Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Synergistic Extraction and Separation of Heavy Lanthanide by Mixtures of Bis(2,4,4-trimethylpentyl)phosphinic Acid and 2-Ethylhexyl Phosphinic Acid Mono-2-Ethylhexyl Ester

Ying Xiong[a]; Xianglan Wang[a]; Deqian Li[a]
[a] Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate School of Chinese Academy of Sciences, Changchun, P.R. China

To cite this Article Xiong, Ying , Wang, Xianglan and Li, Deqian(2005) 'Synergistic Extraction and Separation of Heavy Lanthanide by Mixtures of Bis(2,4,4-trimethylpentyl)phosphinic Acid and 2-Ethylhexyl Phosphinic Acid Mono-2-Ethylhexyl Ester', Separation Science and Technology, 40: 11, 2325 — 2336
To link to this Article: DOI: 10.1080/01496390500202472
URL: http://dx.doi.org/10.1080/01496390500202472

Separation Science and Technology, 40: 2325–2336, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500202472

Synergistic Extraction and Separation of Heavy Lanthanide by Mixtures of Bis(2,4,4-trimethylpentyl)phosphinic Acid and 2-Ethylhexyl Phosphinic Acid Mono-2-Ethylhexyl Ester

Ying Xiong, Xianglan Wang, and Deqian Li
Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate School of Chinese Academy of Sciences, Changchun, P.R. China

Abstract: The extraction of Yb^{3+} from chloride solution has been studied using mixtures of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272) and 2-ethylhexyl phosphinic acid mono-2-ethylhexl ester (P507). The results show that Yb^{3+} is extracted into heptane as $YbA_3(HA)_3$ with Cyanex272, $YbL_3(HL)_3$ with P507, and $YbA_2L_4H_3$ with synergistic mixture. The equilibrium constants, formation constants, and thermodynamic functions have been determined. Extraction mechanism and extraction process are also proposed. The extraction of heavy lanthanide ions by mixtures of Cyanex272 and P507 is studied and the possibility of separating heavy rare earth ions is discussed.

Keywords: Synergistic extraction, ytterbium, Cyanex272, P507, heavy lanthanide

INTRODUCTION

There is a sharp rise in demand of heavy lanthanide metal, due to the quick growth of advanced industries, such as electronics and new ceramics (1, 2). However, it is

Received March 7, 2005, Accepted May 30, 2005
Address correspondence to Deqian Li, Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate School of Chinese Academy of Sciences, Changchun 130022, P.R. China. Tel.: +86-431-5262036; Fax: +86-431-5698041; E-mail: ldq@ciac.jl.cn

generally difficult to separate and purify individual metal from heavy lanthanide because of the similarity in chemical properties of these elements. Therefore, only after a new system has an effective separation ability for heavy lanthanide could highly purified individual heavy rare earth be obtained.

Organophosphorus acids as extractants have been widely studied for solvent extraction in the past three decades. Recently, much effort has been devoted to use bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272), which has a high selectivity, high separation factors of rare earth ions, and a low aqueous acidity in extraction and stripping (3, 4). However, the organic phase caused an increase in viscosity, and low extraction efficiency when Cyanex272 is used. In order to prevent the problems, one of the most effective methods is to modify organic phase by introducing one adduct into Cyanex272.

Synergistic effects are an important phenomenon in the solvent extraction and have been studied extensively. The extraction of Ln(III) with mixtures of P507 and P204 or TOPO, TBP, TPhPO has been studied systematically (5–7). Freiser et al. and Saleh et al. reported the synergistic extraction of tervalent lanthanides by Cyanex272 combined with TOPO, CMPO, or MBDPO (8, 9). Recently, our group has studied the synergistic extraction of Zn^{2+} and Ln(III) by mixtures of Cyanex272 with N1923 and HPMBP, respectively (10, 11). However, most works are concentrated on organic acid and organic base systems (12–14), and few works are focused on organic acid and organic acid systems.

