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Solvent extraction of rare earths from chloride medium with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 and *sec*-octylphenoxyacetic acid

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ABSTRACT

In the present study, the extraction of rare earths with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP, HA) and *sec*-octylphenoxyacetic acid (CA12, H₂B₂) in benzene has been studied from chloride medium. The synergistic enhancement coefficient decreases with increasing atomic numbers of rare earths. The synergistic extraction of lanthanum and neodymium has been studied with the methods of slope analysis and constant mole. The extracted complexes are determined as LaH₂ClA₂B₂ and NdH₃ClA₃B₂, respectively. The equilibrium constants, formation constants, and the thermodynamic functions are calculated. Furthermore, the different extraction effects on rare earths have been employed to discuss the possibilities for the separation of rare earths.

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1. Introduction

The synergistic solvent extraction of rare earths has attracted much attention in the last decades. Synergistic extraction cannot only enhance the extraction efficiency but also improve the selectivity in some cases. Kinds of mixing systems containing two extractants have been investigated for the extraction of rare earths. As a common chelating agent, 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP) is proved to be an excellent synergistic extractant. The mixtures of HPMBP and other extractants such as organophosphorus acids [1–4], neutral organophosphorus extractants [5–8], amines [9], crown ethers [10,11], triazine [12], and calix[*n*]arenes [13] have been employed for the extraction and separation of rare earths. For example, Atanassova and Dukov [10] have studied the synergistic extraction of 14 lanthanoids with HPMBP and dibenzo-18-crown-6 or dibenzo-24-crown-8 in 1,2-dichloroethane. The extracted complexes, equilibrium constants, and separation factors have been determined. The addition of crown ethers to HPMBP system improves the extraction efficiency and the selectivity among the rare earths.

Carboxylic acids have found some applications in the hydrometallurgical processes although they are not as extensively used as organophosphorus extractants. Among carboxylic acids, naph-

thenic acid has been widely employed to separate yttrium from rare earths in China. Compared with naphthenic acid, *sec*-octylphenoxy acetic acid (CA12), an organic carboxylic acid developed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, has several advantages including stable composition, low solubility in the aqueous phase, and not easily emulsified during extraction. Recently, the extraction of rare earths with CA12 and its mixtures with acidic organophosphorus extractants has been reported [14–16]. Sun et al. [14] have studied the extraction of yttrium and heavy lanthanoids with mixtures of CA12 and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272). In our previous work, the extraction of rare earths with mixtures of CA12 and di-(2-ethylhexyl) phosphoric acid (D2EHPA) or bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex301) has been investigated [15,16]. The mixtures of CA12 and D2EHPA or Cyanex301 have higher selectivities for some rare earths than D2EHPA or Cyanex301 alone. However, except these three papers, no other reports have been found about the extraction of rare earths with mixtures of CA12 and acidic extractants. This promotes us to further investigate new mixing systems including CA12 for the extraction and separation of rare earths.

In the present paper, the solvent extraction of rare earths with mixtures of HPMBP and CA12 from chloride medium has been studied. The synergistic coefficient, the extraction mechanism and the thermodynamic functions are determined. Based on the various extraction effects on rare earths, the possibilities of separating them are discussed according to the separation factors.

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2. Experimental

2.1. Reagents and apparatus

HPMBP and CA12 were supplied by Beijing Donghuan chemical plant and Shanghai Rare-Earth Chemical Co., Ltd., respectively. Both of the extractants were dissolved in benzene to the required concentration.

High purity rare earth oxides (>99.95%) 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 rare earths concentrations were maintained at $5 \times 10^{-3} \text{ mol L}^{-1}$. 0.3 mol L^{-1} NaCl was used in all extraction experiments to keep constant ionic strength. All other reagents were of analytical reagent grade.

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

2.2. Extraction procedures

The extraction of rare earths was carried out as follows. Equal volumes (5 mL each) of aqueous and organic solutions were mixed and shaken for 30 min at $293 \pm 1 \text{ K}$ unless otherwise stated. 30 min was determined to be sufficient for equilibrium attainment in preliminary experiments. The solutions were then settled and separated by gravity. After the split of the phase, the concentrations of rare earths in the aqueous phase were determined by spectrophotometry at 654 nm with Arsenazo (III) as an indicator. The concentrations in the organic phase were determined by material balance. Distribution ratios (D) were calculated from these concentrations.

