

Extraction and separation of rare earths from chloride medium with mixtures of 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester and *sec*-nonylphenoxy acetic acid

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Abstract

BACKGROUND: 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEHEHP, H₂A₂) has been applied extensively to the extraction of rare earths. However, there are some limitations to its further utilization and the synergistic extraction of rare earths with mixtures of HEHEHP and another extractant has attracted much attention. Organic carboxylic acids are also a type of extractant employed for the extraction of rare earths, e.g. naphthenic acid has been widely used to separate yttrium from rare earths. Compared with naphthenic acid, *sec*-nonylphenoxy acetic acid (CA100, H₂B₂) has many advantages such as stable composition, low solubility, and strong acidity in the aqueous phase. In the present study, the extraction of rare earths with mixtures of HEHEHP and CA100 has been investigated. The separation of the rare earth elements is also studied.

RESULTS: The synergistic enhancement coefficient decreases with increasing atomic number of the lanthanoid. A significant synergistic effect is found for the extraction of La³⁺ as the complex LaH₂ClA₂B₂ with mixtures of HEHEHP and CA100. The equilibrium constant and thermodynamic functions obtained from the experimental results are 10^{-0.92} (K_{AB}), 13.23 kJ mol⁻¹ (ΔH), 5.25 kJ mol⁻¹ (ΔG), and 26.75 J mol⁻¹ K⁻¹ (ΔS), respectively.

CONCLUSION: Graphical and numerical methods have been successfully employed to determine the stoichiometries for the extraction of La³⁺ with mixtures of HEHEHP and CA100. The mixtures have different extraction effects on different rare earths, which provides the possibility for the separation of yttrium from heavy rare earths at an appropriate ratio of HEHEHP and CA100.

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Keywords: extraction; rare earths; 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester; *sec*-nonylphenoxy acetic acid

INTRODUCTION

2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEHEHP) is an organophosphorus acid that has been employed in the extraction of rare earths. Compared with di-2-ethylhexylphosphoric acid (D2EHPA), a widely used extractant in the rare earths industries, HEHEHP has higher separation factors for rare earths, and a lower aqueous acidity requirement for stripping. However, the viscosity of the organic phase increases and the extraction efficiency decreases in HEHEHP extraction systems. In addition, the lower selectivity for some adjacent lanthanide pairs (Nd/Pr, Gd/Eu, Er/Y, Lu/Yb) has limited its further utilization.

The synergistic effect is an important phenomenon in solvent extraction and has been studied extensively. Many mixing systems involving HEHEHP have been reported.¹⁻⁹ For example, Huang *et al.*¹ have investigated the synergistic extraction of Nd and Sm from a sulfuric acid medium with mixtures of HEHEHP and D2EHPA. The chemical compositions of the extracted complex and the equilibrium constants were determined. Wu *et al.*⁹ employed

mixtures of HEHEHP and 8-hydroxyquinoline for the synergistic extraction of Pr and Nd, and separations of Pr, Nd and La with the mixtures have also been studied.

Sec-nonylphenoxy acetic acid (CA100) is a novel organic carboxylic acid extractant developed by Shanghai Institute of

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Organic Chemistry, Chinese Academy of Sciences. The extractant has several advantages including low solubility and stronger acidity in the aqueous phase.^{10–16} Wang *et al.*¹³ reported that the extraction sequence of rare earths with CA100 is Sc > light (middle) lanthanoids > heavy lanthanoids > Y. However, it is difficult to use CA100 for the separation of Y from heavy rare earths. Sun *et al.*¹⁵ applied the mixture of CA100 and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272) for the extraction of Sc, Y, La, Gd and Yb. The extracted complex of Y with this mixture was determined together with equilibrium constants, formation constants and thermodynamic functions. Dependent on the separation factors, mixtures of these extractants may be of practical value in the separation of rare earths. However, there are few other reports about the extraction of rare earths with mixtures of CA100 and another extractant.

In the present study, the extraction of rare earths with mixtures of HEHEHP and CA100 was investigated. The various extraction effects on different rare earths were reported and considered for the separation of rare earths. In addition, the synergistic extraction of La with the mixture has been studied in detail. The extracted complex, equilibrium constant and thermodynamic parameters have also been determined.

EXPERIMENTAL

Reagents and apparatus

HEHEHP and CA100 were supplied by Shanghai Rare-Earth Chemical Co., Ltd. (Shanghai, China). Both of the extractants were dissolved in *n*-heptane to the required concentration.