In the present work, the synergistic extraction mechanism of Yb^{3+} by mixtures of Cyanex272 and P507 from chloride medium is studied. Effects of the aqueous acidity, the concentration and ratio of the extractants, and experimental temperature are investigated. Data we obtained are analyzed on the basis of slope method to determine the extracted complexes, formation constants, and thermodynamic functions. Furthermore, the separation of heavy Ln(III) with mixtures of Cyanex272 and P507 is discussed. In addition, although impurities that Cyanex272 contains may influence the extraction synergism (15, 16), Cyanex272 is used without purification in this paper in order to combine with the practicality of production.

EXPERIMENTAL

Reagent

P507 (purity >98%) and Cyanex272 (purity >85%) were kindly supplied by Shanghai Organic Chemistry Institute and CYTEC Canada Inc., respectively, and they were used without purification. The extractants were dissolved in heptane to the required concentration. Stock solutions of rare earths were prepared by dissolving their oxide with a purity >99.9% in hydrochloric acid and diluting with distilled water. All extraction experiments were performed at constant ionic strength (0.1 M NaCl). All other reagents employed in this work were of analytical grade.

Apparatus

A pHS-3C digital pH meter made by Shanghai Rex Instruments Factory was used for pH measurements by means of a combined glass-reference electrode. A 722 Model Grating Spectrophotometer made by Shanghai Precision & Scientific Instrument Co. Ltd (SPSIC) was used for measurements of trace element concentration. TJA model POEMS inductive coupled plasma atomic emission spectroscopy (ICP-AES) was used for measurements of individual concentration of mixed rare earth solution.

Procedure

For the equilibrium experiments, equal volumes (5 mL each) of aqueous and organic phases were mixed and shaken for 30 min at 298 $\pm$ 1K (except for the temperature experiments), which was sufficient for equilibrium attainment. After phase separation, the concentration of metal ions in the aqueous phase was determined by spectrophotometer or ICP-AES. The concentration of metal ions in the organic phase was determined by mass balance. The concentrations were used to obtain the distribution ratio, D, was taken as the ratio of the concentration of metal ion in the organic phase to that present in the aqueous phase.

RESULTS AND DISCUSSION

Extraction Yb^{3+} with Cyanex 272 and P507, Respectively

The extraction of Ln(III) with Cyanex272 or P507 has been reported earlier (17, 18), but the extraction of Yb^{3+} in chloride medium has not been discussed in detail. For elucidating the extraction mechanism with Cyanex272 or P507 alone, the conventional slope analysis method has been introduced. As shown in Fig. 1, the plot of logD vs. pH at constant extractant concentration gives a straight line with a slope of about 3.0 both for Cyanex272 and P507. Similarly, at constant aqueous acidity, the plots are linear with slope of about 3.0 both for Cyanex272 and P507 (shown in Fig. 2). The extraction of Yb^{3+} can be expressed by the following equations:

$$Yb^{3+}_{(a)} + 3(H_2A_2)_{(o)} \overset{K_1}{\longleftrightarrow} YbA_3(HA)_{3(o)} + 3H^+_{(a)} \quad (1)$$

$$Yb^{3+}_{(a)} + 3(H_2L_2)_{(o)} \overset{K_2}{\longleftrightarrow} YbL_3(HL)_{3(o)} + 3H^+_{(a)} \quad (2)$$

where H_2A_2 and H_2L_2 represent the dimeric species of Cyanex272 and P507, respectively, due to its larger dimerization constant in heptane (19, 20); K_1 and

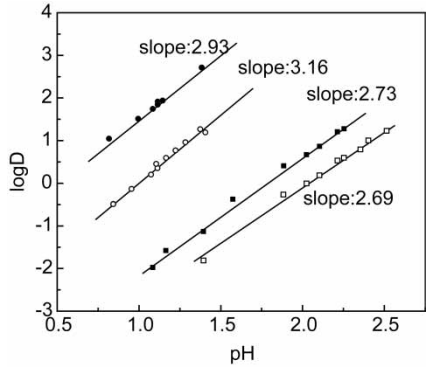

Figure 1. Relationship between distribution ratio D and pH. $[Yb^{3+}] = 3 \times 10^{-4}$ M, $\mu = 0.1$ M. ■, [Cyanex272] = 0.030 M; □, [Cyanex272] = 0.018 M; ●, [P507] = 0.030 M; ○, [P507] = 0.030 M.

