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Separation of ND(III), DY(III) and Y(III) by solvent extraction using D2EHPA and EHEHPA

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ABSTRACT

The equilibrium separation of trivalent rare earth elements (Nd(III), Dy(III), and Y(III)) from hydrochloric acid solution by di-(2-ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexylphosphonic acid mono-2-ethyl hexyl ester (EHEHPA) separately and in mixtures has been studied. The effect of extractant concentration, extractant mixture composition and solution acidity has been investigated. The results show that a mixture of D2EHPA and EHEHPA provide a better separation of Y(III) from Dy(III) when the total extractant concentration is 0.06 and 0.09 mol/L, while the separation is better using pure EHEHPA at higher extractant concentration (0.15 mol/L). The separation of Nd(III) from Y(III) and Dy(III) is higher using pure D2EHPA (0.06 and 0.15 mol/L). The results show that for the complexation of the Nd(III) ions approx. 1–2 hydrogen ions/rare earth element (REE) ion are released to the aqueous phase upon binding approximately 1 extractant dimer on average. For the complexation of Y(III) and Dy(III) ions 2–3 hydrogen ions are released upon binding approximately two extractant dimers on average. Accordingly, under the conditions of this work the complexation involves not only extractant molecule dimers but also monomers or aggregated REE species to some extent, and a fraction of the REE is extracted as chloride complexes.

1. Introduction

There has been an increasing demand for rare earth elements (REE) in the last few decades due to their unique spectroscopic and magnetic properties and wide range of utilization, particularly, in advanced materials (Humphries, 2013; Kołodyńska and Hubicki, 2012). For example, yttrium is used in laser crystals, catalysts, computer monitors, super conductors, and microwave filters. Neodymium is the base of most common solid-state lasers used in material processing and medicine as well as the key element in high strength Nd–B magnet formulations. Dysprosium plays an important role in the manufacturing of laser materials, nuclear reactors, hybrid cars and color television tubes (El-Nadi, 2012; Gupta and Krishnamurthy, 2005; Kołodyńska and Hubicki, 2012; Maestro and Huguenin, 1995; Preston, 1996; Xie et al., 2014; Zhou et al., 2007).

One of the greatest challenges in the recovery of REE from different sources is their separation from each other, which is very difficult due to their chemical similarity (Kołodyńska and Hubicki, 2012; Xie et al., 2014). Among various separation techniques, solvent extraction can be an effective way to separate REE from solution. However, the separation of adjacent REE using conventional solvent extraction processing is still difficult (Nishihama et al., 2002; Xie et al., 2014). Among organophosphorus extractants, di-(2-ethylhexyl)-phosphoric acid (D2EHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA) are the most effective extractants for the separation of rare earth elements (Deshpande et al., 1992; Gupta and Krishnamurthy, 2005; Shaohua et al., 2010). Solvent extraction of REE by D2EHPA in different media such as hydrochloric, sulfuric, and nitric acid solution has been reported (Basualto et al., 2013; Deshpande et al., 1992; Geist et al., 1999; Mason et al., 1964; Sato, 1989). The extraction of lanthanides with D2EHPA from hydrochloric acid and sulfuric acid solutions is similar while the extraction is poorer from nitric acid solution (Gupta and Krishnamurthy, 2005; Xie et al., 2014). Although, the REE extraction efficiency of D2EHPA is high, the difficulty in stripping of loaded extractant has limited its utilization especially for extraction of heavy REE. Recently, considerable attention has been drawn to EHEHPA in separation of REE as an alternative to D2EHPA, because of its high selectivity for rare earth ions. In addition, REE can be stripped at lower acidities in EHEHEPA systems compared to D2EHPA systems (Abdeltawab et al., 2002; Basualto et al., 2013; Gupta and Krishnamurthy, 2005; Sato, 1989; Xie et al., 2014), but the extraction efficiency is lower. The use of different mixtures of acidic organophosphorous extractants in order to improve the extraction efficiency and selectivity of REE has attracted attention in the last decade (Tong et al., 2013; Torkaman et al., 2013; Xiong et al., 2005,2005). In order to obtain an optimized extractant system which could decrease the acidity required for stripping

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the loaded D2EHPA as well as increase the extraction efficiency of EHEHPA, the extraction of REE with mixtures of D2EHPA and EHEHPA has been reported as a promising method (Huang et al., 2008; Nayak et al., 1999; Santhi et al., 1991; Wang et al., 2006; Xinghua et al., 2009; Zhang et al, 2008). Both a higher selectivity and extraction efficiency of REE have been achieved by using mixtures of D2EHPA and EHEHPA (C. Zhang et al., 2014; F. Zhang et al., 2014; Wang et al., 2006).

The extraction of trivalent REE with cationic extractants D2EHPA and EHEHPA has been proposed to follow Eq. (1) (Baes, 1962; Gupta and Krishnamurthy, 2005; Sato, 1989)

$$REE^{3+} + mH_2A_2 = REEA_3(HA)_{2m-3} + 3H^{+} \quad (1)$$

where REE denotes the rare earth element and H_2A_2 refers to the dimeric form of the extractant. It has been proposed that the improved extraction capacity of the mixed system would be due to a breakage of the dimers of D2EHPA and EHEHPA (C. Zhang et al., 2014; F. Zhang et al., 2014). As the hydrochloric acid concentration increases a solvating reaction has been proposed to occur in addition to the cationic exchange reaction in Eq. (1) (Sato, 1989)