3. Results and discussion

3.1. Extraction of rare earths with mixtures of HPMBP and CA12

The mixtures of HPMBP and CA12 in benzene have been employed to extract 14 lanthanoids (except promethium) and yttrium from chloride medium. Under the experimental conditions, the synergistic effects decrease with increasing atomic numbers of lanthanoids, i.e., the mixtures have synergistic effects on light rare earths but antagonistic effects on heavy rare earths. Weak antagonistic extraction effects are found for yttrium. Similar orders have also been reported when rare earths are extracted with mixtures of HPMBP and an acidic organophosphorus extractant, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP), i.e., the synergistic effects decrease with increasing atomic numbers of rare earths. The reason is that extracted complexes with different structures are formed in the extraction processes [1].

So far, much work has been done to study the mechanism of synergistic extraction. However, there are few reports about the mechanism of antagonistic extraction. In Zhang's work [17], the noticeable antagonistic extraction mechanism of palladium (II) with 1-phenyl-3-methyl-4-propionylpyrazolone-5-one and tertiary amine has been studied according to the theory of the corresponding solutions.

In general, the synergistic enhancement coefficient, R , is used to evaluate whether a mixing system has synergistic extraction effect or not [18]:

$$R = \frac{D_{\text{mix}}}{D_{\text{HPMBP}} + D_{\text{CA12}}} \quad (1)$$

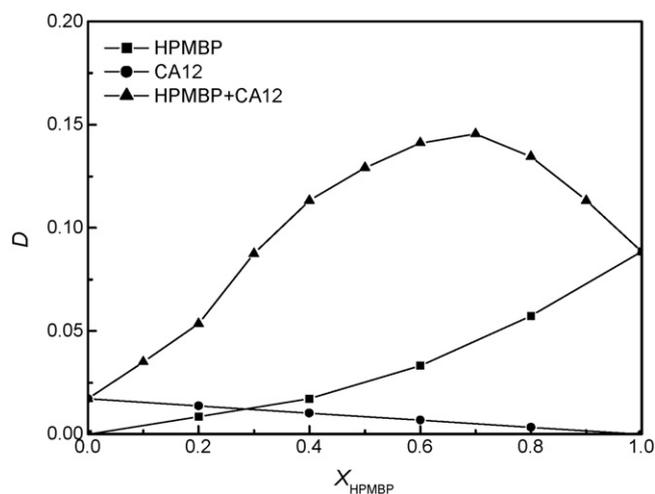


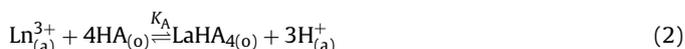
Fig. 1. Synergistic extraction of La^{3+} with mixtures of HPMBP and CA12. [La^{3+}] = $5 \times 10^{-3} \text{ mol L}^{-1}$, pH 3.0, $\mu = 0.3 \text{ mol L}^{-1}$, $C_{\text{HPMBP}} + C_{\text{CA12}} = 0.1 \text{ mol L}^{-1}$.

In the present work, the synergistic effects of rare earths extracted with HPMBP and CA12 have been studied in detail. As representatives, R_{max} of La^{3+} and Nd^{3+} has been calculated as 2.47 and 1.43, respectively. The synergistic extraction of La^{3+} is shown in Fig. 1, where X_{HPMBP} represents the mole fraction of HPMBP in the organic phases.

3.2. Extraction of rare earths with HPMBP

There have been many reports about the extraction of rare earths with HPMBP. According to HSAB theory [19], rare earth ions are hard acids while HPMBP is a hard base. With increasing atomic numbers of lanthanoids, the “harder” is the lanthanoids ion, resulting increasing extraction abilities. Under the experimental conditions in the present work, the extraction ability also follows this order, i.e., the distribution ratio increases with increasing atomic numbers of rare earths. Y is located between Nd and Sm.

The extraction of Ln^{3+} with HPMBP can be written as [6]:



where “a” and “o” represent aqueous and organic phase, respectively. The distribution ratio D_A and the extraction constant K_A have the following relations:

$$\log D_A - 3\text{pH} = 4 \log [\text{HA}]_{(\text{o})} + \log K_A \quad (3)$$

As shown in Table 1, $\log K_A$ values for La^{3+} and Nd^{3+} are calculated to be -4.69 ± 0.05 and -4.31 ± 0.05 , respectively.

3.3. Extraction of rare earths with CA12

The extraction of rare earths with CA12 in *n*-heptane has been studied by some authors [16,20–23], among which the extraction La^{3+} from chloride medium can be expressed as [16]:

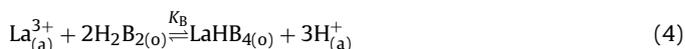


Table 1

Equilibrium constants and formation constants of La^{3+} and Nd^{3+} extracted with HPMBP, CA12, and HPMBP+CA12.