K_2 denote the equilibrium constant; *o* and *a* denote aqueous and organic phase, respectively. The distribution ratio (D_1) is given by

$$D_1 = \frac{[YbA_3(HA)_3]_{(o)}}{[Yb^{3+}](1 + \sum_{i=1}^{2} \beta_i [Cl^-]_i)} \tag{3}$$

where β_i ($i = 1 \sim 2$) are the complex formation constants of Yb^{3+} with chloride ions in the aqueous phase, and the values are 1.15 and 1.59, respectively (21). Then K_1 can be written from Eqs. (1) and (3) as

$$K_1 = \frac{D_1[H^+]^3(1 + \sum_{i=1}^{2} \beta_i [Cl^-]^i)}{[H_2A_2]_{(o)}^3} \tag{4}$$

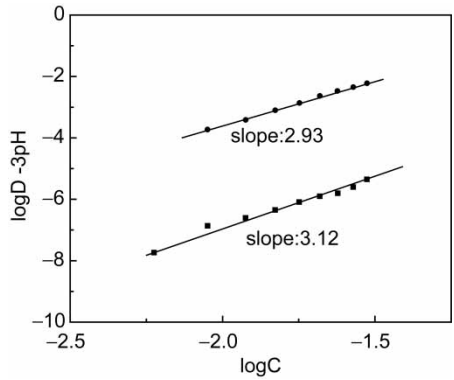

Figure 2. Relationship between distribution ratio D and equilibrium concentration of extractant. $[Yb^{3+}] = 3 \times 10^{-4}$ M, pH = 2.06, $\mu = 0.1$ M. ■, Cyanex272; ●, P507.

where $[H_2A_2]_{(o)} = C_{H_2A_2} - (3 \times D_1 \times C^{3+}_{Yb})/(1 + D_1)$; $C_{H_2A_2}$ and C^{3+}_{Yb} represent the initial concentration of H_2A_2 in the organic phase and the initial concentration of Yb^{3+} in the aqueous phase, respectively. According to Eq. (4), the value of $\log K_1$ is calculated to be -0.89 ± 0.04. In the same way, the value of $\log K_2$ is calculated to be 2.35 ± 0.02.

Extraction Yb^{3+} with Mixtures of Cyanex272 and P507

The synergistic enhancement factors of the extraction of Yb^{3+} with mixtures of Cyanex272 and P507 in heptane, $R = D_{12}/(D_1 + D_2)$ (8, 22), are listed in Table 1. It is obvious that it shows an evident synergistic effect with mixtures of Cyanex272 (<0.021 M) and P507 (0.003 M and 0.006 M), and an anti-synergistic at the other ratio of them. A possible explanation is the favorable or adverse steric effects of the alkyl side-chains in Cyanex272 (8). Moreover, at a ratio of P507 to Cyanex 272 of 1 to 1, the maximal synergistic enhancement could be obtained. The following extraction experiments are measured at a ratio of P507 to Cyanex 272 of 1 to 1 in order to maintain synergistic effect.

If the synergistic extraction equation of Yb^{3+} with mixtures of Cyanex272 and P507 is expressed as

$$Yb^{3+}_{(a)} + nH_2A_{2(o)} + mH_2L_{2(o)} \xleftrightarrow{K_{12}} YbA_{2n}L_{2m}H_{2n+2m-3(o)} + 3H^+_{(a)} \qquad (5)$$

where n and m represent unknown coefficients, then the equilibrium constant (K_{12}) and the distribution ratio (D_{12}) of the synergistic extraction system should be

$$D_{12} = \frac{[YbA_3(HA_3)]_{(o)}[YbL_3(HL)_3]_{(o)}[YbA_{2n}L_{2m}H_{2n+2m-3}]_{(o)}}{[Yb^{3+}](1 + \sum_{i=1}^{2} \beta_i[Cl^-]_i)} \qquad (6)$$

$$K_{12} = \frac{[YbA_{2n}L_{2m}H_{2n+2m-3}]_{(o)}[H^+]^3_{(a)}}{[Yb^{3+}][H_2A_2]^n_{(o)}[H_2L_2]^m_{(o)}}$$

$$= \frac{(D_{12} - D_1 - D_2)[H^+]^3(1 + \sum_{i=1}^{2}(\beta_i[Cl^-]^i)}{[H_2A_2]^n_{(o)}[H_2L_2]^m_{(o)}} \qquad (7)$$

