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Solvent extraction of Ce(III) from nitric acid medium using binary mixture of PC 88A and Cyanex 921

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ABSTRACT

The extraction behaviour of Ce(III) from dilute nitric acid medium using a binary mixture of PC 88A and Cyanex 921 has been investigated. Several process parameters such as contact time, concentration of nitric acid, nitrate ion, extractant, diluents and Ce(III) concentration in aqueous feed, organic to aqueous phase volume ratio and temperature were varied to observe the influence on the extraction and to optimize operating conditions. Experimental results demonstrated that extraction of 0.001 mol/L Ce(III) from 0.001 mol/L HNO_3 was 96.6% with mixture of 0.7 mol/L PC 88A and 0.1 mol/L Cyanex 921. The extraction mechanism was established by applying method of slope analysis. Thermodynamic parameters were calculated from temperature variation studies. The loaded Ce(III) was effectively stripped using 0.6 mol/L HCl or 1.2 mol/L H_2SO_4. Extraction data were analysed using regression method.

1. Introduction

Rare earth elements of high purity have many scientific applications such as catalysts in the production of petroleum and synthetic products, used in magnets, motion picture projectors, lasers, phosphors, and X-ray intensifying screens (Maestro and Huguenin, 1995). Therefore, the production of high purity rare earth elements is necessary for such technologies. A cleaner extraction process is always more desirable to minimize environmental pollution in the metallurgical industry. Mainly organophosphorous compounds are used in the separation of rare earth elements using solvent extraction methods. Nayak and Lahiri (1999a, 1999b) have reported that 0.1% HDEHP and 0.01 M HCl were effectively used for the separation of ^{141}Ce and ^{153}Gd. Nayak and Lahiri (1999a, 1999b) have further investigated the separation of the carrier free radioisotopes of lanthanide series elements. The extraction and separation of rare earth elements depend on the values of stability constant of extracted complexes. The distribution of Ce(IV) species in HNO_3-$HClO_4$ media was studied by Bayulken and Sezai Sarac (1996) and formation constants for nitrato cerium complexes were determined to be 0.52 and 0.65, respectively. In the study of extraction of Y(III) and Eu(III) with PC 88A as extractant ,the stability constants for $Y(NO_3)_3$ and $Eu(NO_3)_3$ complexes were found to be 0.631 and 1.995 kmol m^{-3},-,respectively as reported by Fu and Tanaka (2006) as shown in Table 1.

The extractant PC 88A has higher separation factor for some rare earths as shown in Table 2 (Banda et al., 2014) and low aqueous acidity requirement for stripping (Song et al., 2009). The saponification of PC 88A has the advantage of lowering the effect of high acidity on the extraction process but in turn it gives rise to waste products containing NH_4^+, Ca^{2+} and Na^+ ions causing environmental pollution (Huang et al., 2006). Addition of complexing agents into the aqueous phase was very effective for enhancing the separation factor in the extraction of rare earths (Nishihama et al., 2000, 2003). Complexing agents were costly and recycled with difficulty (Yin et al., 2013). As viscosity of the organic phase increases, the extraction efficiency of PC 88A decreases, lowering its selectivity for some consecutive lanthanide pairs thereby limiting its utilization. Physical properties such as density, viscosity, and interfacial tension of the liquid-liquid system influence the operation of extraction process (Van Delden et al., 2006). An organic solvent is required to dissolve the reaction product, and a diluent is required to control the viscosity and to stop the formation of any third phase (Tamada and King, 2000). The high viscosity of extractant causes aqueous entrainment (Amer and Lewis, 1995) in the organic phase.

The present article describes Ce(III) extraction with a synergistic mixture comprising PC 88A and Cyanex 921(93% of tri-n-octyl phosphine oxide). The effects of shaking time, aqueous phase acidity, concentration of extractants, organic to aqueous phase volume ratio, metal loading capacity, diluent and temperature on the binary extraction system have been investigated. Stripping studies have been undertaken to know reusability of the extractant mixture and also recovery of Ce(III) from the organic extract.

2. Previous studies on applications of synergistic mixtures

To increase the distribution ratio of the metal ion a synergist is usually added which is capable of competing with water molecules for the

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Table 1
Chemical equilibria showing values of stability/formation constants of some lanthanide complexes.

Chemical equilibria	Stability/formation constants	References
$Ce^{4+} + HNO_3 \leftrightarrow Ce(NO_3)^{3+} + H^+$	0.52	Bayulken and Sezai Sarac (1996)
$Ce(NO_3)^{3+} + HNO_3 \leftrightarrow Ce(NO_3)_2^{2+} + H^+$	0.65	Bayulken and Sezai Sarac (1996)
$Y^{3+} + NO_3^- \leftrightarrow Y(NO_3)^{2+}$	0.631	Fu and Tanaka (2006)
$Eu^{3+} + NO_3^- \leftrightarrow Eu(NO_3)^{2+}$	1.995	Fu and Tanaka (2006)

