Korean J. Chem. Eng., **27**(4), 1258-1261 (2010)
DOI: 10.1007/s11814-010-0194-7

Extraction of rare earths using mixtures of *sec*-octylphenoxy acetic acid and organophosphorus acids

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(*Received 30 March 2009 • accepted 25 November 2009*)

Abstract−The extraction of rare earths from nitrate medium using three organophosphorus acids, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP), di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272), and their mixtures with *sec*-octylphenoxy acetic acid (CA12) has been studied in detail. The mixtures have different extraction effects on various rare earths. Synergistic extraction effects are only found when light rare earths and yttrium (III) are extracted with mixtures of D2EHPA and CA12. The possibilities of separating the rare earths with these mixtures are investigated according to the extractabilities. It is feasible and advantageous to separate yttrium (III) from the lanthanoids (III) with HEHEHP + CA12 and D2EHPA+CA12 mixtures at proper extractant ratios. The separation of yttrium (III) from heavy rare earths is also possible with mixtures of Cyanex272 and CA12.

Key words: Extraction, Rare Earths, Organophosphorus Acids, *sec*-Octylphenoxy Acetic Acid, Separation

INTRODUCTION

Separation chemistry and technology of rare earths have been widely investigated because of their wide and important applications in the fields of catalysis, ceramics, magnetics, optics and electronics, etc [1]. In the last decades, kinds of extractants have been applied to the separation of rare earths, among which acidic organophosphorus extractants have attracted much attention. 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP), di-(2-ethylhexyl) phosphoric acid (D2EHPA) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) are extensively used extractants in hydrometallurgical processes for the extraction of rare earths [2-5]. The structures and p*K*a values of HEHEHP, D2EHPA, and Cyanex272 have been reported earlier [6].

However, much further work should be done about the extraction of rare earths with the three organophosphorus extractants mentioned above. In the case of D2EHPA, the extraction capability is high, and the cost is low, but the organic phase is easy to be emulsified in low acidities, and the rare earth ions are difficult to be stripped completely. Compared with D2EHPA, HEHEHP is a better extractant with higher separation factors for rare earth ions, and lower aqueous acidity for stripping. However, the viscosity of the organic phase increases and the extraction efficiency decreases. The practical application of Cyanex272 is strongly affected by their extractability being insufficient and their low loading capacity for rare earths resulting from the low lipophilicity of the coordination compounds formed during extraction. Therefore, there is a growing interest in the development of new extraction systems for the separation of rare earths as a group or from one another. Synergic effect is a well-known phenomenon in solvent extraction, which involves an enhancement of the extraction of a metal ion [7,8]. In recent years, systematic studies have been conducted concerning the synergic phenomenon without following the extraction process. Much attention has been paid to the extraction of rare earths with mixtures containing HEHEHP, D2EHPA, and Cyanex272 [9-22]. For instance, Wu et al. [9] investigated the extraction behaviors of praseodymium (III) using 8-hydroxyquinoline and HEHEHP. The formed complexes and equilibrium constants are determined. The mutual mixtures of HEHEHP, D2EHPA, and Cyanex272 have also been employed for the extraction of rare earths [11,12,14-16]. Huang et al. [11,12] have studied the synergistic extraction of rare earths with mixtures of HEHEHP and D2EHPA from sulfuric acid medium. Wang et al. [14] investigated the extraction of rare earths from chloride medium using mixtures of HEHEHP and five other kinds of organophosphorus acids, D2EHPA, isopropylphosphonic acid 1-hexyl-4-ethyloctyl ester (HHEOIPP), Cyanex272, bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex302), and bis(2,4,4-trimethypentyl) dithiophosphinic acid (Cyanex301). The extractability of the selected extractants for rare earths is proved to decrease in the order: HEHEHP+D2EHPA>HEHEHP+Cyanex301>HEHEHP +HHEOIPP>HEHEHP+Cyanex302>HEHEHP+Cyanex272.

Sec-octylphenoxy acetic acid (CA12) is a carboxylic acid recently developed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. It has several advantages including stable composition, low solubility in the aqueous phase, easy preparation and not easily emulsified during extraction [23]. In our previous work [20], the synergistic extraction of lanthanum (III) with mixtures of D2EHPA and CA12 has been studied. The mixtures exhibit different extraction effects on rare earths, providing possibilities for the separation of yttrium (III) from lanthanoids (III) at proper ratios of D2EHPA and CA12. This prompts us to investigate new synergis-

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tic extraction systems involving CA12 as a synergist in the extraction of rare earths using acidic organophosphorus extractants, with a view to elucidate the selectivity among these trivalent metal ions.