Table 1. Synergistic enhancement factors of Yb^{3+} with mixtures of Cyanex272 and P507 (pH = 2.06, $[Yb^{3+}] = 3 \times 10^{-4}$ M, $\mu = 0.1$ M)

$C_{Cyanex272}$ (M)	0.003	0.006	0.009	0.012	0.015	0.018	0.021	0.024	0.027
C_{P507} (M)	0.027	0.024	0.021	0.018	0.015	0.012	0.009	0.006	0.003
R	1.40	1.33	1.01	1.12	1.86	1.31	1.07	0.93	0.87

Taking logarithms of Eq. (7):

$$\log(D_{12} - D_1 - D_2) = n\log[H_2A_2]_{(o)} + m\log[H_2L_2]_{(o)} + 3pH + \log K_{12} - \log(1 + \sum_{i=1}^{2}(\beta_i[Cl^-]) \quad (8)$$

where

$$[H_2A_2]_{(o)} = C_{H_2A_2} - \frac{C_{Yb^{3+}}[3D_1 + n(D_{12} - D_1 - D_2)]}{1 + D_{12}}$$

$$[H_2L_2]_{(o)} = C_{H_2L_2} - \frac{C_{Yb^{3+}}[3D_1 + m(D_{12} - D_1 - D_2)]}{1 + D_{12}}$$

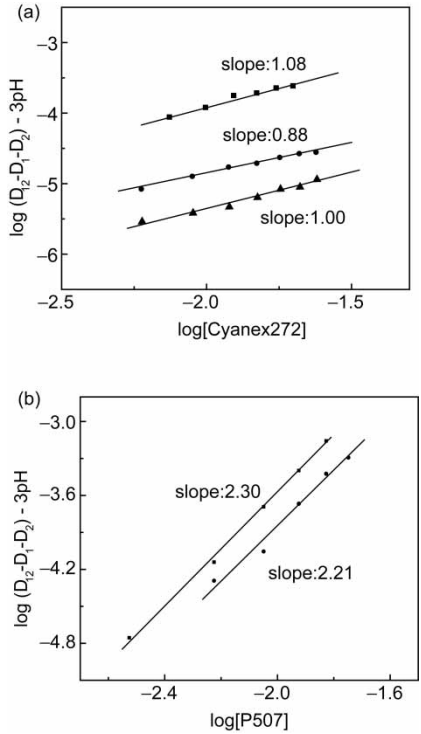

Figure 3. Relationship between distribution ratio D_{12} and equilibrium concentration of Cyanex272 and P507. $[Yb^{3+}] = 3 \times 10^{-4}$ M, $\mu = 0.1$ M, [Cyanex272 + P507] = 0.03 M. (a) ■, [P507] = 0.010 M, pH = 1.20; ●, [P507] = 0.006 M, pH = 2.05; ▲, [P507] = 0.003 M, pH = 2.05; (b) ■, [Cyanex272] = 0.009 M, pH = 1.20; ●, [Cyanex272] = 0.006 M, pH = 1.20.

The coefficients, n and m, are determined by slope analysis. It is clear from the plot (Fig. 3) of $\log(D_{12} - D_1 - D_2)$ vs. $\log[H_2A_2]_{(o)}$ that at a constant Cyanex272 concentration and aqueous acidity, only one H_2A_2 molecule is attached to the synergistic species extracted into the organic phase. In the same way, it is concluded that $2H_2L_2$ molecules in the extracted species in the synergistic extraction reaction. This, in conjunction with the slope of 3 observed in Fig. 4 for the extraction of Yb^{3+} with pH variation experiment at constant extractant concentration, the synergistic extraction reaction can be written as

$$Yb^{3+}_{(a)} + H_2A_{2(o)} + 2H_2L_{2(o)} \overset{K_{12}}{\longleftrightarrow} YbA_2L_4H_{3(o)} + 3H^+_{(a)} \tag{9}$$

The value of K_{12} is calculated to be 1.35 ± 0.08 and is shown in Table 2.