High purity rare earths oxides (>99.99%) were purchased from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China). Stock solutions of the rare earths were prepared from these oxides by dissolving in concentrated hydrochloric acid and diluting with distilled water. The rare earths were analyzed by titration with a standard solution of EDTA at pH 5.5 using xylenol orange as an indicator. All the initial metal concentrations were maintained at 5×10^{-3} mol L⁻¹ with 0.3 mol L⁻¹ NaCl used in all extraction experiments to keep the ionic strength constant ($\mu = 0.3$ mol L⁻¹). All other reagents were of analytical reagent grade.

A PHS-3C digital pH meter (Shanghai Rex Instruments Factory) was used for pH measurements. The concentrations of rare earths were determined by spectrophotometry using a Cintra 10e spectrophotometer (GBC Scientific Equipments, Australia). Deionized water was prepared by the Milli-Q SP system (Millipore, Milford, MA, USA).

Extraction procedures

Equal volumes (5 mL) of aqueous and organic solutions were mixed and shaken for 30 min at 293 ± 1 K (unless otherwise stated), which was determined in preliminary experiments to be sufficient to attain equilibrium. The solutions were then allowed to settle and were separated by gravity. After separating the phases, the concentrations of rare earths in the aqueous phase were determined by spectrophotometry at 654 nm with Arsenazo (III) as an indicator. All the concentrations in the aqueous phase were obtained from three replicate measurements. The concentrations in the organic phase were determined by difference. Distribution ratios (*D*) were calculated from these concentrations.

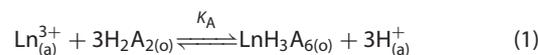
Table 1. Data of concentrations of La³⁺, H₂A₂ and equilibrium constants (pH = 3.0, $\mu = 0.3$ mol L⁻¹)

No.	[La ³⁺] _(a) , (mol L ⁻¹)	log[H ₂ A ₂] _(o)	logK _A	Average logK _A
1	5.0×10^{-3}	-2.02	-3.21	-3.18 ± 0.10
2	4.8×10^{-3}	-1.72	-3.05	
3	4.7×10^{-3}	-1.55	-3.20	
4	4.4×10^{-3}	-1.42	-3.15	
5	4.3×10^{-3}	-1.32	-3.28	

RESULTS AND DISCUSSION

Extraction of rare earths with HEHEHP or CA100 alone

The extraction of rare earths from chloride medium with HEHEHP has been reported,^{17–20} and indicated that extractability increases with increasing atomic number. In the present study, the extraction of 5.0×10^{-3} mol L⁻¹ rare earths ($\mu = 0.3$ mol L⁻¹) has been conducted. The order of the extractability is in accordance with that reported. In general, the extraction of rare earths with HEHEHP (H₂A₂) follows the equation:



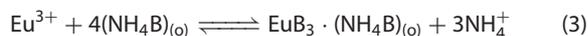
where 'a' and 'o' denote aqueous and organic phase, respectively.

The relationship between the distribution *D_A* and the equilibrium constant *K_A* can be expressed as:

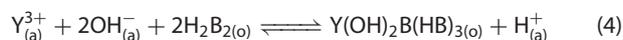
$$\log D_A - 3\text{pH} = 3\log[\text{H}_2\text{A}_2]_{(o)} + \log K_A \quad (2)$$

As a representative example, the analytical data for the extraction of La³⁺ with HEHEHP from 0.3 mol L⁻¹ NaCl solutions are shown in Table 1.

The extraction of rare earths with CA100 has also been reported.^{10–16} Wang *et al.*¹⁴ investigated the extraction of Eu³⁺ from chloride medium with CA100 (H₂B₂) saponified with aqueous ammonia:



The extraction of Y³⁺ with unsaponified CA100 has also been studied, with the following reaction:¹⁵



Apart from these examples, there are no reports of the extraction stoichiometry of rare earths with CA100. In the present work, the extraction of La³⁺ with CA100 was examined in detail. The effects of pH on the extraction were first determined at fixed La³⁺ concentration, ionic strength, and CA100 concentration. Similarly, the effects of [H₂B₂]_(o) on the extraction can also be determined

