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Extraction and Separation of Rare Earth Elements from Nitrate Medium with Mixtures of *sec*-Octylphenoxyacetic Acid and 2,2′-Bipyridyl[†]

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The extraction of rare earth elements (REEs) was investigated with mixtures of *sec*-octylphenoxyacetic acid (CA12, H_2A_2) and 2,2′-bipyridyl (bipy, B) from nitrate medium. The mixing system had synergistic effects on all of the studied REEs and might be employed to the separation of REEs at proper extractant ratios. Methods of slope analysis and constant mole were used to determine the extracted compounds for La and Y as $La(NO_3)_2H_3A_4B$ and $Y(NO_3)_2H_2A_3B$, respectively. Thermodynamic parameters ΔH, ΔG, and ΔS were also calculated, indicating that both the extraction processes of La and Y were endothermic reactions.

Introduction

Rare earth elements (REEs) received increasing attention in high-technology fields ranging from superconductors, supermagnets, cathode-ray tubes, and catalysts to fertilizers in agriculture. Several methods were applied to the determination of REEs, among which spectrophotometry, inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) were proved to be appropriate techniques. However, it is quite difficult or even impossible to determine REEs at extremely low concentration levels. Therefore, various separation and preconcentration methods were developed such as solvent extraction,[1] coprecipitation,[2] adsorption,[3] and so forth. As a traditional method, solvent extraction was widely used in the separation of REEs, among which synergistic extraction, the extraction with a combination of extractants, attracted much attention to enhance extractability and selectivity.[4]

sec-Octylphenoxyacetic acid (CA12) with a chemical formula of $s\text{-}C_8H_{17}C_6H_4OCH_2{-}COOH$ 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 aqueous phase, easy preparation, and low emulsification potential during extraction. The extraction of REEs with CA12 was studied by some authors.[5−13] For instance, when Sm(III) was extracted with CA12 (H_2A_2) from chloride medium, a complex was formed with the structure of $SmA_3\cdot HA$.[7] Recently, several synergistic extraction systems of REEs with two extractants containing CA12 or *sec*-nonylphenoxy acetic acid (CA100) were studied in our laboratory.[5−8,14,15] In acidic nitric solutions, the extraction with REEs with mixtures of CA12 and 1,10-phenthroline (phen),[5] CA12 and di-(2-ethylhexyl)phosphoric acid (D2EHPA),[6] and CA100 and phen[14] were investigated. When phen was added into the CA12 extraction system as a synergist, not only the extractability but also the separation ability could be improved significantly.[5]

2,2′-Bipyridyl (bipy) has a similar structure with phen, which might be expected to improve the extractability and separation ability when used as an adductant in the solvent extraction system. So far, only a few papers were reported about the extraction of REEs with mixing systems containing bipy.[16−21] For instance, Inoue et al.[16] investigated the extraction equilibrium behavior of a series of trivalent lanthanide ions, La, Pr, Eu, Ho, and Yb, from tartrate aqueous solutions using a chloroform solution containing *N*-*p*-methoxybenzoyl-*N*-phenylhydroxylamine combined with an adductant, phen or bipy. The stoichiometry, the extraction constants, and the separation factors of the systems were determined. Therefore, as a continuation of our work about the extraction of REEs, it is of interest to investigate the extraction behavior of REEs with other extracting agents containing bipy. The present work was directed to the synergistic solvent extraction of REEs with CA12 and bipy. The synergistic effect, the extraction mechanism of La and Y, and the thermodynamic parameters in the synergistic extraction were mainly investigated.

Experimental Section

Reagents and Apparatus. CA12 and bipy were supplied by Shanghai Rare-earth Chemical Co., Ltd. and Sinopharm Chemical Reagent Shanghai Co., Ltd., respectively. Both of the extractants were used without further purification and dissolved in *n*-heptane to the required concentrations.

High-purity rare earth oxides with mass fractions greater than 0.9995 were obtained from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China). Stock solutions of REEs were prepared from their oxides by dissolution in concentrated nitric acid and diluting with distilled water. All of the initial REEs concentrations were maintained at $0.005\ mol\cdot L^{-1}$. The pH of the aqueous phase was adjusted by the addition of HNO_3 or NaOH solutions. All extraction experiments were performed at a constant ionic strength with $NaNO_3$ ($\mu = 0.6\ mol\cdot L^{-1}$). All other reagents were of analytical reagent grade.