The following hypothetical synergistic reaction can be derived from the Eqs. (1), (2), and (9):

$$YbA_3(HA)_{3(o)} + 2H_2L_{2(o)} \overset{\beta_1}{\longleftrightarrow} YbA_2L_4H_{3(o)} + 2H_2A_{2(o)} \tag{10}$$

$$YbL_3(HL)_{3(o)} + H_2A_{2(o)} \overset{\beta_2}{\longleftrightarrow} YbA_2L_4H_{3(o)} + H_2L_{2(o)} \tag{11}$$

where β_1 and β_2 are formation constants that can be expressed as

$$\log \beta_1 = \log K_{12} - \log K_1 \tag{12}$$

$$\log \beta_2 = \log K_{12} - \log K_2 \tag{13}$$

The values of β_1 and β_2 are shown in Table 2, which indicates that Eq. (10) contributes more to the synergistic extraction. The extracted complexes $YbA_3(HA)_3$ is more prone to form the final synergistic complex $YbA_2L_4H_3$. A possible explanation is that the extracted complex of Yb^{3+}

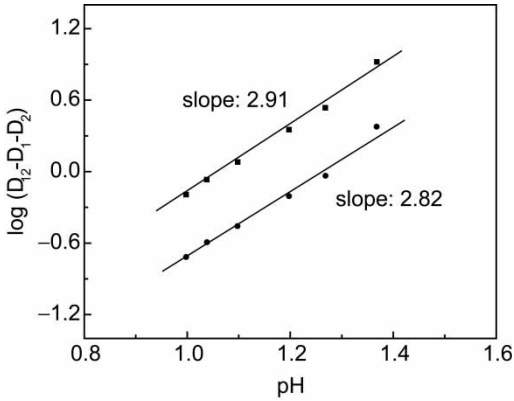

Figure 4. Relationship between distribution ratio D_{12} and pH. $[Yb^{3+}] = 3 \times 10^{-4}$ M, $\mu = 0.1$ M. ■, [Cyanex272] = [P507] = 0.015 M; ●, [Cyanex272] = [P507] = 0.009 M.

Table 2. Equilibrium constants and formation constants for the extraction of Yb^{3+} with mixtures of Cyanex 272 and P507 ($[Yb^{3+}] = 3 \times 10^{-4}$ M, $\mu = 0.1$ M)

$\log K_1$	$\log K_2$	$\log K_{12}$	$\log \beta_1$	$\log \beta_2$
-0.89 ± 0.04	2.35 ± 0.02	1.35 ± 0.08	2.24 ± 0.06	-1.0 ± 0.05

with Cyanex272 is less stable than that with P507, consequently, the substitutional reaction of $YbA_3(HA)_3$ with H_2L_2 is easier than that of $YbL_3(HL)_3$ with H_2A_2.

Effect of Temperature on Synergistic Extraction

The distribution ratios of the extraction of Yb^{3+} by mixtures of Cyanex272 and P507 or by one extractant have been studied at different temperatures (293 K–318 K) at other constant conditions. The ΔH is obtained from the slope of the plot of logD vs. $1000/T$ (Fig. 5) using the Van't hoff equation in the form (23)

$$\log D = -\frac{\Delta H}{2.303R} \cdot \frac{1}{T} + C \tag{14}$$

where R is the gas constant and C is a constant for a solution of constant ionic strength. The free energy change (ΔG) and the entropy change (ΔS) of the

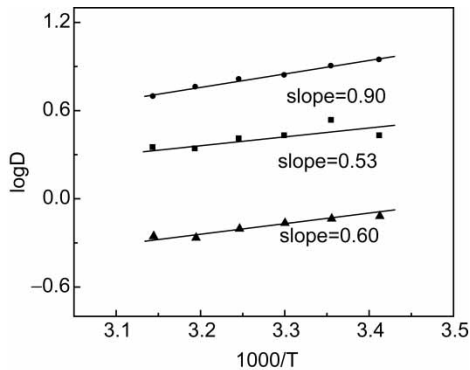

Figure 5. Relationship between distribution ratio D and temperature. $[Yb^{3+}] = 3 \times 10^{-4}$ M, $\mu = 0.1$ M. ■, [Cyanex272] = 0.018 M, pH = 2.05; ▲, [P507] = 0.018 M, pH = 1.36; ●, [Cyanex272 + P507] = 0.018 M, pH = 1.30.