first coordination sphere of the metal ion. These synergists contain uncharged electron donor atoms and hydrophobic hydrocarbon chains. Coordination sites of the extracted species must be saturated either by additional molecules of water (hydration) or by the undissociated ligand (self-adduct). According to the HSAB concept, hard cations coordinate to various hard ligands mainly by electrostatic interactions. Synergistic extraction shows promising effect in the field of solvent extraction (Xu et al., 1963). Nayak et al. (1999) have reported the synergistic extraction of neodymium and carrier free promethium by the mixture of HDEHP and PC 88A. The solvent extraction of rare earths from nitrate medium using binary mixture of DEHPA and CA12 was studied (Qiong et al., 2009). Strong synergistic effect was observed enabling separation of Y(III) from other rare earths. Reddy et al. (1999) have studied the extraction of La-(III) and Nd-(III) from nitrate solution using mixture of Cyanex301 and Cyanex923. They concluded that Cyanex923 enhances both extraction efficiency and selectivity. Extraction of rare earth metal ions using mixture of acidic organophosphorus extractants from chloride medium shows Cyanex reagents have low loading capacity due to low lipophilicity of coordination compounds formed during extraction (Sole and Hiskey, 1992, Wang et al., 2006). With the addition of CA100 to PC 88A, synergistic coefficient decreases with increase in atomic number of lanthanides. Free energy change (ΔG) found to be positive indicating non-spontaneity of the extraction process (Naizhong et al., 2009). A mixture of PC 88A and DEHPA, PC 88A and Cyanex 272 shows a synergistic effect while mixture of PC 88A and Cyanex 301, PC 88A and Cyanex302 do not show any synergistic effect in chloride medium (Xianglan et al., 2006). Synergistic mixture of DEHPA and PC 88A in kerosene has been used for the extraction of La(III), Nd(III), Sm(III), Gd(III) from H_2SO_4 medium (Zhang et al., 2008a). Synergistic coefficient was maximum for Gd(III) at pH 2.0. Mixture proved to be more effective for heavy rare earths than lighter ones and separation occurs at low acidity. No stripping data are available with binary extractant system. Synergistic extraction of Ce(IV) from H_2SO_4 medium using PC 88A and DEHPA in kerosene was reported (Xinghua et al., 2009). Maximum synergistic coefficient for Ce(IV) was obtained at mole fraction 0.6 of PC 88A. Extraction of Ce(III) from chloride medium was 87% with mixture of HFAA-TOPO in cyclohexane (Murthy et al., 1998). Zhang et al. (2008b) have studied the solvent extraction of Ce(IV) and fluoride from sulphate solution using DEHPA and Cyanex 923 in n-heptane and it was seen that Ce(III) was not extracted by the mixture. Panda et al. (2013) have reported that synergistic enhancement for the extraction of Nd(III) from nitric acid medium is higher with a binary mixture of 0.1 M Cyanex 272 and Cyanex 923 as compared to that with mixture of 0.1 M Cyanex 272 and Cyanex 921 from 0.001 M HNO_3 solution.

Table 2
Separation factors with PC 88A and DEHPA.

Extractants	Concentration in M	$\beta_{Pr/La}$	$\beta_{Nd/La}$
PC 88A	0.5	6.4	8.3
	0.7	7.3	9.5
DEHPA	0.5	6.0	6.9
	0.7	5.7	6.2

3. Experimental

3.1. Materials

The commercial extractants, PC 88A (Daihachi Chem. Ind., Japan) and Cyanex 921 (Cytec. Inc.,Canada) were used as received. All other reagents used were of analytical reagent grade. The aqueous phase was prepared by dissolving required amount of $Ce(NO_3)_3$ in double distilled water. The mixture of PC 88A and Cyanex 921 diluted with kerosene was taken as the organic phase except for diluent variation. For stripping experiments the metal- PC 88A + Cyanex 921 complex loaded organic phase and stripping solution containing various mineral acids of desired concentrations were considered.

3.2. Procedure and calculation

The extraction experiments were carried out in duplicate by equilibrating equal volumes of aqueous phase containing Ce(III) in HNO_3 and organic phase with the binary mixture of extractants in diluent in a separating funnel using a mechanical shaker. The cerium ion concentration in the aqueous phase was measured by Arsenazo (III) method (Savvin, 1961) using UV–visible spectrophotometer (ELICO). The concentration of Ce(III) in the organic phase was calculated from the difference in its concentration in the aqueous phase before and after the extraction using mass balance. The extraction performance was evaluated in terms of distribution ratios (D_{mix}) and the percentage of extraction (%E). These terms are calculated as follows, for an organic /aqueous phase ratio of 1, where 'final' refers equilibrium concentration:

$$D_{mix} = \frac{\left[Ce^{3+}{}_{(org)}\right]_{final}}{\left[Ce^{3+}{}_{(aq)}\right]_{final}} = \frac{\left[Ce^{3+}{}_{(aq)}\right]_{initial} - \left[Ce^{3+}{}_{(aq)}\right]_{final}}{\left[Ce^{3+}{}_{(aq)}\right]_{final}} \tag{1}$$

$$\%E = \frac{\left[Ce^{3+}{}_{(aq)}\right]_{initial} - \left[Ce^{3+}{}_{(aq)}\right]_{final}}{\left[Ce^{3+}{}_{(aq)}\right]_{initial}} \times 100 \tag{2}$$

The concentrations of various reagents used in the test program are listed in Table 3.

4. Results and discussion

4.1. Influence of contact time on Ce(III) extraction

The effect of contact time on the extraction was studied by varying it from 1 min to 30 min. The compositions of aqueous phase with Ce(III) and HNO_3 and the organic phase containing PC 88A and Cyanex 921 for this study are given in Table 3. The extraction percentage of Ce(III) was increased from 23.1% to 49.5% when time was varied from 1 min to 5 min and further increase in time did not have any influence on the extraction. Therefore, in all subsequent studies 5 min contact time was maintained (Fig .1).

4.2. Stoichiometry of extraction

The extraction percentage of Ce(III) decreased from 49.5% to 3.8% with the increase in nitric acid concentration from 0.001 mol/L to 1.0 mol/L. This trend can be explained by the fact that at higher acid concentration, complex formation between the acid and the extractant becomes significant lowering the extraction. The extractant complexed with acid is no longer able to solvate the metal ions compared with the free extractant. Tan et al. (1999) have reported the adduct formation

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