



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 phases 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-earth ions 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 200,000.

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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)phosphonic 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 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

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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-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 Pamuktschiewa, 1976; Bagreev and Popov, 1985; Gorski et al., 1991; Maeck et al., 1961). Typical examples of such extractants are quaternary ammonium salts, e.g., tricaprilmethylammonium 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 tricaprilmethylammonium 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-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 tricaprilmethylammonium 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: $\text{SO}_4^{4-} < \text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{ClO}_4^- < \text{SCN}^-$. 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. 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 ($[M]_{\text{IL}}$) by the total concentration in the aqueous phase ($[M]_{\text{aq}}$) 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 (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.

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

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

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

In its most general form, the split-anion extraction separates rare-earth 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

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