Table 3. Thermodynamic parameter for the extraction of Yb^{3+} with the Cyanex272 and P507 system ($[Yb^{3+}] = 3 \times 10^{-4}$ M, $\mu = 0.1$ M)

	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
Cyanex272	−9.42	−40.70 ± 0.30	3.01 ± 0.39
P507	−11.60	−19.52 ± 0.28	−5.64 ± 0.20
Cyanex272 + P507	−17.31	−15.38 ± 0.20	−12.61 ± 0.16

system are defined as follows:

$$\Delta G = -RT \ln K \tag{15}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{16}$$

The thermodynamic values in the 293 K to 318 K temperature range are obtained using Eqs. (15) and (16), and shown in Table 3. The signs of the ΔH and ΔS change show that the synergistic extraction is enthalpy driven, and more order in this system owing to the reduction of the number of particles resulted from the formation of the synergistic complex.

Extraction of Heavy Ln(III) with Mixtures of Cyanex272 and P507

The extraction of Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}, and Y^{3+} from chloride mixed solutions by mixtures of Cyanex272 and P507 is investigated

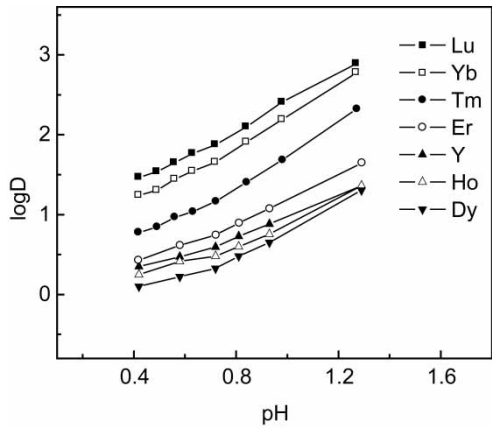

Figure 6. Distribution ratios for heavy Ln(III) and Y^{3+} extraction with mixtures of Cyanex272 and P507 at different pH. $[M^{3+}] = 0.5$ M, $\mu = 0.1$ M, [Cyanex272 + P507] = 1.5 M.

Table 4. Separation factors for adjacent heavy lanthanide with the Cyanex272 and P507 system ($\mu = 0.1$ M)

	Separation factors ($\beta = D_{Z+1}/D_Z$)				
Extractant	Ho/Dy	Er/Ho	Tm/Er	Yb/Tm	Lu/Yb
Cyanex272 (25)	2.07	2.23	2.66	2.4	1.32
P507 (26)	1.62	1.25	1.33	1.12	1.13
Cyanex272 + P507	1.32	1.50	2.65	3.04	1.6

(shown in Fig. 6). The separation factors for adjacent heavy lanthanide are calculated and given in Table 4. It demonstrates that the separation coefficients (β_z^{z+1}) of heavy Ln(III) using the mixtures of Cyanex272 and P507 as an extractant are higher than those obtained using P507. It is also clear that the extraction of heavy Ln(III) with the mixtures can be considered to more effectively separate Tm^{3+}, Lu^{3+}, and Yb^{3+}, but less effectively separate Ho^{3+}, Er^{3+}, and Tm^{3+} than Cyanex272. On the other hand, the extraction ability of rare earth ions with the mixtures (shown in Table 1) is higher than that of the sum of Cyanex272 and P507 alone. The results indicate that the mixture has better separation ability for heavy lanthanide as well as higher extraction efficiency.

In addition, conforming to the order of Cyanex272 and P507 alone, Y^{3+} is located between Ho^{3+} and Er^{3+}, and the extraction ability of rare earth elements by the mixtures increases with decreasing ionic radii of the lanthanide ions (shown in Fig. 6), which can be explained by HSAB theory (24). Rare earth ions are hard acids while the mixtures is a hard base. The smaller is the ionic radius, the harder is the rare earth ion, which results in the increasing extraction ability with decreasing ionic radii of the lanthanide ions.