Table 2. Equilibrium constants and formation constants of La³⁺ extracted with HEHEHP and CA100

logK _A	logK _B	logK _{AB}	logβ ₁	logβ ₂	logβ ₃
-3.18 ± 0.10	-4.88 ± 0.07	-0.92 ± 0.04	2.26	3.96	6.22

Table 3. Separation factors of rare earths in HEHEHP and HEHEHP + CA100 systems

Extractant	Separation factors ($\beta_{Y/Ln}$)													
	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	21.65	9.56	6.90	3.04	2.95	2.62	2.46	1.45	1.23	1.07	0.83	0.64	0.48	0.31
HEHEHP+CA100	3.80	3.22	2.50	1.41	2.06	1.65	1.90	1.23	1.48	0.80	0.62	0.72	0.33	0.24

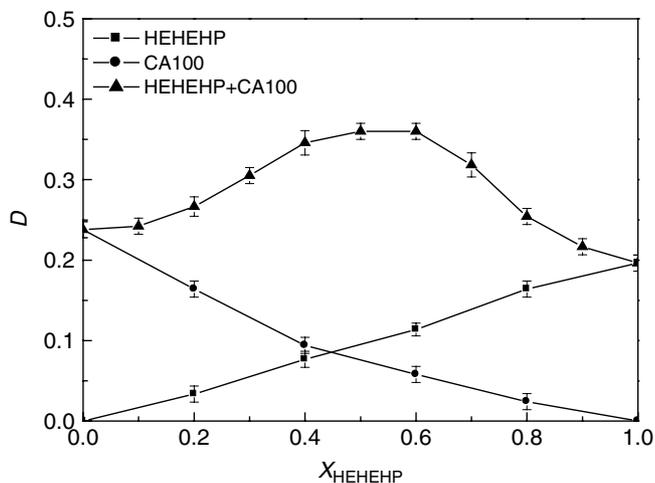


Figure 1. Synergistic extraction of La^{3+} with HEHEHP + CA100: $[\text{La}^{3+}] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$, $\text{pH} = 3.0$, $\mu = 0.3 \text{ mol L}^{-1}$, $[\text{HEHEHP}]_{(o)} + [\text{CA100}]_{(o)} = 0.05 \text{ mol L}^{-1}$.

when La^{3+} concentration, pH value, and ionic strength are fixed. Thus, the extraction reaction of La^{3+} with CA100 was shown to be:



The equilibrium constant, K_B , is calculated as shown in Table 2.

Extraction of rare earths with mixtures of HEHEHP and CA100

The extraction of 15 lanthanoids (except Pm) and Y was studied with mixtures of HEHEHP and CA100. The extraction effects decrease with increasing atomic number of the lanthanoids. The mixture has antagonistic effects on Y extraction similar to that for the heavy rare earths. Such results can be employed to consider the separation of rare earths. Table 3 shows the separation factor values between Y and lanthanoids. It is evident that the mixture is better than HEHEHP alone for the separation of Y and the heavy rare earths. However, there is no potential for the separation of Y from light and medium rare earths with mixtures of HEHEHP and CA100.

Since there are synergistic effects for the light rare earths, the extraction stoichiometry was studied in detail. The extraction of La^{3+} with mixtures of HEHEHP and CA100 is chosen as representative. In Fig. 1, significant synergistic effects on the extraction of La^{3+} with mixtures of HEHEHP and CA100 can be observed. The synergistic enhancement coefficient can be calculated as follows:²¹

$$R = \frac{D_{\text{mix}}}{D_A + D_B} \quad (6)$$

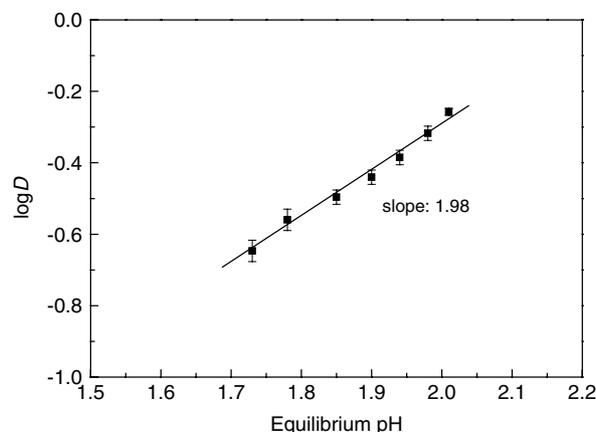
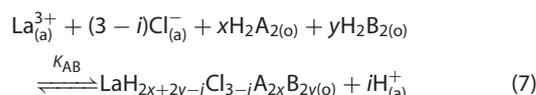


