4 M MgCl ₂ +Yb
pre-saturated	0.10	0.035	0.0056
1 wash step	0.018	0.011	0.0029
2 wash steps	0.009	0.005	0.0024

¹ Thiocyanate concentrations were measured with UV-VIS absorption spectroscopy.

² The Yb spike concentration was approximately 10 g/L.

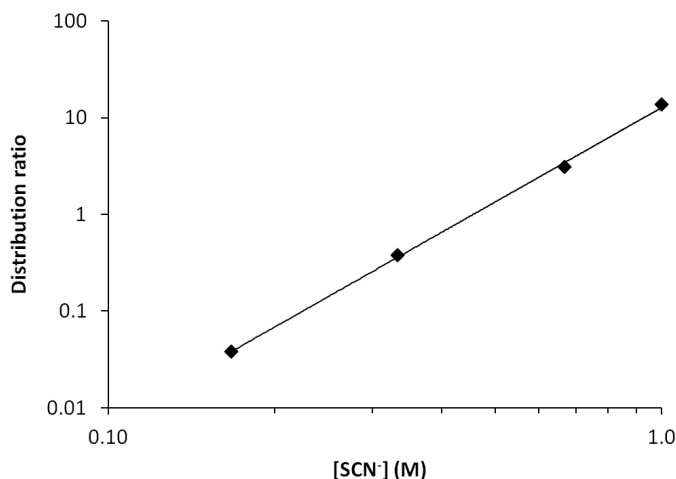


Figure 8: Distribution ratios for 50 mM dysprosium in a 6 M chloride solution, using [C101][ClO₄] as initial ionic liquid (log-log). The X-axis displays the added thiocyanate concentration, which was varied by increasing the initial aqueous thiocyanate concentration.

4.8. Influence of thiocyanate concentration

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 suited 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 (Figure 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 (Figure 9). 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. Equation 4 can now be modified

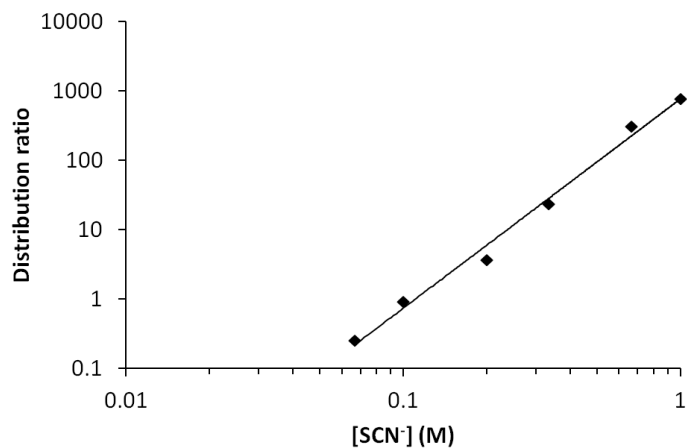
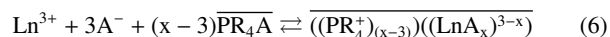
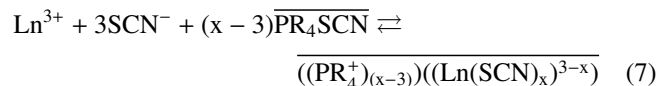


Figure 9: Distribution ratios for 50 mM dysprosium in a 6 M chloride solution, using [C101][SCN] (water washed) as initial ionic liquid (log-log). The X-axis displays the added thiocyanate concentration, which was varied by increasing the initial aqueous thiocyanate concentration.

into equation 6, which assumes that a small amount of A⁻ anions are 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 ($x \geq 3$).



The reactions can now be expressed in terms specific to the thiocyanate extraction (equation 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.