CONCLUSIONS

Mixtures of Cyanex272 and P507 show evident synergistic effects when used to extract Yb^{3+} from chloride solutions at comparatively lower concentration of Cyanex272, and the maximal synergistic enhancement could be obtained at a ratio of P507 to Cyanex 272 of 1 to 1. That is, the mixture has a higher extraction efficiency than those of both P507 and Cyanex272. The stoichiometry of the extracted complexes has been determined to be $YbA_3(HA)_3$ with Cyanex272, $YbL_3(HL)_3$ with P507, and $YbA_2L_4H_3$ with synergistic mixture. The equilibrium constants and formation constants have been calculated, which shows that the extracted complexes $YbA_3(HA)_3$ are more prone to form the final synergistic complex $YbA_2L_4H_3$. The thermodynamic parameters of the synergistic extraction process are also determined, and the extraction is an exothermic process. The extraction mixed solution

of heavy Ln(III) with mixtures of P507 and Cyanex272 is investigated, which indicates that the mixture has better separation abilities for heavy lanthanide.

ACKNOWLEDGMENTS

The authors wish to thank Shanghai Organic Chemistry Institute and CYTEC Canada Inc. for supplying the P507 and Cyanex272. This project is supported by the National Program entitled Basic Research of Rare Earths (G1998061301), National "863" project (2002AA647070) and National Natural Science Foundation of China (20371046).

REFERENCES

1. Turanov, A.N., Karandashev, V.K., Khaaritonov, A.V., Yarkevich, A.N., and Safronova, Z.V. (2000) Extraction of scandium, rare-earth elements and yttrium from nitric acid solutions by selected diphosphine dioxides. *Solvent Extr. Ion Exch.*, 18 (6): 1109–1134.
2. Bourdet, G.L. and Casagrande, O. (2005) Theoretical comparison of ytterbium doped sesquioxydes under pulsed diode pumping. *Optics Communication*, 244 (1): 327–332.
3. Wang, Z.H., Meng, S.L., and Li, D.Q. (1995) Extraction separation of rare earth elements(III) with bis(2,4,4-trimethylpentyl)phosphinic acid. *Chin. J. Anal. Chem.*, 23 (4): 391–394.
4. Zhang, X.F. and Li, D.Q. (1993) Extraction of rare-earth ions(III) with bis(2,4,4-trimethylpentyl)phosphinic acid. *Chin. J. Appl. Chem.*, 10 (4): 72–74.
5. Tachimori, S. and Nakamura, H. (1978) Application of synergistic MEHPA-DEHPA mixed solvent to the extraction of lanthanides(III). *J. Radioanal. Nucl. Chem.*, 44 (1): 37–47.
6. Reddy, B.V., Reddy, L.K., Reddy, A.S., Reddy, M.L.P., Sujatha, S., Ramamohan, T.R., and Damodaran, A.D. (1994) Synergistic solvent extraction of Eu(III) and Tb(II) with mixtures of various organophosphorus extractants. *J. Radioanal. Nucl. Chem.*, 178 (1): 109–120.
7. Santhi, P.B., Reddy, M.L.P., Ramamohan, T.R., and Damodaran, A.D. (1991) Liquid-liquid extraction of yttrium (III) with mixtures of organophosphorus extractants: theoretical analysis of extraction behaviour. *Hydrometallurgy*, 27: 169–177.
8. Komatsu, Y. and Freiser, H. (1989) Extraction separation of trivalent lanthanide metals with bis(2,4,4-trimethylpentyl)phosphinic acid. *Anal. Chim. Acta*, 227: 397–404.
9. Saleh, M.I., Bari, M.F., Sadd, B., Saleh, M.I., Bari, M.F., and Saad, B. (2002) Solvent extraction of lanthanum(III) from acidic nitrate-acetato medium by cyanex 272 in toluene. *Hydrometallurgy*, 63: 75–84.
10. Jing, S. and Li, D.Q. (1994) Study of synergistic extraction of rare earth element(III) with BTMPPA and HPMBP. *Chinese Journal of Applied Chemistry*, 11 (3): 49–53.
11. Wang, Y.G., Wang, L.G., and Li, D.Q. (2003) Synergistic extraction of zinc(II) with mixtures of CA-100 and cyanex272. *Separation Science and Technology*, 38 (10): 2291–2306.

