Hydrometallurgy 146 (2014) 128–132

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Solvent extraction studies on rare earths from chloride medium with organophosphorous extractant dinonyl phenyl phosphoric acid

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ARTICLE INFO

Article history:
Received 6 December 2013
Received in revised form 14 March 2014
Accepted 22 March 2014
Available online 3 April 2014

Keywords:
DNPPA
Solvent extraction
Rare earths
Diluent
Temperature

ABSTRACT

Extraction behaviour of rare earths, La, Dy and Y, from hydrochloric acid medium by di-nonyl phenyl phosphoric acid (DNPPA) has been investigated over a wide range of experimental conditions such as feed acidity, feed concentration, DNPPA concentration, diluents, temperature, stripping reagents. The slope analysis method indicated the formation of $[RE(HA_2)_3]$ type of neutral species in the organic phase. The extraction reaction of rare earths with DNPPA was found to be exothermic with ΔH values being −10.6 kJ/mol (La), −12.9 kJ/mol (Dy) and −17.5 kJ/mol (Y). The ΔS values were found to be −42.5 (La), −37.3 (Dy) and −43.0 (Y) J/mol K. The free energy change (ΔG) were found to be −2.2 (La), −1.6 (Dy) and −4.5 (Y) KJ/mol at 303 K. Stripping of rare earth was >90% from rare earth loaded DNPPA by sulphuric acid (7 M) in a single contact at room temperature (303 K). Extraction of rare earths in different diluents followed the order: petrofin ~ dodecane > dichlorobenzene >xylene > chlorobenzene. The extraction efficiency for rare earths by DNPPA increased with increase in atomic number: La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy < HoY < Er < Tm < Lu. Separation factors between these metal ions were calculated and compared with extractants such as di-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexyl 2-ethylhexyl phosphonic acid (EHEHPA). DNPPA was found to be stable even after 10 cycles of repeated extraction/stripping operations.

1. Introduction

Rare earths (RE) are widely used in phosphor materials, magnetic substances, alloys, catalysts, optoelectronic materials, superconductors, solid oxide fuel cells and in nuclear applications. The high value of these elements depends on their effective separation into high purity compounds. It is generally known that the difficulties encountered in the separation and recovery of rare earths from each other is due to their similar physical and chemical properties. Solvent extraction is one of the major techniques for separation of the rare earth elements. The organophosphorous extractants such as 2-ethylhexyl 2-ethyhexylphosphonic acid (EHEHPA), di-2-ethyl hexyl phosphoric acid (D2EHPA), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), tri-n-octyl phosphine oxide (Cyanex 921) and a mixture of four trialkylphosphine oxides: R_3PO, $R_2R'PO$, RR'_2PO and R'_3PO where R is n-octyl and R′ is n-hexyl chain (Cyanex 923) have been been extensively researched for the extraction and separation of rare earths (Anitha et al., 2008; Duan et al., 2010; Panda et al., 2012; Reddy et al., 1998; Sato, 1989; Thakur et al., 1993). The organophosphorous extractants have been commercially employed for this purpose due to their solvation properties as well as their chemical stability and low aqueous solubility. Di-nonyl phenyl phosphoric acid (DNPPA) is an organo phosphorus extractant ($pK_a = 2.54$), aromatic analogue of D2EHPA, and extracts metal ions by cation exchange mechanism (Kul et al., 2008). DNPPA is a stronger extractant compared to D2EHPA and EHEHPA. Metal ion extraction at higher acidities was feasible in the case of DNPPA. In this context, DNNPA was evaluated as an alternative extractant in our laboratory. Mishra et al. have studied the extraction behaviour of uranium from aqueous acidic solutions of nitrate, perchlorate, sulphate, chloride and phosphate with DNPPA in combination with TOPO (Biswas et al., 2012; Mishra et al., 2005; Singh et al., 2004). Singh et al. have reported the recovery of yttrium from phosphoric acid medium with DNPPA and TOPO by solvent extraction (Singh et al., 2012). Recently, DNNPA solvent was explored to extract Nd(III) from nitric acid medium in supported liquid membrane cell and hollow fibre contactor (Ambare et al., 2013; Anitha et al., 2013). There is no information available in the literature pertaining to the use of DNPPA extractant in the separation of rare earths from hydrochloric acid medium. Therefore, an attempt has been made in the present study to investigate the feasibility of using DNPPA for the extraction of rare earths from chloride medium. The effect of different experimental variables such as acidity, metal ion concentration, DNPPA concentration, temperature, stability, etc. on extraction has been investigated in detail. Separation factors between rare earth elements were evaluated and compared with those of commercial extractants like