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 (Figure 10). The distribution ratios in the sulfate matrix were fairly

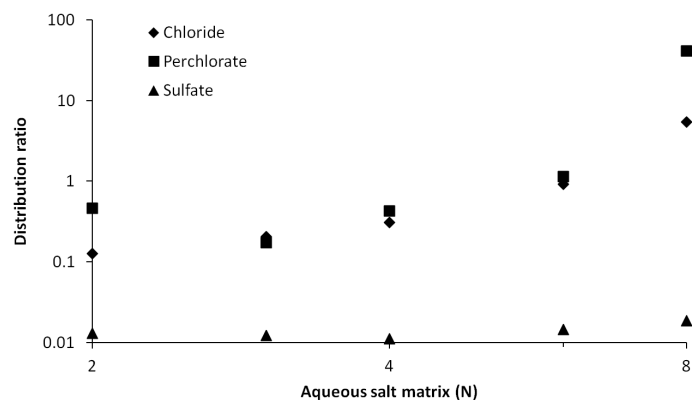


Figure 10: Distribution ratios for 50 mM dysprosium when using [C101][SCN] (pre-saturated) as an initial ionic liquid with varying concentrations of chloride, perchlorate and sulfate (equivalence factor of 0.5 for sulfate).

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. 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 sulfate and chloride both have a very strong tendency to be highly hydrated, and since many anions are between chloride and perchlorate in the Hofmeister series, one can assume that chloride is closer to sulfate than to perchlorate in the Hofmeister series. The sulfate anions are less likely to enter the ionic liquid phase than chloride or perchlorate, but it is also likely that complexation of rare-earth ions with sulfate ions in the aqueous phase reduces the distribution ratios. The distribution ratios for the anions correspond to the order in the Hofmeister series (sulfate < chloride < perchlorate). This can be explained by the influence of the anions on the distribution of thiocyanate anions, an increased tendency to reside in the IL likely increases the amount of thiocyanate available for complexation and thereby the distribution ratio. The fact that the extraction behavior in chloride and perchlorate media is similar, except at high or low matrix concentration, is an indication that rare-earth complexes with mixed anions are not a dominant effect.

4.10. General Discussion

Rare-earth ions cannot be efficiently extracted and separated from chloride feed solutions by basic extractants (anion exchangers) in their chloride form. However, this study shows that rare-earth ions can be extracted from chloride feed solutions by hydrophobic ionic liquids with nitrate or thiocyanate anions, provided that the chloride concentration in the aqueous feed solution is sufficiently high. The electrical neutrality is maintained during the extraction process, since chloride ions also enter the ionic liquid phase, no ionic liquid components are lost to the aqueous phase due to extraction. In this sense, the extraction mechanism is similar to that of extraction of rare earth

by neutral extractants. There is even more similarity with the extraction mechanism of *binary extractants* (quaternary ammonium or phosphonium salts of acidic extractants). (Grinstead et al., 1969; Grinstead and Davis, 1970; Davis and Grinstead, 1970; Kholkin et al., 1994; Belova and Kholkin, 1998; Belova et al., 2009, 2012). Such types of extractant 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 of the formation of easily extracted complexes of rare-earth ions with nitrate or thiocyanate ligands compared to chloride ligands. 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 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 and thiocyanate) exhibit such different extraction behaviour for rare earths 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.

To develop an efficient separation process, the extraction parameters need to be optimized for each different aqueous feed solution. This is due to that the rare-earth concentrations are different in most rare-earth resources and the loading of the organic phase is a crucial parameter in split-anion extraction. The separation factors are raised due to the crowding generated by the extracted heavier rare earths that prevent extraction of lighter rare earths. The preferential order of this extraction 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 concentration 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 composition 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 the rare earths by thiocyanate ionic liquids compared to nitrate ionic liquids. Additionally, the thiocyanate ions have a stronger tendency to stay in the ionic liquid phase than nitrate ions, due to the position of the thiocyanate ions at the end of the Hofmeister series. However, there is a fundamental difference between extraction with thiocyanate

ions versus nitrate ions that concerns 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).

A remark on the stability of the thiocyanate ionic liquids is that prolonged exposure to sunlight and high temperatures leads to some degradation of the thiocyanate ions (H_2S formation). However, no degradation was observed (consistent distribution ratios and no H_2S observed) in samples that were stored in the dark and at low temperatures. Additional research on the degradation of thiocyanate ions is required to assess the long-term stability of these thiocyanate ionic liquids (Li et al., 2012).

5. Conclusions

This paper describes a fundamentally new approach to the separation of mixtures of rare earths by solvent extraction, which enables efficient extraction of trivalent rare-earth ions from chloride feed solution, without the need of using acidic extractants. The rare-earth ions are extracted 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 phase comprise different anions. Thiocyanate 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 anions 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 separations factors for pairs of neighbouring rare-earth ions compared to the quaternary ammonium ionic liquid [A336][SCN]. However, [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].

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