The concentrations of REEs were determined by spectrophotometry using a Cintra 10e spectrophotometer (GBC Scientific Equipments, Australia). A pHs-3C digital pH meter was employed for pH measurements (Shanghai Rex Instruments Factory, China).

Extraction Procedures. Equal volumes (5 mL) of aqueous and organic phases were mixed and shaken in equilibrium tubes using a mechanical shaker for 30 min at 298 ± 1 K unless otherwise stated, which was sufficient for equilibrium attain-

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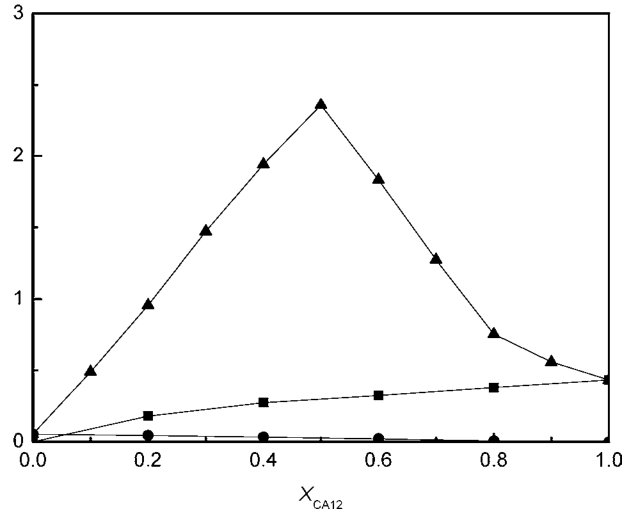

Figure 1. Synergistic extraction of La^{3+} with CA12, bipy, and CA12 + bipy. $[La^{3+}] = 5 \cdot 10^{-3}$ mol·L^{-1}, $\mu = 0.6$ mol·L^{-1}, pH = 3.0, $C_{CA12} + C_{bipy} = 0.05$ mol·L^{-1}; -■-, CA12; -●-, bipy; -▲-, CA12 + bipy.

Table 1. Synergistic Coefficients of REEs

X_{CA12}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
R (La)	5.3	7.4	8.8	9.5	9.7	6.5	4.0	2.1	1.4
R (Nd)	4.8	7.7	10.6	11.2	9.8	7.3	4.1	1.8	1.2
R (Eu)	6.8	12.1	15.3	15.7	12.5	8.2	5.3	2.6	1.3
R (Gd)	9.0	16.1	20.7	20.0	15.6	10.4	6.7	3.2	1.4
R (Er)	9.2	17.0	19.8	20.8	17.0	10.8	6.9	3.4	1.5
R (Y)	6.7	9.6	11.1	11.3	8.9	6.7	4.7	2.8	1.1

ment. After phase separation, the concentrations of REEs in the aqueous phase were determined by spectrophotometry at 654 nm with Arsenazo(III) as an indicator. The concentrations in the organic phases were determined by difference. Distribution ratios (*D*) were calculated from these concentrations.

Results and Discussion

Extraction of RE^{3+} with Mixtures of CA12 and bipy. The extraction of REEs, La, Nd, Eu, Gd, Er, and Y, with CA12, bipy, and their mixtures were investigated. As a representative, the distribution ratios of La were shown in Figure 1. When the total concentration of CA12 and bipy was fixed at 0.05 mol·L^{-1}, the distribution ratios of REEs in the mixing system changed with changing mole fractions of CA12 (X_{CA12}). The synergistic enhancement factor, *R*, could be obtained according to the synergistic extraction theory:[22]

$$R = \frac{D_{mix}}{D_{CA12} + D_{bipy}} \qquad (1)$$

where D_{mix}, D_{CA12}, and D_{bipy} represented the distribution ratios when REEs were extracted with CA12 + bipy, CA12, and bipy, respectively. $R > 1$ meant synergistic extraction, whereas $R < 1$ meant antagonistic extraction. Table 1 showed the *R* values at various X_{CA12} for the REEs. It could be concluded that the mixtures had synergistic effects on all of the REEs.