Figure 2. Effect of pH on the extraction of La^{3+} with HEHEHP + CA100: $[\text{La}^{3+}] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$, $\mu = 0.3 \text{ mol L}^{-1}$, $[\text{HEHEHP}]_{(o)} = 0.02 \text{ mol L}^{-1}$, $[\text{CA100}]_{(o)} = 0.03 \text{ mol L}^{-1}$.

where D_{mix} , D_A , and D_B denote the distribution ratios of La^{3+} when extracted with HEHEHP + CA100, HEHEHP, and CA100, respectively. R can thus be obtained as 1.69.

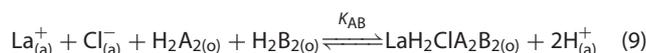
If the synergistic extraction of La^{3+} with mixtures of HEHEHP and CA100 is expressed as:^{22,23}



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

$$\log D_{AB} = x \log[\text{H}_2\text{A}_{2(o)}] + y \log[\text{H}_2\text{B}_{2(o)}] + \log K_{AB} + ipH + (3 - i) \log[\text{Cl}^-]_{(a)} \quad (8)$$

Similar to the method employed in the extraction of La^{3+} with CA100 alone, a series of experiments were carried out to investigate the extraction stoichiometry of La^{3+} with HEHEHP + CA100. At fixed concentrations of HEHEHP and CA100, plots of $\log D_{AB}$ versus pH were obtained (Fig. 2), giving a straight line with a slope of about 2. When the pH and the concentration of one extractant are fixed, the relationship between D_{AB} and the concentration of the other extractant can be obtained. Results are shown in Fig. 3, the slopes of the plots of $\log D_{AB} - 2\text{pH}$ versus $\log[\text{H}_2\text{A}_{2(o)}]$ and $\log[\text{H}_2\text{B}_{2(o)}]$ are both about 1. Therefore, Equation (7) can be deduced:



From which the equilibrium constant, K_{AB} , can be calculated (Table 2).

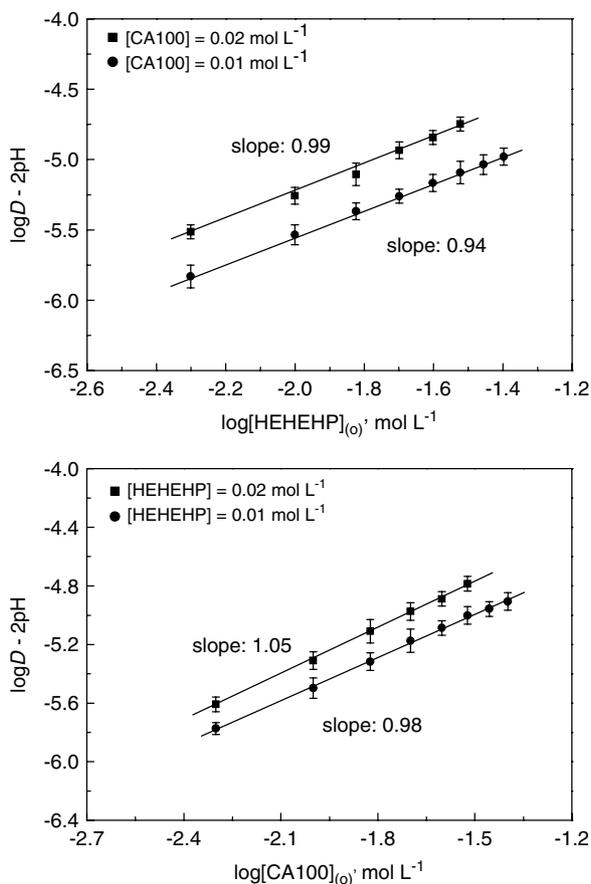
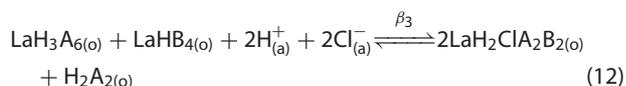
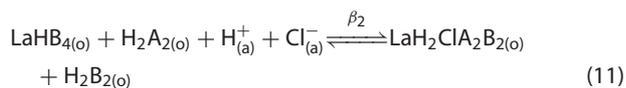
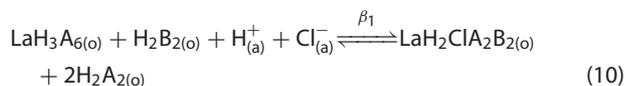


Figure 3. Effect of extractant concentration on the extraction of La^{3+} with HEHEHP and CA100: $[\text{La}^{3+}] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$, $\text{pH} = 3.0$, $\mu = 0.3 \text{ mol L}^{-1}$.