In the present work, the extraction of rare earths from nitrate medium with HEHEHP, D2EHPA, Cyanex272 and their mixtures with CA12 is investigated systematically. The differences of the extractabilities are studied according to the structures of the extractants, and a possible explanation is given. The separation abilities of rare earths using the organophosphorus extractants with and without CA12 have been studied and compared with each other.

EXPERIMENTAL

1. Reagents and Apparatus

HEHEHP, D2EHPA and CA12 were supplied by Shanghai Rare-Earth Chemical Co., Ltd. Cyanex272 was kindly supplied by the CYTEC Canada, Inc. All the extractants were used as received and dissolved in *n*-heptane to the required concentration. The concentrations of the extractants were determined by titration with standard sodium hydroxide. Stock solutions of rare earths were prepared from their oxides by dissolving in concentrated nitric acid and diluting with distilled water. The rare earths were analyzed by titration with a standard solution of EDTA with xylenol orange as indicator. The pH values of the aqueous phase were measured with a pHS-3C digital pH meter (Shanghai Rex Instrument Factory, China). All extraction experiments were performed at constant ionic strength ($NaNO_3$=0.6 mol·L^{-1}). All the other reagents were of analytical grade. Deionized water was prepared by the Milli-Q SP system (Millipore, Milford, MA, USA).

2. Experimental Procedures

For the equilibrium experiments, 5 mL of the aqueous and the organic solution, respectively, was mixed and shaken for 30 min at 293±1 K. After the phase separation, the concentration of rare earths in the aqueous phase was determined by titration with EDTA and that in the organic phase by difference. The distribution ratio was calculated as the ratio of the concentration of rare earths in the organic phase to that in the aqueous phase.

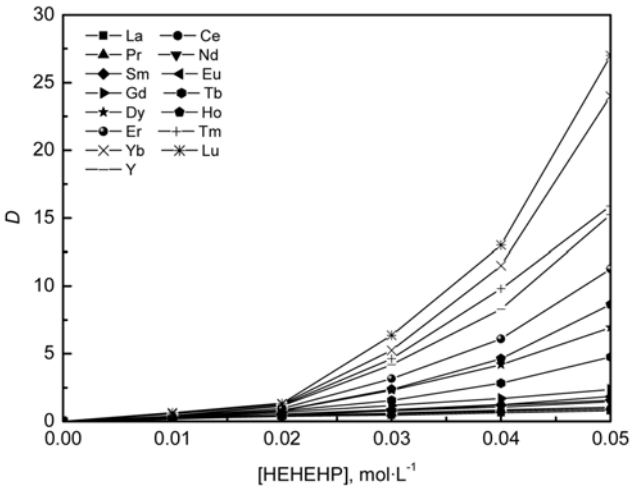

Fig. 1. Extraction of RE^{3+} with HEHEHP: [RE^{3+}]=5.0×10^{-3} mol·L^{-1}, pH=3.0, μ=0.6 mol·L^{-1}.

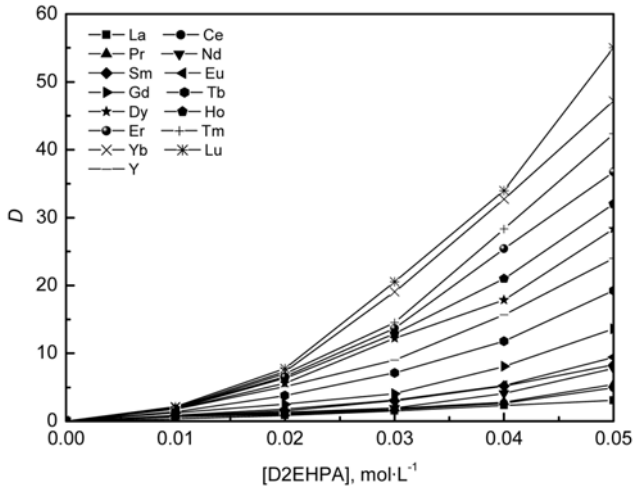

Fig. 2. Extraction of RE^{3+} with D2EHPA: [RE^{3+}]=5.0×10^{-3} mol·L^{-1}, pH=3.0, μ=0.6 mol·L^{-1}.