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http://dx.doi.org/10.1016/j.hydromet.2014.03.015

D2EHPA and EHEHPA. It was observed in this study DNPPA extracts RE even at higher acidities. Recycle tests have also been performed to evaluate the stability of DNPPA for rare earth extraction.

2. Experimental

DNPPA was synthesised in our laboratory by a method described elsewhere (Kosolapoff, 1950). Diester and monoester content of DNPPA was estimated by potentiometric titration. The % diester and mono ester in DNPPA were >95% and <0.5% respectively. DNPPA was dissolved in Petrofin to prepare the organic solvent. The stock solutions of mixture of rare-earth ions, which were prepared by digesting the corresponding rare earth oxide in minimum concentrated hydrochloric acid and evaporated to near dryness and then made up with distilled water. Feed solutions were made by diluting the stock solution. All other chemicals used were of analytical reagent grade. ICP-AES (JY Ultima 2) was used for analysis of rare earths.

The extraction experiments were carried out in separatory funnel by equilibrating equal volumes (10 ml) of aqueous (0.01 M La, feed acidity: 3 M HCl) and organic phases (0.2 M DNPPA) for different contact time periods to obtain the equilibration time. After equilibrium, the contents were allowed for phase disengagement. Metal ion concentrations in the aqueous phase before and after extraction were determined by ICP-AES after suitable dilutions. The concentration of RE(III) in organic phase was obtained by mass balance. The plot of % extraction of La versus contact time is shown in Fig. 1. From the data it is evident that a contact time of 3 min is sufficient to reach equilibrium. However, contact time of 5 min was maintained in all experiments so as to ensure that equilibrium has been attained. The distribution ratio (D) represents the ratio of RE(III) in the organic phase to that in the aqueous phase. The distribution ratio (D) was calculated as $(C_i - C_f) / C_f$, where C_i is the metal ion concentration in the aqueous phase before extraction and C_f is the metal ion concentration in the aqueous phase after extraction. The percentage extraction of metal ion (% E), was calculated by $\% E = 100 \times D \times R / (1 + D \times R)$, R is the phase ratio (volume of the organic phase to volume of aqueous phase). When volumes of aqueous and organic phases are equal, $\% E = 100 \times D / (1 + D)$. All the experiments were carried out at room temperature (301 K) except when effect of temperature on the distribution equilibrium was studied. Stripping experiments were carried out by shaking equal volumes of (5 ml) the organic phase loaded with the extracted metal for 15 min with a known volume of the aqueous acid solution under study. The concentration of the metal ion in the aqueous phase was determined and the stripping percent (% stripping) was calculated by the following relation: $\% \text{Stripping} = [C_s / (C_i - C_f)] \times 100$, where C_s is the stripped metal ion concentration in the aqueous phase after stripping For temperature variation effect, care was taken to keep the temperature constant throughout the studies by monitoring at regular intervals using a thermometer and also by preheating the solutions. In all the experiments each data point represents a mean value of three independent measurements with standard deviation of ±5%.