$$REE^{3+} + 3Cl^{-} + m'H_2A_2 = REECl_3(HA)_{2m'}. \quad (2)$$

Complexes of the form $YCl(HB_2)_2$ (B: EHEHPA) has been suggested to form under certain conditions when extracting Y(III) by EHEHPA and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) (C. Zhang et al., 2014; F. Zhang et al., 2014). The composition and structure of REE extractant complexes formed in the organic phase during extraction with D2EHPA have been studied by various techniques such as small angle neutron scattering, X-ray absorption spectroscopy and IR spectroscopy (Basualto et al., 2013; Gannaz et al., 2006; Jensen et al., 2001). Basualto et al. (2013) studied the extraction of the light rare earth cations La(III), Ce(III), Pr(III) and Nd(III) with D2EHPA and found that the number of extractant dimers that coordinated with the REE were in the range of 1.05 (Pr(III)) to 2.42 (Ce(III)) by evaluating the equilibrium concentration data. Evidence for formation of dimeric, ligand bridged 6:2 complexes and multinuclear species in the form $[NdC_3]_n$ have been found, when extracting Nd(III) by D2EHPA (C) at high Nd(III) to extractant concentration, by performing small angle neutron scattering, X-ray absorption spectroscopy and IR spectroscopy measurements (Gannaz et al., 2006; Jensen et al., 2001).

The structural formulas of the two extractants D2EHPA and EHEHPA are shown in Fig. 1. Both D2EHPA and EHEHPA form dimers in nonpolar diluents; the branched alkyl chains and the presence of oxygen donors favor the dimerization. The acidity constants (K_a) in aqueous solutions and dimerization constants (K_2) in heptane are given in Table 1.

The cations coordinate 8 (Y(III)) or 9 (Nd(III), Dy(III)) water molecules in the aqueous phase and the ionic radii of the hydrated Nd(III), Dy(III) and Y(III) ions are 1.175 Å, 1.075 Å and 1.02 Å respectively (D'Angelo et al., 2011; Persson, 2010). The cations will form complexes with chloride ions to some extent in the aqueous phase. Stability constants for REE chlorides can be found in literature (Fernández-Ramirez et al., 2008; Haas et al., 1995; Luo and Byrne, 2001; Spahiu and Bruno, 1995; Wood, 1990). The REE chloride and hydroxide stability constants from the Medusa database are tabulated in Table 2 (Medusa, 2013). These are valid at zero ionic strength and at 25 °C. In Medusa the activity coefficients are calculated by a modified version of the model by Helgeson et al. (1981), which is valid up to ionic strengths of about 0.3 mol/L.

Table 1
Thermodynamic data for D2EHPA and EHEHPA at 25 °C.

Extractant	pK_a (predicted, I = 0)[a]	pK_a (0.2 mol/L (H, Na)ClO_4)[b]	Log K_2 (heptane)[b]
D2EHPA	1.47 ± 0.5	1.9	7.82
EHEHPA	2.95 ± 0.1	2.1	7.23

[a] Reference: SciFinder, calculated using Advanced Chemistry Development Software v11.02.
[b] Reference: Kolarik (2010).

Though there are numerous investigations on the extraction of REE with mixtures of extractants, to our knowledge, available data on the extraction of rare earths by mixtures of D2EHPA and EHEHPA are scarce, and the separation of Y(III), Dy(III) and Nd(III) by such mixtures has not been reported. The aim of this study was to investigate the extraction and separation of Nd(III), Dy(III) and Y(III) from hydrochloric acid solution using D2EHPA, EHEHPA and their mixtures. EHEHPA was added to the D2EHPA extraction system in order to enhance the selectivity of Y(III) over Dy(III).

2. Experimental

2.1. Reagents

The extractants di-(2-ethylhexyl) phosphoric acid (D2EHPA, CAS No. 298-07-7, 97 wt.%) and 2-ethylhexylphosphonic acid-mono-2-ethylhexyl ester (EHEHPA, CAS No. 14802-03-0, 95 wt.%) were supplied by Sigma-Aldrich and Daihachi Chemical Industry Co., respectively. All extractants were used as received without further purification. The extractants and their mixtures were dissolved in n-heptane (p.a.) to the desired concentration.

Stock solutions of Nd(III), Dy(III) and Y(III) were prepared by dissolving the respective REE oxide (99%), provided by Treibacher, in concentrated hydrochloric acid, and diluting with distilled water.

2.2. Solvent extraction

Solvent extraction experiments were carried out in a glass beaker placed on a magnetic stir plate. The pH of the aqueous solution was adjusted to the desired value by adding dilute ammonium hydroxide or hydrochloric acid solution. For each experiment, 10 mL of aqueous phase with known pH value was mixed with 10 mL of the extractant mixture at room temperature and mixed for 20 min using a magnetic stirrer (300 rpm). After equilibration, the mixture was transferred to a separation funnel where the phases were allowed to separate. After complete phase separation, the pH of the aqueous phase (equilibrium pH) was measured. The reported pH values are the measured proton activities at the specific ionic strength of each solution. The concentrations of metal ions in the aqueous solutions were determined by ICP-OES analysis (Thermo Fisher iCAP 6500) and the concentrations of metal

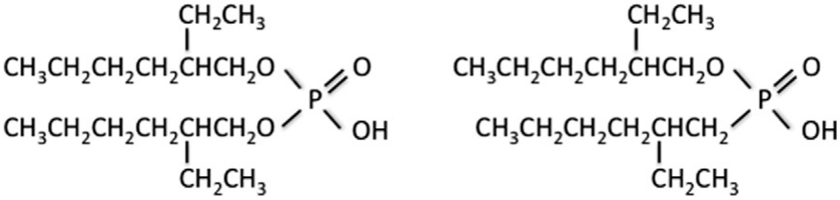

Fig. 1. Structural formula for D2EHPA (left) and EHEHPA (right).