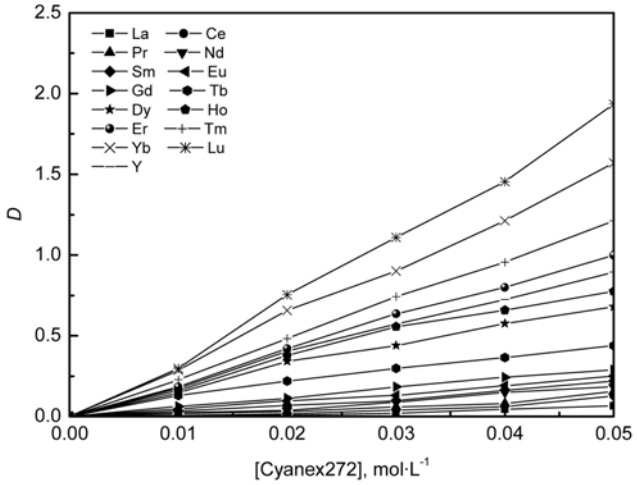

Fig. 3. Extraction of RE^{3+} with Cyanex272: [RE^{3+}]=5.0×10^{-3} mol·L^{-1}, pH=3.0, μ=0.6 mol·L^{-1}.

RESULTS AND DISCUSSION

1. Extraction of Rare Earths with HEHEHP, D2EHPA or Cyanex272

Figs. 1-3 show the extraction of rare earths with single HEHEHP, D2EHPA, or Cyanex272 extractant. In all the three systems, the extraction capacity increases with increasing atom numbers of lanthanoids. Y locates between Tb and Dy, Er and Tm, Ho and Er when extracted with HEHEHP, D2EHPA, and Cyanex272, respectively. The extraction order of the rare earths may be explained based on the structures of the three acidic organophosphorus extractants. According to HSAB theory [24], both rare earth ions and HEHEHP, D2EHPA, Cyanex272 are hard bases. The extractants are more prone to react with the rare earth ions with high atomic numbers. In addition, the increase of C-P numbers within the extractants results in increasing p*K*a values (3.24, 4.51, and 6.37 for D2EHPA, HEHEHP, and Cyanex272, respectively) and activities of the functional group P(O)OH. Therefore, as to a certain rare earth element, the extrac-

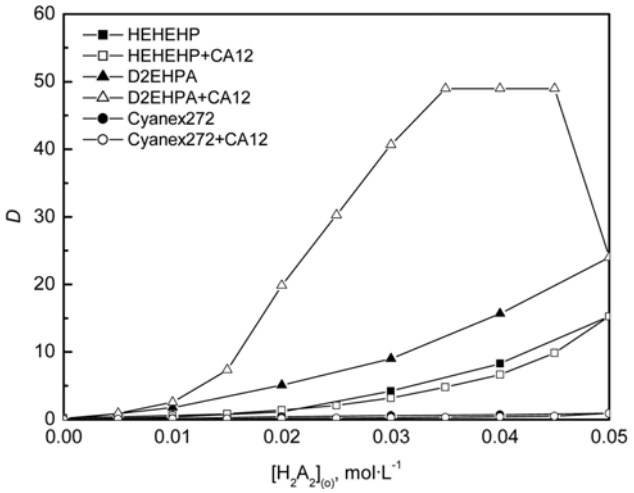

Fig. 4. Extraction of Y^{3+} with organophosphorus acids and their mixtures with CA12: $[Y^{3+}]=5.0\times10^{-3}$ mol·L^{-1}, pH=3.0, μ= 0.6 mol·L^{-1}, $[H_2A_2]+[CA12]=0.05$ mol·L^{-1}.

tion ability follows the order: D2EHPA>HEHEHP>Cyanex272. This order is also shown in Figs. 1-3.

3. Extraction of Rare Earths with Mixtures of HEHEHP and CA12

The extraction of rare earths with mixtures of HEHEHP and CA12 has been investigated. Results show that the mixtures have weak synergistic effects on light rare earths (La, Ce, and Pr), but weak antagonistic effects on other rare earths. Weak antagonistic effect is also found for Y when extracted with the mixtures, which is shown in Fig. 4.

4. Extraction of Rare Earths with Mixtures of D2EHPA and CA12

The synergistic extraction of La with mixtures of D2EHPA and CA12 has been investigated in detail in our previous work [20]. The methods of slope and constant moles are employed to determine the extracted complex, equilibrium constant, and thermodynamic functions. The extraction reaction is as the following:

$$La^{3+}_{(a)}+2NO^{-}_{3(a)}+H_2A_{2(o)}+\frac{1}{2}H_2B_{2(o)} \xrightleftharpoons{K_{AB}} La(NO_3)_2H_2A_2B_{(o)}+H^{+}_{(a)} \quad (1)$$

where H_2A_2 denotes D2EHPA, H_2B_2 denotes CA12. The synergistic enhancement coefficient, calculated according to Xu et al.'s theory [25], is determined as 3.63. The logarithm of equilibrium constant, $\log K_{AB}$, is calculated as 0.80. In addition, the extraction of Ce, Nd, Dy, Lu, and Y is investigated. The mixtures have synergistic effects on Ce, Nd, and Y, but neither synergistic nor antagonistic effects on Dy, and weak antagonistic effects on Lu are found.

