

Synergistic extraction and separation study of rare earth elements from nitrate medium by mixtures of *sec*-nonylphenoxy acetic acid and 2,2'-bipyridyl

Shujuan Fan,^a Miaomiao Tian,^a Naizhong Song,^a Qiong Jia^{a*} and Wuping Liao^b

Abstract

BACKGROUND: Synergistic extraction has been proven to enhance extractability and selectivity. Numerous types of synergistic extraction systems have been applied to rare earth elements, among which *sec*-nonylphenoxyacetic acid (CA100) has proved to be an excellent synergistic extractant. In this study, the synergistic enhancement of the extraction of holmium(III) from nitrate medium by mixtures of CA100 (H₂A₂) with 2,2'-bipyridyl (bipy, B) in *n*-heptane has been investigated. The extraction of all other lanthanides (except polonium) and yttrium by the mixtures in *n*-heptane has also been studied.

RESULTS: Mixtures of CA100 and bipy have significant synergistic effects on all rare earth elements, for example holmium(III) is extracted as Ho(NO₃)₂HA₂B with the mixture instead of HoH₂A₅, which is extracted by CA100 alone. The thermodynamic functions, ΔH° , ΔG° , and ΔS° have been calculated as 2.96 kJ mol⁻¹, -6.23 kJ mol⁻¹, and 31.34 J mol⁻¹ K⁻¹, respectively.

CONCLUSION: Methods of slope analysis and constant molar ratio have been successfully applied to study the synergistic extraction stoichiometries of holmium(III) by mixtures of CA100 and bipy. Mixtures of these extractants have also shown various synergistic effects with other rare earth elements, making it possible to separate them. Thus CA100 + bipy may be used to separate yttrium from other lanthanides at appropriate ratios of the extractants.

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Keywords: synergistic extraction; *sec*-nonylphenoxyacetic acid; 2,2'-bipyridyl; rare earth elements

INTRODUCTION

Carboxylic acids have been applied to the extraction of rare earth elements (REEs), among which naphthenic acid is a well-known extractant for the separation of yttrium from REEs under some conditions because it is readily available and cheap. Naphthenic acid has some shortcomings, such as a complex composition, instability in process applications, and easy emulsification. *Sec*-nonylphenoxyacetic acid (CA100) is a carboxylic acid recently developed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The extraction of divalent transition metals and REEs with CA100 has been reported elsewhere.^{1–11} Compared with naphthenic acid, CA100 has several advantages including low solubility in the aqueous phase, stable composition, and little tendency to emulsify during extraction.

Synergistic extraction, that is extraction with two or more kinds of extractants, has been proven to enhance extractability and selectivity. Over recent decades, synergistic extraction systems have been applied many times to the separation of REEs. Various mixtures of two extractants have been investigated for the extraction of REEs, including carboxylic acids,^{1,5,7–18} acidic organophosphorous extractants,^{19–21} neutral organophosphorous extractants,^{22–24} crown ethers,^{25,26} and amines (ammonium salts).²⁷ Among these reagents, CA100 has been proved to be

an excellent synergistic extractant. For example, Wu *et al.*⁹ investigated the extraction of Ho, Y, and Er with mixtures of bis (2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) with various organic extractants including CA100, and the stoichiometry of the synergistic extraction of Y with this mixture has been studied. Compared with other mixed systems, the mixture of Cyanex 302 and CA100 has been proven to be an excellent separation system. Sun *et al.*¹¹ studied the synergistic extraction of REEs from hydrochloride medium using a mixture of CA100 and bis (2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272). The mixtures are considered of practical value in the extraction and separation of REEs and in previous work, the extraction and separation of REEs with CA100 and its mixtures with 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEHEHP)

* Correspondence to: Qiong Jia, College of Chemistry, Jilin University, Changchun 130022, P. R. China. E-mail: jiaqiong@jlu.edu.cn

^a College of Chemistry, Jilin University, Changchun 130022, P. R. China

^b State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) were investigated in detail^{8,13} and the equilibrium constants and thermodynamic functions obtained.

