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Extraction of Rare Earths(III) from Nitrate Medium with Di-(2-ethylhexyl) 2-ethylhexyl Phosphonate and Synergistic Extraction Combined with 1-Phenyl-3-Methyl-4-Benzoy l-Pyrazolone-5

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Abstract: The extraction of trivalent rare earths (RE) from nitrate solutions with di-(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP, B) and synergistic extraction combined with 1-phenyl-3-methyl-4-benzoyl -pyrazolone-5 (HPMBP, HA) were investigated. The extraction distribution ratios demonstrate a distinct "tetra effect," and Y lies between Tb and Dy when DEHEHP is used as a single extractant for RE. According to the corresponding separation factors (SF_{12}) for adjacent pairs of rare earths, it could be concluded that DEHEHP could be employed for the separation of La from the other rare earths, and Y from light rare earths. The present work has also found that mixtures of HPMBP and DEHEHP have an evident synergistic effect for RE(III). Taking Y(III) as an example, a possible synergistic extraction mechanism is proposed. The enhancement of extraction in the binary system can be explained due to the species $Y(NO_3) \cdot A_2 \cdot HA \cdot B$ formed. The synergistic enhancement coefficients (R), extraction constants, formation constants and thermodynamic functions of the reaction were calculated.

The extraction of heavy rare earths (HRE = Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} and Lu^{3+}) has also been investigated using such a binary system and compared with that of Y(III). The results show that the synergistic extraction distribution ratios follow the order:

$$Y^{3+} < Tb^{3+} \approx Dy^{3+} \approx Ho^{3+} < Er^{3+} < Tm^{3+} < Yb^{3+} < Lu^{3+}$$

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The separation factors ($SF_{RE/Y}$) between Y and HRE were calculated and compared with the single extraction system. The possibility of separating Y(III) from heavy rare earths is discussed according to the separation factors.

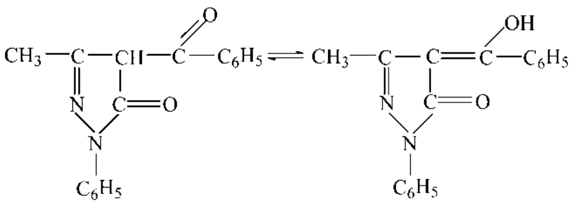
Keywords: Synergistic extraction, rare earths, Yttrium(III), HPMBP, DEHEHP

INTRODUCTION

Rare earth elements (including yttrium) have attracted much more attention due to their wide range of applications in various important fields such as electronics, magnetism, metallurgy and phosphors, catalysts, glass, laser, nuclear energy, astronavigation, and ceramic technology (1), With increasing demand for rare earths (RE) and their compounds individually and collectively, the extraction and separation of these elements has also gained considerable attention. However, owing to the extreme similarity in the chemical properties for these rare earth elements, their separation is very difficult to achieve. Actually, solvent extraction plays an important role as a separation and purification technique for rare earths (2). Thus, it is desirable to develop new extraction systems for the separation of rare earths as a group or from one another. Some synergistic extraction systems for the extraction of RE(III) have been reported (3–9).

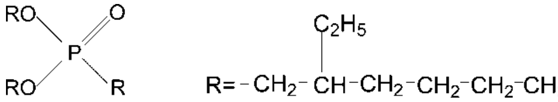
Synergistic extraction sometimes not only enhances the extraction efficiency but also improves the selectivity significantly, which attracts more and more attention of separation scientists. The equilibrium for synergistic extraction is discussed in several monographs on solvent extraction (10–12,) and a synergistic system with a combination of chelating extractant and neutral extractant generally produces a good synergistic effect (10).

1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP, HA) is one of common chelating agents and also is an excellent synergistic reagent. Its chemical structure is shown as follow:



There are extensive reports about the synergistic extraction of rare earths by mixtures of HPMBP and some other extractants, such as high molecular weight amines (13–15), acidic alkylphosphorous extractants(16–18) and neutral organophosphorous ester (19, 23). Han, et al. (19) have studied the synergistic extraction of Nd(III) by a combination of HPMBP with di-(1- methylheptyl) methyl phosphonate (P350). Jia, et al.(20) have investigated synergistic extraction of La(III) from nitrate medium by mixtures of HPMBP and triisobutyl phosphine sulphide (TIBPS).

Di(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP, B), a kind of neutral organophosphate, has attracted considerable attention. Its chemical structure is as follows:



Our laboratory has systematically studied the extraction of RE(III), Ce(IV) and Th(IV) by DEHEHP.(21, 22) The results show that DEHEHP has moderate extractability compared with some other organophosphorous esters and good physico-chemical properties as an extractant for rare earths, such as being completely miscible with all common hydrocarbon diluents even at low ambient temperatures, low aqueous solubility, good resistance to hydrolysis, and high purity (>99%) so on. However, so far, there have been no systematic reports about the extraction of Y(III) and other RE(III) by mixtures of HPMBP and DEHEHP.

In the present work, it has been found that mixtures of HPMBP and DEHEHP have an evident synergistic effect for RE(III). Taking Y(III) as an example, a possible synergistic extraction mechanism is proposed. The equilibrium constants, formation constants, and thermodynamic constants were calculated. The extraction of heavy rare earths (Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}) has also been investigated using such a binary system and compared with that of Y(III). The advantages in separation selectivity of the binary system are discussed according to the separation factors.