In this work, the extraction of the other rare earths, i.e., Pr, Sm, Eu, Gd, Tb, Ho, Er, Tm, and Yb have also been conducted. It can be concluded that there are not evident synergistic effects on these rare earths.

5. Extraction of Rare Earths with Mixtures of Cyanex272 and CA12

Under similar experimental conditions, the mixtures of Cyanex272 and CA12 are employed for the extraction of rare earths. Results show that the mixtures have antagonistic effects on all the rare earths. The antagonistic extraction of Y with the mixtures is also shown in Fig. 4. In Sun et al.'s work [21], synergistic effects have been found for Ho, Y, Er, Tm, Yb, and Lu when the ions are extracted from chloride medium with mixtures of Cyanex272 and CA12, with synergistic enhancement coefficients (R_{max}) as 5.12 (Ho), 5.34 (Y), 7.04 (Er), 7.50 (Tm), 13.12 (Yb), and 17.58 (Lu), respectively. This implies that the medium is a very important factor affecting the extraction effects. Many similar results have been found in previous papers. For example, the mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP) and triisobutylphosphine sulfide (TIBPS) have synergistic effects on La in both hydrochloric and nitric solutions, but the synergistic enhancement coefficients are different (2.40 and 1.82 for HCl and HNO_3, respectively) [26,27].

6. Separation of Rare Earths with Mixtures of Organophosphorus Acids and CA12

The different extraction effects on rare earths with mixtures of the organophosphorus acids and CA12 can be considered for the separation of the trivalent metal ions. As is well known, the separation and purification of rare earths is difficult due to their similar chemical and physical properties. In addition, the separation of Y from lanthanoids is another difficult problem. In our previous work, the separation of Y from La, Ce, Nd, Dy, and Lu has been investigated with mixtures of D2EHPA and CA12. The selectivity between Y and lanthanoids with D2EHPA+CA12 is higher than that with D2EHPA alone. In Table 1, the separation factors of Y to lanthanoids with HEHEHP, D2EHPA, Cyanex272 and their mixtures with CA12 are determined. It is evident the separation of Y from lanthanoids is enhanced with HEHEHP+CA12 and D2EHPA +CA12. However, the separation of Y from heavy rare earths (Ho, Er, Tm, Yb, and Lu) can be performed with Cyanex272+CA12.

CONCLUSIONS

The extraction of yttrium and 15 lanthanoids (except promethium) from nitrate medium with organophosphorus acids, HEHEHP,

Table 1. Separation factors between Y and lanthanoids with organophosphorus acids and their mixtures with CA12

$\beta_{Y/Ln}$	Y/La	Y/Ce	Y/Pr	Y/Nd	Y/Sm	Y/Eu	Y/Gd	Y/Tb	Y/Dy	Y/Ho	Y/Er	Y/Tm	Y/Yb	Y/Lu
HEHEHP	3.10	2.91	2.85	2.73	2.59	2.05	1.64	1.47	1.44	1.37	1.18	0.95	0.89	0.85
HEHEHP+CA12	3.71	3.60	3.54	3.71	3.96	3.54	3.49	3.79	4.17	4.51	4.80	4.17	4.43	6.75
D2EHPA	6.16	4.98	4.39	3.93	3.40	2.87	2.03	1.35	0.91	0.80	0.78	0.73	0.70	0.66
D2EHPA+CA12	10.37	8.90	8.42	8.58	10.17	10.70	8.67	6.36	4.63	4.61	4.58	4.36	4.07	4.63
Cyanex272	51.14	26.41	13.25	10.49	5.91	4.19	3.58	1.84	1.19	1.07	0.96	0.83	0.62	0.54
Cyanex272+CA12	19.24	10.20	5.21	4.26	2.45	1.79	1.55	0.82	0.54	0.50	0.46	0.41	0.31	0.28

D2EHPA, and Cyanex272 with and without CA12 as an added reagent in *n*-heptane diluent has been carried out in the present work. The different extraction abilities with the organophosphorus acids are discussed according to their structures. The various extraction effects on rare earths have been found with the mixtures of organophosphorus acids and CA12. The possibilities of separating yttrium from lanthanoids have been discussed according to the separation factors. HEHEHP+CA12 and D2EHPA+CA12 systems are possible to separate yttrium from lanthanoids, while Cyanex272+CA12 can only be considered to separate yttrium from heavy rare earths.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. Zhenfeng CUI and Ms. Jinling SONG of Changchun Institute of Technology. This project was supported by a grant from Jilin Provincial Science & Technology Department (20090121).

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