On the basis of the different synergistic effects on different REEs, mixtures of CA12 and bipy could be considered to separate REEs. Table 2 showed the separation factors of lanthanoids to Y ($\beta_{Ln/Y}$), indicating that the mixtures of CA12 and bipy could be used for the separation of Y from Ln at appropriate ratios of the extractants. Compared with the single CA12 extractant, mixtures of CA12 and bipy had better separation factors when used for the separation of Y from middle and heavy lanthanoids.

Table 2. Separation Factors of REEs ($\beta_{Ln/Y}$) in CA12 and CA12 + bipy, $C_{CA12} = C_{bipy} = 0.05$ mol·L^{-1}

extractant	La/Y	Nd/Y	Eu/Y	Gd/Y	Er/Y
CA12	2.9	2.2	1.9	1.4	1.0
CA12 + bipy	2.6	2.0	2.4	2.4	1.9

Table 3. Analytical Data of $[La^{3+}]_{(a)}$, $[H_2A_2]_{(o)}$, and K_A (pH = 3.0, μ = 0.6 mol·L^{-1})

no.	$[La^{3+}]_{(a)}$ / mol·L^{-1}	$\log[H_2A_2]_{(o)}$ / mol·L^{-1}	D_A	log K_A	average log K_A
1	0.0043	−2.10	0.23	−4.15	−4.19 ± 0.04
2	0.0042	−1.75	0.27	−4.23	
3	0.0040	−1.56	0.33	−4.20	
4	0.0038	−1.43	0.38	−4.16	
5	0.0037	−1.33	0.43	−4.18	

Extraction Stoichiometries of RE^{3+} with CA12 and CA12 + bipy. La^{3+} and Y^{3+} were selected as representatives to study the extraction stoichiometries. The extraction of RE^{3+} with CA12 from nitrate medium was studied in our previous work with the following equation:[6]

$$RE_{(a)}^{\;\;3+} + 2H_2A_{2(o)} \overset{K_A}{\rightleftharpoons} REA_3 \cdot HA_{(o)} + 3H_{(a)}^{\;\;+} \qquad (2)$$

where "a" and "o" represented the aqueous and organic phases, respectively. The distribution ratio D_A, the equilibrium constant K_A, and their relationship could be obtained as:

$$D_A = \frac{[REA_3 \cdot HA]_{(o)}}{[RE^{3+}]_{(a)}} \qquad (3)$$

$$K_A = \frac{[REA_3 \cdot HA]_{(o)}[H^+]^3_{(a)}}{[RE^{3+}]_{(a)}[H_2A_2]^2_{(o)}} \qquad (4)$$

$$\log D_A - 3\text{pH} = 2 \log[H_2A_2]_{(o)} + \log K_A \qquad (5)$$

In the present work, the extraction of La^{3+} and Y^{3+} with single CA12 extractant was investigated to obtain the equilibrium constants. Table 3 listed the equilibrium data of La^{3+}, that is, $[La^{3+}]_{(a)}$, $[H_2A_2]_{(o)}$, and K_A. The equilibrium constant, log K_A could be calculated as −4.19 and −6.01 for La^{3+} and Y^{3+}, respectively.

When bipy was added into the CA12 extraction systems for La^{3+}, the following synergistic extraction reaction was expressed as:

$$La_{(a)}^{\;\;3+} + (3 - i)NO_{3(a)}^{\;\;-} + xH_2A_{2(o)} + yB_{(o)} \overset{K_{AB}}{\rightleftharpoons} La(NO_3)_{3-i}H_{2x-i}A_{2x}B_{y(o)} + iH_{(a)}^{\;\;+} \qquad (6)$$

The relationship between the distribution ratio D_{AB} and the equilibrium constant K_{AB} could be described by:

$$\log D_{AB} = x \log[H_2A_2]_{(o)} + y \log[B]_{(o)} + i\text{pH} + \log K_{AB} + (3 - i) \log[NO_3^{\;-}]_{(a)} \qquad (7)$$

A series of experiments were carried out to determine the extraction stoichiometries. First, the relationship between D_{AB} and pH was determined at fixed ionic strength and concentrations of REEs and extractants. Results were shown in Figure 2, indicating that log D_{AB} versus pH gave a straight line with a slope of around 1.0. Second, the influence of the concentration of one extractant was investigated at a fixed pH value, ionic strength, and concentration of the other extractant. The plots of log D_{AB} − pH versus $\log[CA12]_{(o)}$ or $\log[bipy]_{(o)}$ were shown