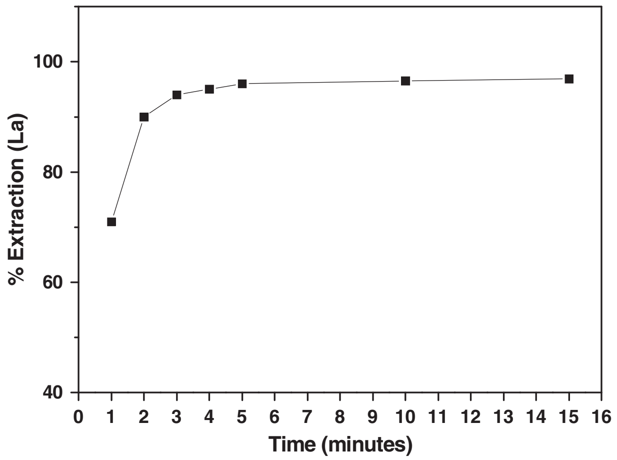

Fig. 1. Effect of time on extraction of La. $[\text{La(III)}] = 0.01$ M, $[H^+] = 3$ M, $[\text{DNPPA}] = 0.2$ M, O / A = 1.

3. Results and discussion

3.1. Effect of aqueous acidity on distribution ratio of rare earths

Effect of HCl concentration from 0.5 to 5 M in the aqueous phase containing 0.01 M rare earth (La, Dy or Y) was studied using 0.2 M DNPPA at aqueous to organic phase ratio (A:O) of 1:1. The D values decreased gradually with increased feed acidity in the aqueous phase. The % extraction (Y) at 0.5 and 3 M acidities was found to be 99.99 and 95.8% respectively. This observation was attributed to the acidic nature of DNPPA and that of rare earth loading in the organic phase. The decrease in rare earth extraction with aqueous phase acidity is typical of acidic extractants suggesting the involvement of cation exchange mechanism. Similar observations have been reported during the extraction of rare earth elements using other acidic extractants such as D2EHPA and EHEHPA in different aqueous media (Mishra et al., 2000; Singh et al., 2004). The conventional slope analysis method was used to establish the extraction behaviour of RE by DNPPA. A plot of log D ($_{La/Dy/Y}$) vs $\log[H^+]$ at constant DNPPA resulted in straight lines with a slope of approximately '−3' indicating three H^+ ions are discharged in the reaction with RE (Fig. 2). The relation between D and $[H^+]$ obtained for La, Dy and Y are shown below:

$$\log\ D_{La} = 1.18 - 3.11\ \log\left[H^+\right] \tag{1}$$

$$\log\ D_{DY} = 2.79 – 2.90\ \log\left[H^+\right] \tag{2}$$

$$\log\ D_Y = 4.20 - 3.03\ \log\left[H^+\right]. \tag{3}$$

The correlation coefficient (r) for regression equations was found to be >0.99. At lower acidities, the extraction of RE was near quantitative and RE in the raffinate phase was found to be below detection limits. Hence, 3 M HCl was chosen as feed acidity for subsequent experiments.

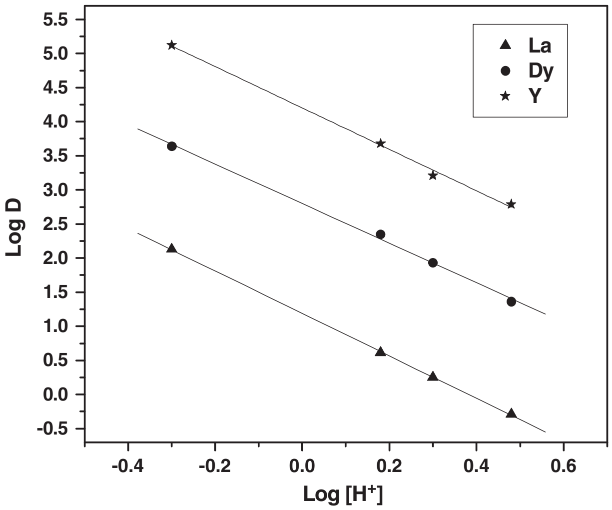

Fig. 2. Effect of feed acidity on distribution ratio of La, Dy and Y. $[\text{RE(III)}] = 0.01$ M, $[\text{DNPPA}] = 0.2$ M, O / A = 1.