12. Reddy, M.L.P., Bharathi, J.R.B., and Peter, S. (1999) Synergistic extraction of rare earths with bis(2,4,4-trimethylpentyl) dithiophosphinic acid and trialkyl phosphine oxide. *Talanta*, 50 (1): 79–85.
13. Jia, Q., Zhan, C.H., Li, D.Q., and Niu, C.J. (2004) Extraction of zinc(II) and cadmium(II) by using mixtures of primary amine N1923 and organophosphorus acids. *Separation Science and Technology*, 39 (5): 1111–1123.
14. Yuan, C.Y., Ma, H.L., Pan, C., and Rickelton, W.A. (1996) Proceedings of the International Solvent Extraction Conference (ISEC'1996), *Synergistic Extraction of Rare Earths Based on Cyanex272*; Shallcross, D.C., Paimin, R. and Prvcic, L.M., eds.; Australia; Vol. 1, 733–738.
15. Li, K. and Freiser, H. (1986) Extraction of lanthanide metals with bis(2,4,4-trimethylpentyl)phosphinic acid. *Solvent Extr. Ion Exch.*, 4 (4): 739–755.
16. Reddy, M.L.P., Ramamohan, T.R., and Iyer, C.S.P. (1998) Enhanced extraction and separation of trivalent lanthanides and yttrium with bis(2,4,4-trimethylpentyl) phosphinic acid and trialkyl phosphine oxide. *Solvent Extr. Res. Dev.*, 5: 1–15.
17. Wang, Z.H., Ma, G.X., and Li, D.Q. (1998) Extraction and separation of heavy rare earth(III) with extraction resin containing di(2,4,4-trimethylpentyl) phosphinic acid (cyanex272). *Solvent Extr. Ion Exch.*, 16 (3): 813–828.
18. Ma, E.X., Yan, X.M., Wang, S.Y., Long, H.Y., and Yuan, C.Y. (1981) Extraction of lanthanide by 2-ethylhexyl phosphinic acid mono-2-ethylhexl ester. *Science in China Series B: Chemistry*, 5: 565–573.
19. Binghua, Y. and Nagaosa, Y. (1996) Solvent extraction of metal ions and separation of nickel(III) from other metal ions by organophosphorus acid. *Solvent Extr. Ion Exch.*, 14 (5): 849–870.
20. Sheng, J.L., Xi, Z.K., Gao, Z.L., Sun, S.X., Song, Q.S., and Guo, L.X. (1984) Studies on the interfacial properties of liquid-liquid extraction II. Interfacial properties of HEH(EHP) in water-diluent system. *Chin. J. Appl. Chem.*, 1 (4): 57–62.
21. Stability constant of metal ion complexes. The chemical society: London, 1971, 137–140, Supplement No. 1.
22. Xu, G.X., Wang, W.Q., and Wu, J. (1963) Extraction chemistry of the nuclear fuel(I):Synergistic extraction with chelating and complexing extractants. *Atomic Energy Science and Technology*, 7: 487–508.
23. Out, E.O. (1999) The thermodynamics of synergistic extraction of bismuth by 2-ethylhexyl phenylphosphonic acid and micelles of dinonyl naphthalene sulfonic acid. *Thermochim. Acta*, 329: 117–121.
24. Pearson, R.G. (1963) Hard and soft acids and bases. *J. Am. Chem. Soc.*, 85: 3533–3539.
25. Li, D.Q. and Ni, J.Z. (2001) Separation of Rare Earth. In *Handbook of Solution Extraction*; Wang, J.D. and Chen, J.Y., eds.; Chemical Industry Press: Beijing, 546–556.
26. Balint, B.J. (1991) *Proceeding of the 2nd International Conference on Rare Earth Development and Application*; Xu, G.X. et al, eds.; International Academic Publishers: Beijing, 386–387.