	$\log K_A$	$\log K_B$	$\log K_{AB}$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
La^{3+}	-4.69 ± 0.04	-7.13 ± 0.04	-1.92 ± 0.03	2.77	5.21	7.98
Nd^{3+}	-4.31 ± 0.04	-7.63 ± 0.05	0.59 ± 0.04	4.90	8.22	13.12

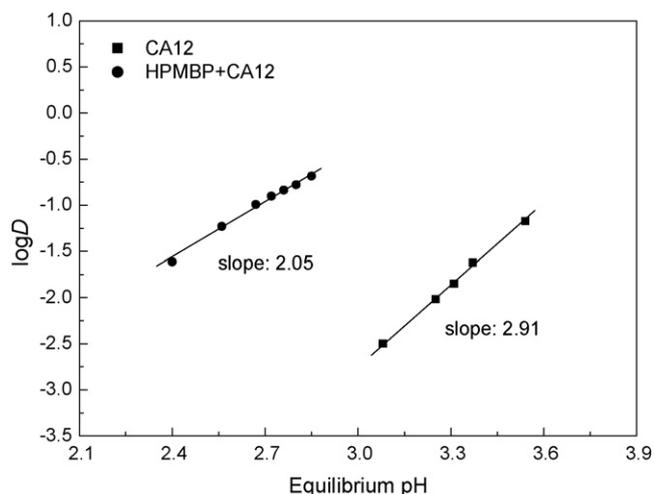
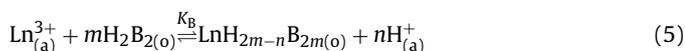


Fig. 2. Relationship between distribution ratio D_{AB} and equilibrium pH. $[La^{3+}] = 5 \times 10^{-3} \text{ mol L}^{-1}$, $\mu = 0.3 \text{ mol L}^{-1}$, $C_{HPMBP} = 0.04 \text{ mol L}^{-1}$, $C_{CA12} = 0.06 \text{ mol L}^{-1}$.

In the present study, benzene is employed as the diluent instead of *n*-heptane. The diluent is well known to be an important factor which may affect the extraction of metal ions. In order to investigate the extraction stoichiometry of La^{3+} extracted with CA12 in benzene, the following reaction is employed:

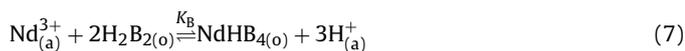


The relationship between the distribution ratio D_B and the extraction constant K_B can thus be described:

$$\log D_B - npH = m \log [H_2B_2]_{(o)} + \log K_B \quad (6)$$

Fig. 2 shows the plots of $\log D_B$ versus pH at fixed La^{3+} concentration, CA12 concentration, and ionic strength. The effects of $[H_2B_2]_{(o)}$ on the extraction of La^{3+} with CA12 can also be determined when La^{3+} concentration, pH value, and ionic strength are fixed. Results of m and n values indicate that Eq. (4) can still be used to express the extraction stoichiometry of La^{3+} when extracted with CA12 in benzene.

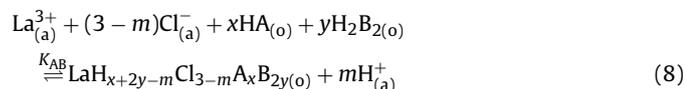
In the same way, the extraction stoichiometry of Nd^{3+} with CA12 can also be obtained:



The equilibrium constant, K_B , has been calculated as shown in Table 1.

3.4. Synergistic extraction mechanism of rare earths with mixtures of HPMBP and CA12

If the synergistic extraction of La^{3+} from chloride medium with mixtures of HPMBP and CA12 in benzene is expressed as:



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

$$\log D_{AB} = x \log [HA]_{(o)} + y \log [H_2B_2]_{(o)} + mpH + \log K_{AB} + (3 - m) \log [Cl^-]_{(a)} \quad (9)$$