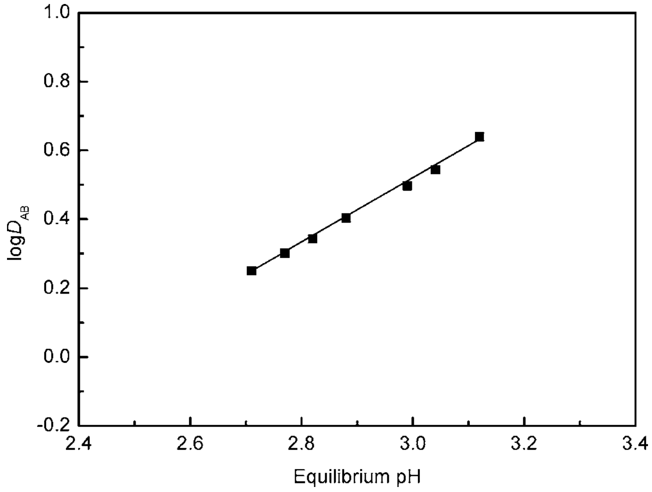

Figure 2. Relationship between distribution ratio D_{AB} and equilibrium pH. $[La^{3+}] = 5 \cdot 10^{-3}\ mol \cdot L^{-1}$, $\mu = 0.6\ mol \cdot L^{-1}$, $C_{CA12} = 0.025\ mol \cdot L^{-1}$, $C_{bipy} = 0.025\ mol \cdot L^{-1}$.

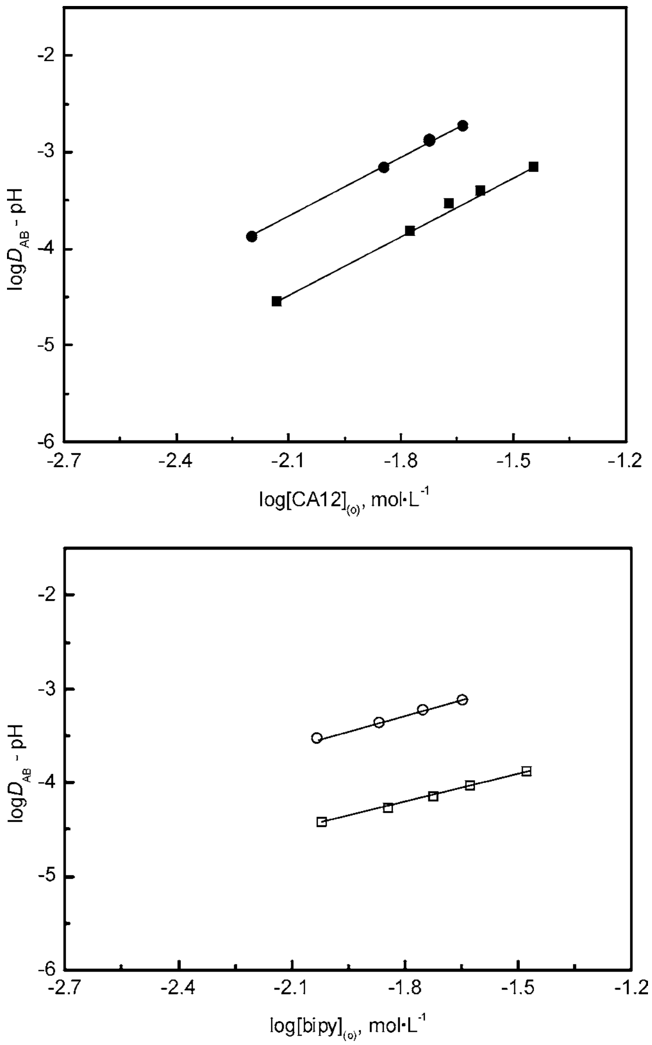

Figure 3. Relationship between distribution ratio D_{AB} and equilibrium concentration of CA12 and bipy in CA12 + bipy systems. $[La^{3+}] = 5 \cdot 10^{-3}\ mol \cdot L^{-1}$, pH = 3.0, $\mu = 0.6\ mol \cdot L^{-1}$; -■-, [bipy] = $0.01\ mol \cdot L^{-1}$; -●-, [bipy] = $0.02\ mol \cdot L^{-1}$; -□-, [CA12] = $0.01\ mol \cdot L^{-1}$; -○-, [CA12] = $0.02\ mol \cdot L^{-1}$.