Much attention has been paid to the synergistic extraction of lanthanide and actinide elements with chelating reagents as extractants. The formation of mixed ligand chelates involving the chelating extractants and various adducts not only provide better extractability, but also improve separation. The extraction of REEs from acidic nitric solutions with binary mixtures of 1, 10-phenanthroline (phen) with *sec*-octylphenoxyacetic acid (CA12) and CA100 have been studied in the laboratory.^{7,16} 2,2'-bipyridyl (bipy) has a similar structure to phen, and has also proven to be an excellent synergistic. Recently, the synergistic extraction of REEs with mixtures of CA12 and bipy was investigated.¹⁸ When bipy is added to the CA12 extraction system the extractability and separation ability can be significantly improved. However, there are few other reports on the extraction of REEs with mixtures of bipy and other extractants.^{28–33}

In the present work, a novel synergistic extraction system using CA100 and bipy has been developed for the extraction of REEs from nitrate medium. The effects of aqueous acidity, ratio of the extractants, and experimental temperature are discussed. The selectivity of REEs has also been analyzed.

EXPERIMENTAL

Reagents and apparatus

CA100 and bipy were supplied by the Shanghai Rare-earth Chemical Co. Ltd and the Sinopharm Chemical Reagent Shanghai Co. Ltd, respectively. Both of the extractants were used without further purification and dissolved in *n*-heptane at the required concentration.

High purity REE oxides (>99.95%) were purchased from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China) and stock solutions prepared from these oxides by dissolution in concentrated nitric acid and diluting with distilled water. The REEs were analyzed by titration with a standard solution of EDTA at pH 5.5 using xylenol orange as an indicator. All the initial REE concentrations were maintained at $5.0 \times 10^{-3} \text{ mol L}^{-1}$ and the pH of the aqueous phase was adjusted by the addition of HNO₃ or NaOH solutions. All extraction experiments were performed at constant ionic strength with NaNO₃ ($\mu = 0.6 \text{ mol L}^{-1}$). All other reagents were of analytical reagent grade.

A pH-3C digital pH meter was employed for pH measurements (Shanghai Rex Instruments Factory, China). The concentrations of REEs were determined by spectrophotometry using a TU 1810 spectrophotometer (Beijing Purkinje General Instruments Co. Ltd, China).

Extraction procedures

Equal volumes (5 mL) of aqueous and organic solutions were mixed and shaken for 30 min at $293 \pm 1 \text{ K}$ unless otherwise stated. Preliminary experiments showed this was sufficient time to achieve equilibrium. The solutions were then allowed to settle by gravity and after separation of the phases, 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 phase were obtained by mass balance. All the experimental work was carried out in triplicate and the average result was presented. Distribution ratios (*D*) were calculated from these concentrations.

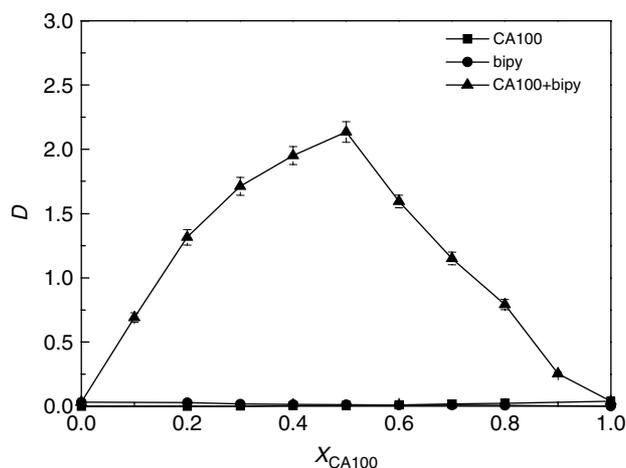


Figure 1. Extraction of Ho³⁺ by CA100, bipy, and CA100 + bipy: [Ho³⁺] = $5 \times 10^{-3} \text{ mol L}^{-1}$, pH = 3.0, $\mu = 0.6 \text{ mol L}^{-1}$, [CA100]_(o) + [bipy]_(o) = 0.05 mol L^{-1} .

Stripping test

The loaded organic phase was equilibrated with nitric acid of different concentrations. The mixtures were shaken at $293 \pm 1 \text{ K}$ for 30 min. The aqueous solution was separated from the organic phase and the REE concentrations were quantified to evaluate the stripping ratio, $St = ([\text{REEs}]_{a,e} / [\text{REEs}]_{o,i}) \times 100\%$, where [REEs]_{a,e} and [REEs]_{o,i} represented the equilibrium concentration of REEs in stripping acid and the initial concentration of REEs in the organic phase, respectively.