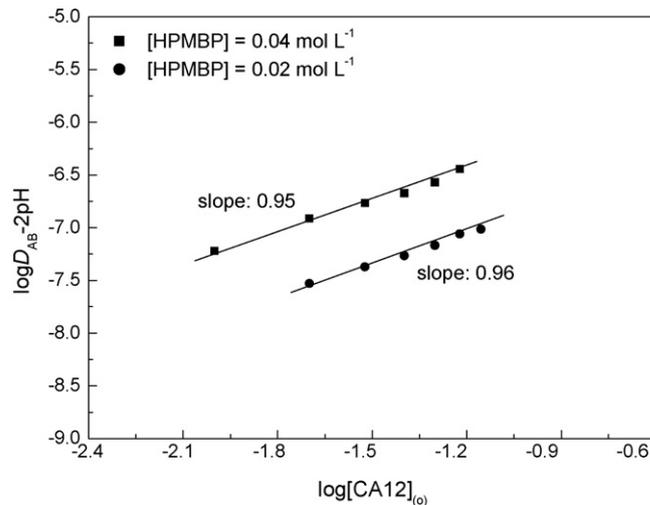
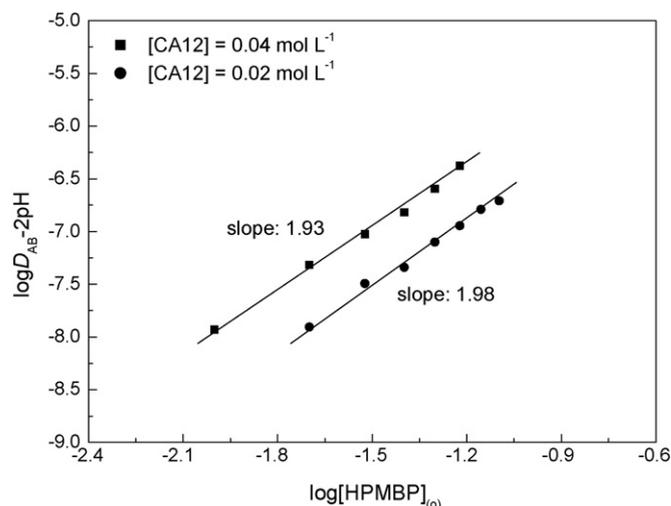


Fig. 3. Relationship between distribution ratio D_{AB} of La^{3+} and equilibrium concentration of HPMBP and CA12 in the mixtures of HPMBP and CA12. $[La^{3+}] = 5 \times 10^{-3} \text{ mol L}^{-1}$, $pH = 3.0$, $\mu = 0.3 \text{ mol L}^{-1}$.

where,

$$[HA]_{(o)} = C_{HA} - C_{La^{3+}} \times \frac{4D_A + xD_{AB}}{1 + D_A + D_B + D_{AB}} \quad (10)$$

$$[H_2B_2]_{(o)} = C_{H_2B_2} - C_{La^{3+}} \times \frac{2D_B + yD_{AB}}{1 + D_A + D_B + D_{AB}} \quad (11)$$

In order to gain insight into the extraction stoichiometry of La^{3+} with mixtures of HPMBP and CA12, D_{AB} has been determined at various acidities at fixed concentrations of HPMBP and CA12. The plots of $\log D_{AB}$ versus pH give a straight line with a slope of about 2.0 as shown in Fig. 2. Similarly, when the concentration of one extractant is varied at fixed pH value and fixed concentration of the other extractant, the plots of $\log D_{AB} - 2pH$ versus the concentration of extractants can also be obtained. Results are shown in Fig. 3. The plots are linear with slopes of about 2.0 and 1.0 for $\log [HA]_{(o)}$ and $\log [H_2B_2]_{(o)}$, respectively. Based on these results, Eq. (8) can be obtained as:



$\log K_{AB}$ can be calculated as shown in Table 1.

It can be seen from Eq. (12) that Cl^- forms the final extracted complex, which is similar to some previous reports. According to Xu's book [24], Cl^- may be regarded to participate in the solvent extraction reaction. Li and Ni [25] have also determined the formed

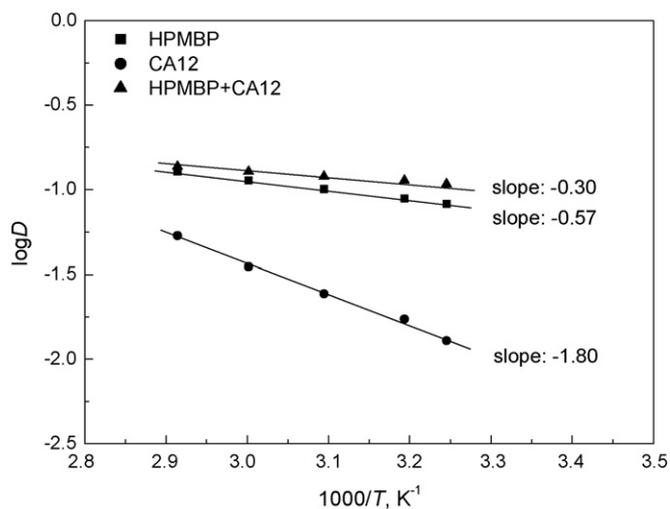
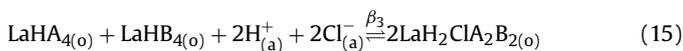
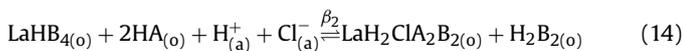
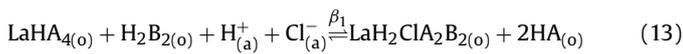