in Figure 3, giving a straight line with slopes of about 2.0 and 1.0 for CA12 and bipy, respectively. Therefore, eq 6 could be rewritten as:

$$\mathrm{La_{(a)}}^{3+} + 2\mathrm{NO_{3(a)}}^{-} + 2\mathrm{H_2A_{2(o)}} + \mathrm{B_{(o)}} \overset{K_{AB}}{\rightleftharpoons} \mathrm{La(NO_3)_2H_3A_4B_{(o)}} + \mathrm{H_{(a)}}^{+} \tag{8}$$

Table 4. Thermodynamic Parameters of La^{3+} and Y^{3+} Extracted with CA12 + bipy Systems

	ΔH / $kJ \cdot mol^{-1}$	ΔG / $kJ \cdot mol^{-1}$	ΔS / $J \cdot mol^{-1} \cdot K^{-1}$
CA12 + bipy−La^{3+}	10.07	−10.22	68.05
CA12 + bipy−Y^{3+}	8.31	−6.28	48.93

Similarly, the following equation could be obtained for Y^{3+} when extracted with mixtures of CA12 and bipy:

$$\mathrm{Y_{(a)}}^{3+} + 2\mathrm{NO_{3(a)}}^{-} + \frac{3}{2}\mathrm{H_2A_{2(o)}} + \mathrm{B_{(o)}} \overset{K_{AB}}{\rightleftharpoons} \mathrm{Y(NO_3)_2H_2A_3B_{(o)}} + \mathrm{H_{(a)}}^{+} \tag{9}$$

The equilibrium constant, log K_{AB} could be obtained as the following:

$$\text{For La}^{3+}\text{: } \log K_{AB} = \log D_{AB} - 2\log[\mathrm{H_2A_2}]_{(o)} - \log[\mathrm{B}]_{(o)} - \mathrm{pH} - 2\log[\mathrm{NO_3}^{-}]_{(a)} \tag{10}$$

$$\text{For Y}^{3+}\text{: } \log K_{AB} = \log D_{AB} - \frac{3}{2}\log[\mathrm{H_2A_2}]_{(o)} - \log[\mathrm{B}]_{(o)} - \mathrm{pH} - 2\log[\mathrm{NO_3}^{-}]_{(a)} \tag{11}$$

$\log K_{AB}$ of La^{3+} and Y^{3+} could be calculated as 1.79 and 1.10, respectively.

Temperature Dependency of the Synergistic Extraction. The influence of temperature on the extraction of La^{3+} and Y^{3+} with mixtures of CA12 and bipy was studied within the temperature range of (293.15 to 333.15) K. The relationship between log D and $[T^{-1}/K^{-1}]$ was determined at fixed pH values and concentrations of CA12 and bipy. The distribution ratio of La^{3+} and Y^{3+} increased with increasing temperature. The change in enthalpy (ΔH) could be determined according to the equation:[10]

$$\frac{\Delta \log D}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \tag{12}$$

The change in Gibbs energy (ΔG) and the change in entropy (ΔS) of the system could be obtained as well:

$$\Delta G = -RT \ln K \tag{13}$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \tag{14}$$

ΔH, ΔG, and ΔS at 298.15 K were calculated and shown in Table 4. The values of ΔH in CA12 + bipy systems were positive, indicating that the extraction procedures of La^{3+} and Y^{3+} with the mixtures were endothermically driven. In addition, the signs of ΔS for La^{3+} and Y^{3+} were also positive. This indicated that the mixture system was more disordered, which was in accordance with the theory of increasing entropy from the view of statistics.

Conclusions

The extraction behavior of REEs (La, Nd, Eu, Gd, Er, and Y) from nitrate medium was investigated using CA12, bipy, and their mixtures. Mixtures of CA12 and bipy had higher extraction efficiency than CA12 or bipy alone. The stoichiometries of the extracted complexes for La and Y were determined by graphical and numerical methods. The equilibrium constants and thermodynamic parameters were investigated. The synergistic extraction of La and Y were both determined as endothermic processes. The various extraction effects on different REEs were considered to separate REEs, indicating the mixtures of CA12 and bipy might be of practical value for the separation of lanthanoids and yttrium.

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