RESULTS AND DISCUSSION

Extraction of Ho³⁺ by mixtures of CA100 and bipy

Figure 1 shows the distribution ratios of Ho³⁺ by CA100, bipy, and their mixtures, in which X_{CA100} denotes the mole fraction of CA100. When the total concentration of CA100 and bipy is fixed at 0.05 mol L^{-1} , the distribution ratios of Ho³⁺ in the mixed system change with changing mole fractions of CA100. The synergistic enhancement coefficient can be calculated as follows:

$$R = \frac{D_{\text{mix}}}{D_A + D_B} \quad (1)$$

where D_{mix} , D_A and D_B represent the distribution ratios of Ho³⁺ when extracted by CA100 + bipy, CA100, and bipy, respectively. The calculated values of *R* thus obtained are shown in Table 1 and when $R > 1$ synergistic extraction occurs whereas $R < 1$ indicates antagonism. It is evident that the mixtures of CA100 and bipy have synergistic effects on the extraction of Ho³⁺ (Fig. 1).

Extraction stoichiometries of Ho³⁺ with CA100 and CA100 + bipy

In previous work,⁷ the extraction of RE³⁺ by CA100 (H₂A₂) in benzene from nitrate medium has been established as:



where 'a' and 'o' represent the aqueous and organic phases, respectively.

Table 1. Synergistic coefficients of REEs in CA100 + bipy systems ($[CA100]_{(o)} + [bipy]_{(o)} = 0.05 \text{ mol L}^{-1}$)

X_{CA100}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
R (La)	5.5	8.8	11.9	15.6	15.9	11.5	6.9	3.4	1.5
R (Ce)	7.3	11.1	16.0	20.2	20.3	15.2	9.5	5.2	2.1
R (Pr)	7.5	13.6	19.9	22.8	22.9	13.5	7.4	2.9	1.0
R (Nd)	8.5	17.3	26.3	32.5	35.4	22.2	14.1	7.5	3.2
R (Sm)	12.0	25.1	36.4	47.4	47.6	29.4	17.5	8.3	3.5
R (Eu)	4.5	11.3	18.7	25.7	28.4	22.0	14.5	7.7	4.1
R (Gd)	12.2	26.7	36.7	38.0	38.1	29.7	18.5	10.5	4.2
R (Tb)	34.1	52.2	54.2	57.3	58.1	34.6	19.7	10.2	3.5
R (Dy)	44.1	69.3	68.4	66.2	66.4	43.2	23.1	12.5	4.6
R (Ho)	21.9	40.8	51.9	58.0	62.1	45.5	32.1	21.7	6.8
R (Er)	20.0	46.7	59.0	71.5	71.6	52.1	35.7	21.2	8.9
R (Tm)	15.5	26.1	47.8	60.9	66.4	49.2	34.4	18.7	6.7
R (Yb)	21.0	45.8	67.3	76.1	76.2	56.7	34.2	18.3	5.9
R (Lu)	8.4	17.3	35.9	47.3	53.8	48.0	36.6	27.2	13.6
R (Y)	4.4	7.2	9.9	12.4	15.6	10.0	6.4	3.6	2.4

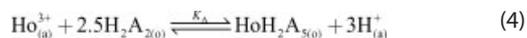
Table 2. Analytical data of Ho^{3+} concentrations, CA100 concentrations, and equilibrium constants ($pH = 3.0$, $\mu = 0.6 \text{ mol L}^{-1}$)

No.	$[Ho^{3+}]_{(a)}$, mol L^{-1}	$\log[H_2A_2]_{(o)}$, mol L^{-1}	$\log K_A$	Average $\log K_A$
1	4.51×10^{-3}	-2.00	-4.96	-4.90 ± 0.08
2	4.50×10^{-3}	-1.70	-4.98	
3	4.49×10^{-3}	-1.60	-4.92	
4	4.47×10^{-3}	-1.52	-4.91	
5	4.42×10^{-3}	-1.40	-4.84	
6	4.35×10^{-3}	-1.30	-4.82	

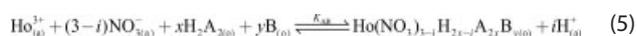
The extraction equation of RE^{3+} by CA100 in *n*-heptane from chloride medium has also been obtained as follows:⁵



In the present work, the extraction of Ho^{3+} by CA100 in *n*-heptane from nitrate medium has been studied by slope analysis and the method of constant molar ratio. The analytical data obtained is shown in Table 2. Thus the extraction stoichiometry of Ho^{3+} by CA100 can be expressed by:



When bipy (B) is added to the CA100 extraction systems for Ho^{3+} , the following synergistic extraction reaction is obtained:



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

$$\log D_{AB} = x \log[H_2A_2]_{(o)} + y \log[B]_{(o)} + ipH + \log K_{AB} + (3-i) \log[NO_3^-]_{(a)} \quad (6)$$