Fig. 4. Relationship between distribution ratio D and temperature. $[La^{3+}] = 5 \times 10^{-3} \text{ mol L}^{-1}$, $\text{pH} = 3.0$, $\mu = 0.3 \text{ mol L}^{-1}$, $C_{\text{HPMBP}} = 0.04 \text{ mol L}^{-1}$, $C_{\text{CA12}} = 0.06 \text{ mol L}^{-1}$.

complex containing Cl^- when rare earths are extracted with primary amine N1923 from chloride medium. In addition, it should be noted that the extraction reactions cannot offer the ideas about the structure and the coordination numbers of the extracted complexes. Some instruments such as IR, NMR, and element analysis may be employed for this goal.

From Eqs. (2), (4), and (12), the following formation reactions can be described:



where β_1 , β_2 and β_3 are formation constants as the followings:

$$\log \beta_1 = \log K_{\text{AB}} - \log K_{\text{A}} \quad (16)$$

$$\log \beta_2 = \log K_{\text{AB}} - \log K_{\text{B}} \quad (17)$$

$$\log \beta_3 = 2 \log K_{\text{AB}} - \log K_{\text{A}} - \log K_{\text{B}} \quad (18)$$

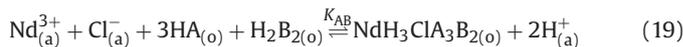
The $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ values are also shown in Table 1.

Similarly, the synergistic extraction mechanism of Nd^{3+} with mixtures of HPMBP and CA12 in benzene from chloride medium can also be obtained. The relationships between distribution ratio D_{AB} and equilibrium pH or equilibrium concentrations of HPMBP and

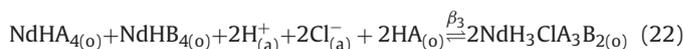
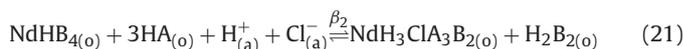
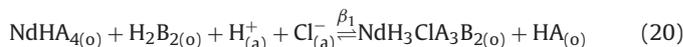
Table 2
Thermodynamic parameters of La^{3+} extracted with HPMBP, CA12 and HPMBP + CA12 systems.

Extractant	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
HPMBP	10.94	26.32	-52.45
CA12	34.55	40.01	-18.62
HPMBP + CA12	5.80	10.77	-16.99

CA12 have been determined. The synergistic extraction of Nd^{3+} with mixtures of HPMBP and CA12 can be obtained as the followings:



The following formation reactions can be derived:



The equilibrium constants and formation constants have also been calculated and shown in Table 1.

It can be seen from Table 1 that β_1 , β_2 , β_3 values for both La^{3+} and Nd^{3+} follow the order: $\beta_1 < \beta_2 < \beta_3$, indicating that Eqs. (15) and (22) contribute most to the synergistic extraction equations among the formation reactions. It implies that the complexes formed in single HPMBP and CA12 extraction systems are more prone to form the final synergistic compound, $\text{LaH}_2\text{ClA}_2\text{B}_2$ or $\text{NdH}_3\text{ClA}_3\text{B}_2$.

3.5. Influence of temperature

At fixed pH, ionic strength, and concentrations of La^{3+} and extractants, the influence of temperature on the extraction of La^{3+} has been studied. Results are shown in Fig. 4, based on which the change of enthalpy of the reaction, ΔH , can be determined according to the equation:

$$\frac{\Delta \log D}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \quad (23)$$

The change of Gibbs free energy, ΔG , and the change of entropy, ΔS of the system at 293 K can be obtained as well.

$$\Delta G = -RT \ln K \quad (24)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (25)$$

ΔH , ΔG and ΔS can be calculated as shown in Table 2. The ΔH , ΔG and ΔS values of La^{3+} when extracted with HPMBP or CA12 alone are also shown in Table 2. The signs of ΔH in HPMBP, CA12,

Table 3
Separation factors of rare earths in HPMBP and HPMBP + CA12 systems.

Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	
La	2.25/1.74	2.44/1.52	4.20/3.14	4.44/2.37	7.59/3.23	9.87/3.37	11.80/3.49	13.30/3.63	14.75/3.53	16.29/4.42	18.10/3.24	20.72/3.94	22.00/3.48	6.28/2.68
Ce		1.09/0.87	1.87/1.80	1.97/1.36	3.38/1.86	4.39/1.94	5.25/2.00	5.92/2.08	6.56/2.03	7.25/2.54	8.05/1.86	9.21/2.26	9.79/2.00	2.79/1.54
Pr			1.72/2.06	1.81/1.56	3.10/2.12	4.04/2.22	4.83/2.29	5.44/2.38	6.03/2.32	6.66/2.90	7.40/2.13	8.47/2.58	9.00/2.29	2.57/1.76
Nd				1.06/0.75	1.81/1.03	2.35/1.07	2.81/1.11	3.17/1.16	3.51/1.13	3.88/1.41	4.31/1.03	4.93/1.25	5.23/1.11	1.50/0.86
Sm					1.71/1.36	2.23/1.42	2.66/1.47	3.00/1.53	3.32/1.49	3.67/1.86	4.08/1.37	4.67/1.66	4.96/1.47	1.42/1.13
Eu						1.30/1.04	1.55/1.08	1.75/1.12	1.94/1.09	2.15/1.37	2.38/1.00	2.73/1.22	2.90/1.08	0.83/0.83
Gd							1.35/1.07	1.49/1.05	1.65/1.31	1.83/0.96	2.10/1.17	2.23/1.03	0.64/0.80	
Tb								1.13/1.04	1.25/1.01	1.38/1.27	1.53/0.93	1.76/1.13	1.86/1.00	0.53/0.77
Dy									1.11/0.97	1.22/1.22	1.36/0.89	1.56/1.09	1.65/0.96	0.47/0.74
Ho										1.10/1.25	1.23/0.92	1.40/1.11	1.49/0.99	0.43/0.76
Er											1.11/0.73	1.27/0.89	1.35/0.79	0.39/0.61
Tm												1.14/1.22	1.22/1.08	0.35/0.83
Yb													1.06/0.29	0.30/0.68
Lu														0.29/0.77

HPMBP + CA12 systems are all positive, indicating that all the three procedures are endothermically driven.

3.6. Separation of rare earths with mixtures of HPMBP and CA12

In Section 3.1, the different extraction effects of rare earths with mixtures of HPMBP and CA12 have been shown. Such results can be employed to consider the separation of rare earths. Since Y^{3+} is widely known to be difficult to be separated from lanthanoids because of their similar chemical properties, the separation of Y^{3+} from Ln^{3+} has also been investigated with HPMBP + CA12 mixtures and compared with that with HPMBP alone. Results of the separation factors are shown in Table 3. The separation factor value of Lu/Yb with HPMBP + CA12 is much higher than that with HPMBP alone, indicating that the mixtures may be of practical value for the separation of Lu and Yb. There is small gain for the separation of Pr/Ce, Nd/Pr, Sm/Nd, Er/Ho, Tm/Er, and Yb/Tm with the mixtures since the separation factor values in HPMBP + CA12 system are only a little larger than those in single HPMBP system. Worse selectivities have been obtained for other rare earths pairs with the mixtures than with HPMBP. Although great potential cannot be expected for the separation of most rare earths, the synergistic combinations of HPMBP and CA12 show some advantages in comparison with HPMBP alone if both the extraction efficiency and the metal separation are taken into account. Because under the same experimental conditions, the values of the distribution ratios in the mixing system are greater than those in single HPMBP system, the extraction process may be carried out at lower pH values.

4. Conclusions

The mixtures of HPMBP (HA) and CA12 (H_2B_2) in benzene have evident synergistic effects on light rare earths from chloride medium. The extracted complexes of La^{3+} and Nd^{3+} with the mixtures are determined to be $LaH_2Cl_2A_2B_2$ and $NdH_3Cl_3B_2$, respectively. The equilibrium constants, formation constants and thermodynamic parameters have been determined. The synergistic extraction of La^{3+} is endothermically driven. The various extraction effects on different rare earths have been considered to separate rare earths, indicating the mixtures of HPMBP and CA12 may be of practical value for the separation of Lu and Yb.

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