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Synergistic extraction of cerium from sulfuric acid medium using mixture of 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester and Di-(2-ethyl hexyl) phosphoric acid as extractant

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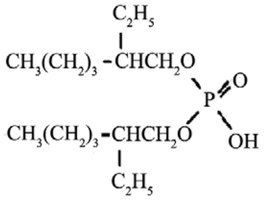
Abstract: Synergistic extraction of cerium(IV) from sulfuric acid medium using mixture of 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester(HEH/EHP, HL) and Di-(2-ethyl hexyl) phosphoric acid (HDEHP, HA) as extractant was investigated. The results indicated that the maximum synergistic enhancement coefficients were obtained at the mole fraction of HEH/EHP=0.6, and cerium(IV) was extracted into organic phase in the form of $Ce(SO_4)_{0.5}HL_2A_2$. A cation exchange mechanism was proposed for the synergistic extraction of Ce(IV). The equilibrium constants and thermodynamic functions such as ΔG, ΔH, and ΔS were determined in the extraction of Ce(IV) from sulfuric medium using mixture of HEH/EHP and HDEHP.

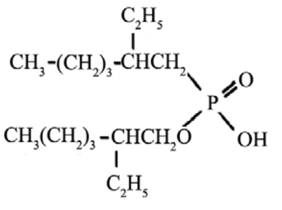
Keywords: synergistic extraction; cerium; HEH/EHP; HDEHP; sulfuric acid medium; rare earths

It is well known that the bastnaesite is one of the main sources of cerium and other light rare earths[1,2]. The advanced technology for bastnaesite treatment is oxidation roasting, leaching with sulfuric acid, then recovering rare earth, fluorine, and thorium by solvent extraction, which is considered as a simple and continuous process with high yield and products purity[3,4]. Cerium is oxidized into Ce(IV), and it can be leached out with sulfuric acid and be extracted using organoPhos-phorous acidic extractants.

HEH/EHP and HDEHP are widely used organophosphorous acidic extractants, their formulas are as mentioned above.



HDEHP



HEHEHP

HDEHP has higher pKa value than HEH/EHP, so it holds the advantages of higher extraction capacity and formation of less emulsion. However, the stripping properties of extracted metal ions are not so good as HEH/EHP, especially for the loaded thorium(IV) and middle and heavy rare earths. Compared with the single extractant of HDEHP and HEH/EHP, it is a promising solution to use mixture of HDEHP and HEH/EHP as extractant for Ce(IV) and other rare earths extraction from the sulfuric acid leached solution.

In Ref.[5], extraction mechanism of Ce(IV) using HDEHP has been investigated. Li et al investigated the extraction mechanism of Ce(IV) using several kinds of extractants (single extractant system) from nitric acid, hydrochloric acid, and sulfuric acid medium, including: HEH/EHP[6], N1923[7], Cyanex 923[8], and so on. Few reports have been found to study the synergistic extraction of Ce(IV) with mixture systems of organophosphorous acidic extractants.

Therefore, the synergistic extraction behaviors of Ce(IV) with HEH/EHP and HDEHP as the extractant were investigated in this article. The synergistic effect, the extraction mechanism of Ce(IV), and the thermodynamic parameters in the synergistic extraction were mainly investigated.

1 Experimental

1.1 Reagents and apparatus

HEH/EHP and HDEHP are supplied by Luoyang Zhongda Chemical Co., Ltd. The extractants were purified

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by washing with 2% Na_2CO_3, 0.2 mol/L H_2SO_4 and distilled water, respectively, before they were dissolved into sulfonate kerosene to prepare the organic solvent. Stock solution of Ce(IV) was prepared by dissolving $Ce(SO_4)_2 \cdot nH_2O$ (>99.9%) into sulfuric acid and diluted with distilled water. The concentration of Ce(IV) was determined by the method of Ammonium Ferrous Sulfate $[(NH_4)_2Fe(SO_4)_2]$ reductometry, by using N-phenylanthanilic acid and dibenzeneammonia sulfonate acid sodium as the indicators. The acidity was determined by neutralization titration by standard sodium hydroxide solution using mixed indicators of methyl red and bromocresol green after masking the metal ions by Ca-EDTA solution.