At fixed concentrations of CA100, bipy, and ionic strength, the effects of varying the pH on the extraction of Ho^{3+} gave a straight

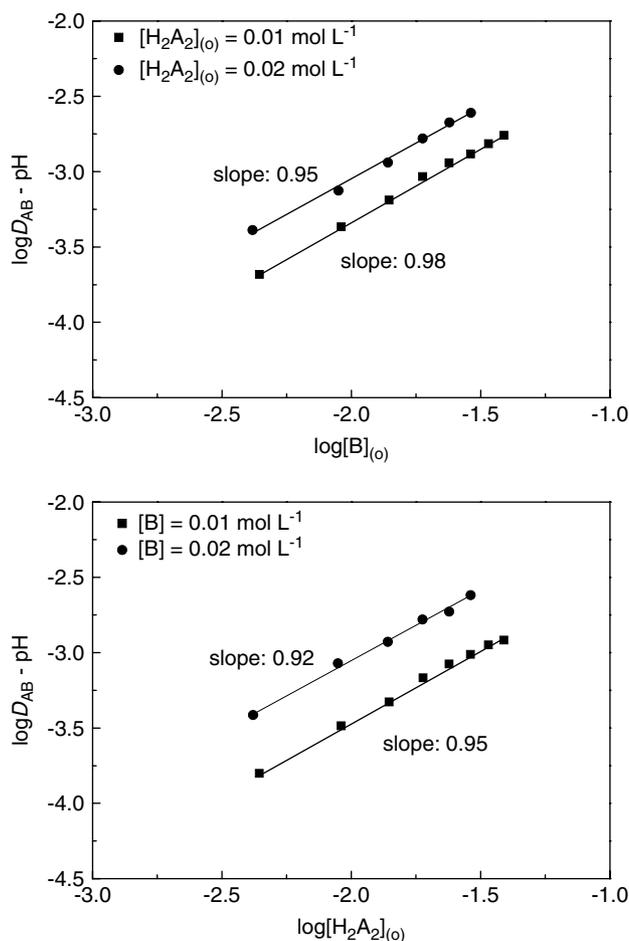


Figure 2. Relationship between distribution ratio and extractant concentration: $[Ho^{3+}] = 5 \times 10^{-3} \text{ mol L}^{-1}$, $pH = 3.0$, $\mu = 0.6 \text{ mol L}^{-1}$.

line with a slope of about 1.0. When the concentration of one extractant was varied and the pH and the concentration of the other extractant fixed, the relationship between $\log D_{AB} - pH$ and extractant concentrations can be obtained. As shown in Fig. 2, the straight lines of the plots of $\log D_{AB} - pH$ versus $\log[H_2A_2]_{(o)}$ and $\log[B]_{(o)}$ both have a slope value of about 1.0. Based on these results, Equation (5) can be rewritten as:



and the equilibrium constant ($\log K_{AB}$) of Ho^{3+} can be calculated as 1.11 ± 0.04 .

Influence of temperature on the extraction of Ho^{3+} by mixtures of CA100 and bipy

The effect of temperature on the extraction of Ho^{3+} by the mixtures of CA100 and bipy has been studied with the other parameters, aqueous acidity and concentrations of CA100 and bipy, fixed. The plots of $\log D$ versus $[1000/T \text{ (K)}]$ gave a straight line with a slope of -0.15 . The change of enthalpy (ΔH°), the change of Gibbs free energy (ΔG°), and the change of entropy (ΔS°) can thus be

Table 3. Separation factors of Ln to Y in CA100 and CA100 + bipy systems

Extractant	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/Y
CA100	3.6	2.7	2.5	2.2	2.0	1.8	1.4	1.0	0.9	0.6	0.5	0.4	0.4	0.3
CA100 + bipy	3.0	2.9	3.2	4.5	5.1	4.4	3.2	3.2	3.2	3.1	2.6	2.8	2.2	2.6

obtained from

$$\frac{\Delta \log D}{\frac{1}{\Delta T}} = \frac{-\Delta H^\circ}{2.303R} \quad (8)$$

$$\Delta G^\circ = -RT \ln K \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \Rightarrow \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (10)$$

where ΔG° and ΔS° are determined when T is 293 K.