Based on Equations (1), (5) and (9), the formation reactions can be derived as follows:



where β_1 , β_2 and β_3 are the formation constants:

$$\log \beta_1 = \log K_{AB} - \log K_A \quad (13)$$

$$\log \beta_2 = \log K_{AB} - \log K_B \quad (14)$$

$$\log \beta_3 = 2 \log K_{AB} - \log K_A - \log K_B \quad (15)$$

The values of β_1 , β_2 and β_3 were obtained (Table 2), giving the order $\beta_1 < \beta_2 < \beta_3$. This implies that Equation (12) contributes most to the synergistic extraction. Thus the extracted complexes of La^{3+} with HEHEHP and CA100, i.e. LaH_3A_6 and LaHB_4 , are more prone to form the final synergistic complex, $\text{LaH}_2\text{ClA}_2\text{B}_2$.

The influence of temperature on the extraction of La^{3+} with HEHEHP + CA100 was also studied. The relationship between \log

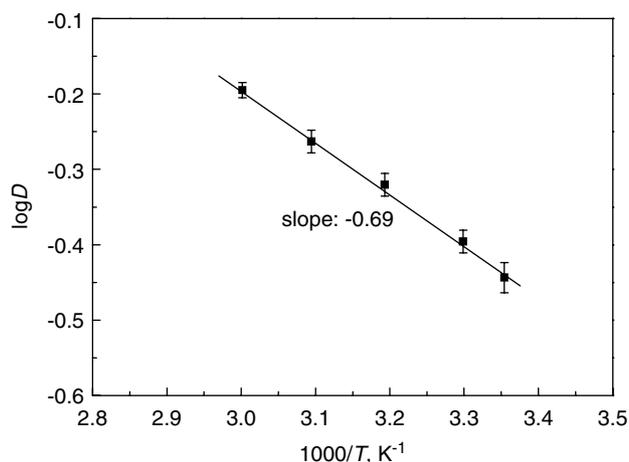


Figure 4. Relationship between distribution D and temperature: $[\text{La}^{3+}] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$, $\text{pH} = 3.0$, $\mu = 0.3 \text{ mol L}^{-1}$, $[\text{HEHEHP}]_{(o)} = 0.02 \text{ mol L}^{-1}$, $[\text{CA100}]_{(o)} = 0.03 \text{ mol L}^{-1}$.

D and $[1000/T (\text{K})]$ was determined at fixed pH values and fixed concentrations of HEHEHP and CA12 (Figure 4). The distribution ratio of La^{3+} increases with increasing temperature. The change of enthalpy (ΔH), the change of Gibbs free energy (ΔG), and the change of entropy (ΔS) can thus be obtained as follows:

$$\frac{\Delta \log D}{\Delta \frac{1}{T}} = \frac{-\Delta H}{2.303R} \quad (16)$$

$$\Delta G = -RT \ln K \quad (17)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (18)$$

where ΔG and ΔS are determined when T is 298.15 K.

The ΔH , ΔG , and ΔS values were calculated as $13.23 \text{ kJ mol}^{-1}$, 5.25 kJ mol^{-1} , and $26.75 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. It can be seen that the sign of ΔH is positive, indicating that La^{3+} extraction in the HEHEHP + CA100 system is endothermic.

CONCLUSIONS

The extraction of rare earths with mixtures of HEHEHP and CA100 was investigated in the present work. The extraction effects decrease with increasing rare earths atomic number, i.e. the mixture has synergistic effects on the light rare earths but antagonistic effects on the heavy rare earths. Weak antagonistic effects have also been found for Y extraction with the mixture. Thus the separation ability of Y and heavy rare earths is a little enhanced. The synergistic extraction of La^{3+} with the mixture was studied in detail and extraction reaction, equilibrium constants, formation constants and thermodynamic parameters were obtained. The synergistic extraction is shown to be endothermic.

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