1.2 Extraction procedure

Equal volumes (15 ml) of aqueous and organic solutions were put into separation funnels, then they were put into a THZ-D Model constant temperature oscillator to heat for 15 min, then mixed and shaken for 15 min to reach distribution equilibrium. All the operation temperatures were (20±1) °C, except the temperature experiments. After two phases are separated, the concentration of Ce(IV) in the aqueous phase was determined. The concentration in the organic phase was obtained by mass balance. Then, the distribution ratio D was obtained by $[Ce(IV)]_{(o)}/[Ce(IV)]_{(a)}$.

2 Results and discussion

2.1 Synergistic extraction effect of Ce(IV) with mixture of HEH/EHP and HDEHP

Effect of the various composition in the mixture of HEH/EHP and HDEHP on the Ce(IV) extraction was first investigated. The distribution ratio of Ce(IV) at different mole fraction of HEHEHP is shown in Fig.1, whereas the total concentration of HEHEHP and HDEHP was fixed at 0.1 mol/L. The distribution ratio varies with the variant ratio of HEH/EHP in the organic phases. Synergistic effect using mixture of HEH/EHP and HDEHP can be observed obviously.

The distribution ratio of D_1, D_2, and D_T for HEH/EHP, HDEHP, and their mixture, respectively, were obtained by experiments, then the synergistic enhancement coefficient, $R=D_T/(D_1+D_2)$, was obtained according to Xu's method[9].

Synergistic enhancement coefficients (R) of Ce(IV) extraction at variant equilibrium acidity and mole fraction of HEH/EHP are shown in Table 1.

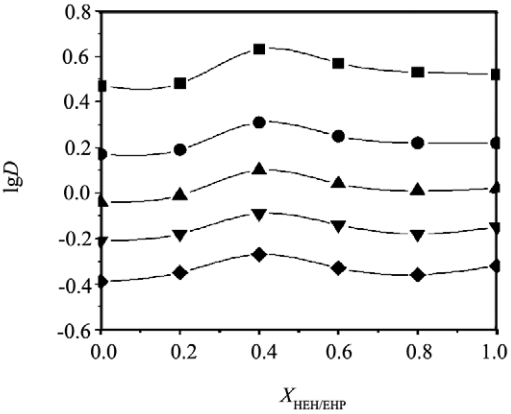

Fig.1 Synergistic extraction of Ce(IV) by mixture of HEH/EHP and HDEHP; [Ce(IV)]=0.024 mol/L; $[HEH/EHP+HDEHP]_{(O)}$= 0.10 mol/L; $[H^+]_e$=(■) 0.52 mol/L; (●) 0.69 mol/L; (▲) 0.83 mol/L; (▼) 0.98 mol/L; (◆)1.15 mol/L

Table 1 Synergistic enhancement coefficient of Ce(IV) at different equilibrium acidity and HEH/EHP mole fraction in extractant

$X_{HEH/EHP}$ $[H^+]$/(mol/L)	0.2	0.4	0.6	0.8
0.52	4.22	8.16	8.93	3.65
0.69	3.64	6.64	7.25	3.61
0.83	3.31	5.79	6.28	3.57
0.98	3.03	5.13	5.52	3.54
1.15	2.78	4.54	4.84	3.50

It can be seen that the maximum value of R appears at $X_{HEHEHHP}$=0.6 for variant acidity conditions but not at the $X_{HEHEHHP}$=0.4 at which the distribution ratio reaches maximum value for each acidity condition as shown in Fig.1. This may be due to the fact that the synergistic extraction and the reactions by HEH/EHP and HDEHP alone exist simultaneously in the mixture system, the three reactions affect R and determine the largest synergistic effects.

2.2 Synergistic extraction mechanism of Ce(IV) with mixture of HEH/EHP and HDEHP

If the synergistic extraction of Ce(IV) by the mixture of HEH/EHP and HDEHP from sulfuric acid medium is expressed as:

$$Ce^{4+}+\frac{4-x}{2}SO_4^{2-}+m\,H_2L_{2(o)}+n\,H_2A_{2(o)} \xleftrightarrow{K_{12}} Ce(SO_4)_{\frac{4-x}{2}}H_{2m+2n-x}L_{2m}A_{2n(o)}+x\,H^+ \quad (1)$$

Then, the distribution ratio, D_{12} of the synergistic reaction, and the equilibrium constant, K_{12} of the synergistic extraction reaction should be:

$$D_{12}=D_T-D_1-D_2=\frac{[Ce(SO_4)_{\frac{4-x}{2}}H_{2m+2n-x}L_2A_2]_{(o)}}{[Ce^{4+}]} \quad (2)$$