The values of ΔH° , ΔG° , and ΔS° were respectively 2.96 kJ mol⁻¹, -6.23 kJ mol⁻¹, and 31.34 J mol⁻¹ K⁻¹. The sign of ΔH° in this system is positive, indicating that the synergistic procedure is endothermically driven; in addition, the sign of ΔS° is also positive, in accordance with increasing entropy from the statistical approach.

Separation factors for REEs with mixtures of CA100 and bipy

The extraction of REEs using mixtures of CA100 with bipy have been studied in detail. Table 1 shows the R values at various X_{CA100} for the REEs and it can be seen that the mixtures have synergistic effects on all the REEs. In previous work, similar synergistic effects were shown for the extraction of REEs with CA12 and bipy from nitrate medium.¹⁸ However, the synergistic coefficients of REEs in the CA100 + bipy system are much higher than those for the CA12 + bipy system. On replacing bipy by phen, synergistic effects were also found for REEs⁷ but again the synergism with CA100 + phen was not as strong as those in the current system. The reason why a mixture has significant synergistic or antagonistic effects on the extraction of metal ions is not clear. In the mixed system, in addition to the synergistic extraction reaction there are also the reactions between the metal ions and the single extractant so all three extraction processes exist simultaneously and determine the final overall extraction.

The difference in the synergism enhancement for different REEs can be considered as a way of separating them. If D_M and D_N represent the distribution ratios of M and N under the same extraction conditions, then the separation factor between M and N can be expressed as:

$$\beta_{M/N} = \frac{D_M}{D_N} \quad (11)$$

The separation factors of Ln³⁺ and Y³⁺ ($\beta_{Ln/Y}$) by CA100 and CA100 + bipy are shown in Table 3 and it can be seen that the selectivity between most lanthanoids and Y³⁺ with CA100 + bipy is higher than that with CA100 alone. Therefore, mixtures of CA100 and bipy may be used for the separation of Y³⁺ from Ln³⁺ at an appropriate ratio of the extractants.

Stripping properties

The loading capacities of REEs by CA100 + bipy have also been investigated. An organic phase composed of 0.025 mol L⁻¹

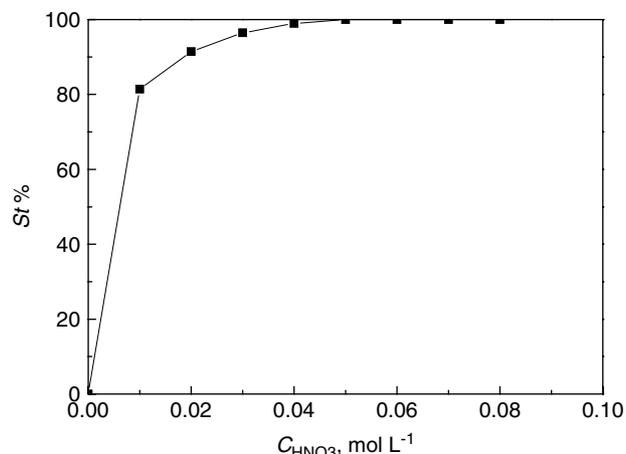


Figure 3. Relationship between stripping concentration of HNO₃ and stripping ratio: [CA100]_(o) = [bipy]_(o) = 0.025 mol L⁻¹, [Ho³⁺] = 5.0 × 10⁻³ mol L⁻¹.

CA100 + 0.025 mol L⁻¹ bipy loaded with 5.0 × 10⁻³ mol L⁻¹ Ho³⁺ has been back-extracted with HNO₃. The results shown in Fig. 3, indicate that the majority of REEs can be stripped in one single stage if the concentration of nitric acid is greater than 0.05 mol L⁻¹. Therefore, the low stripping acidity in the CA100 + bipy mixed system will have potential in practical applications.

CONCLUSIONS

The synergistic extraction of Ho³⁺ from nitrate medium with mixtures of CA100 and bipy has been investigated by graphical and numerical methods and the extracted complex shown to be Ho(NO₃)₂HA₂B. The equilibrium constant has been calculated and an extraction stoichiometry proposed. The synergistic extraction of Ho³⁺ is an endothermic reaction.

Mixtures of CA100 with bipy have also been applied to the extraction of other REEs from nitrate medium. The mixtures show different effects on the extraction of different REEs. Furthermore, the mixtures of CA100 with bipy have been proven according to their separation factors to have great potential for the separation of Y from other lanthanides.

ACKNOWLEDGEMENTS

The authors wish to thank Professor Zhenfeng Cui and Ms Chao Liu from Changchun Institute of Technology. This project was supported by a grant from Jilin Provincial Science and Technology Department (20090121).

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