EXPERIMENTAL

Reagents

HPMBP, with a purity > 99% and supplied by Shanghai (China) Chemistry Reagent Factory, was used as received. DEHEHP, kindly supplied by Tianjin (China) Baicheng chemical plant, was purified using a method similar to Cyanex923 (23) washed by Na_2CO_3, HNO_3 solutions and distilled water in turn. The extractants were dissolved in benzene or heptane to the required concentration. All the other reagents were of analytical grade.

Stock solutions of rare earths were prepared by dissolving their oxides (purity > 99.9%) in HNO_3, respectively. The metal ions were analyzed by titration with a standard solution of EDTA with xylenol orange as an indicator. The aqueous phase was kept at a constant ionic strength (μ) with $LiNO_3$. The pH (2, 3) of the aqueous phase was controlled by a buffer solution of ammonium acetate–hydrochloric acid during the extraction.

Methods

Distribution ratios were determined by shaking equal volumes of aqueous and organic phases together for 30 min at 298 ± 1 K (except for temperature experiments), which was sufficient for attaining equilibrium. After the phases separating by gravity, the concentration of metal ions in the aqueous phase was determined by titration with EDTA and that of metal ions in the organic phase was determined by material balance. From these concentration values, the distribution ratio D was calculated.

RESULTS AND DISCUSSION

Extraction of RE^{3+} by HPMBP and DEHEHP Alone

The extraction of RE^{3+} by HPMBP has been studied earlier (24–27). All of these results show that HPMBP can extract RE^{3+} as the following equation at a lower concentration of HPMBP (27):

$$RE^{3+}_{(a)} + 3HA_{(o)} \overset{k_1}{\longleftrightarrow} REA_{3(o)} + 3H^{+}_{(a)} \qquad (1)$$

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

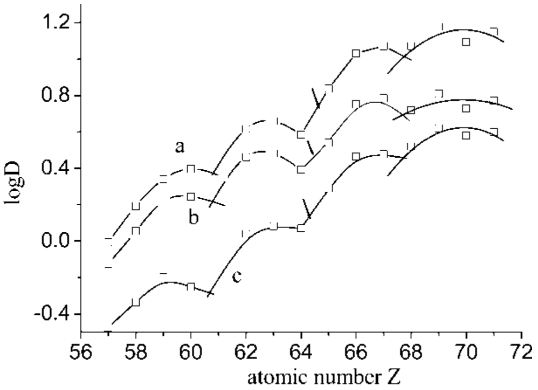


Figure 1. The relationship between atom number Z and logD at different conditions. $RE^{3+} = 1.0 \times 10^{-3}$ mol/L, DEHEHP (in heptane) = 0.42 mol/L, a: $pH_e = 2.50$, $LiNO_3 = 2.61$ mol/L; b: $pH_e = 1.89$, $LiNO_3 = 2.61$ mol/L; c: $pH_e = 2.50$, $LiNO_3 = 1.74$ mol/L.

Table 1. Separation factors (SF_{12}) among rare earth elements in nitrate medium with DEHEHP

		1													
	SF_{12}	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Y	Dy	Ho	Er	Tm	Yb	Lu
2	La	1.583	2.221	2.527	4.193	4.630	3.904	6.991	8.621	10.93	12.01	12.01	15.30	12.61	16.85
	Ce		1.402	1.595	2.648	2.923	2.465	4.414	5.443	6.900	7.584	7.584	9.658	7.959	10.64
	Pr			1.138	1.888	2.084	1.758	3.147	3.881	4.920	5.407	5.407	6.886	5.675	7.585
	Nd				1.659	1.832	1.545	2.767	3.412	4.325	4.753	4.753	6.053	4.989	6.668
	Sm					1.104	0.931	1.667	2.056	2.606	2.865	2.865	3.648	3.006	4.018
	Eu						0.843	1.510	1.862	2.361	2.594	2.594	3.304	2.723	3.639
	Gd							1.791	2.208	2.799	3.076	3.076	3.917	3.228	4.315
	Tb								1.233	1.563	1.718	1.718	2.188	1.803	2.410
	Y									1.268	1.393	1.393	1.774	1.462	1.954
	Dy										1.099	1.099	1.400	1.153	1.542
	Ho											1.000	1.274	1.050	1.403
	Er												1.274	1.050	1.403
	Tm													0.824	1.102
	Yb														1.337

The extraction of RE^{3+} in HNO_3 solutions by DEHEHP - heptane in the presence of $LiNO_3$ had been studied systematically. Figure 1 shows the relationship between distribution ratio D and atomic number Z. The arrowhead indicates the position of Y in the extraction list and lies between Tb and Dy. The distribution ratios are found to be a distinct "tetra effect. (28)" Compared with the three plots in Fig. 1, it can also be determined that the effect of ionic strength on the distribution ratio is larger than that of pH_e. Table 1 summarizes the calculated separation factors (SF_{12}) for adjacent pairs of rare earths at $pH_e = 2.50$ and 2.61 mol/L $LiNO_3$. From the values of separation factors, it could be concluded that DEHEHP could be employed for the separation of La from the other rare earths, and Y from light rare earths under certain conditions.

Taking La, Ce, Nd, Gd, Yb, and Y as examples, a series of experiments were carried out to determine the extraction mechanism.

Figure 2 presents the effect of extractant concentrations on the logD of La, Ce, Nd, Gd, Yb, and Y, and the slopes of linear fitting curves from the experimental data are also showed. The results show that three molecules of DEHEHP are associated with the extraction reaction under the present experimental conditions, but Gd is an exception. This might be mainly due to the nephelauxetic and half-full effect in the 4f orbit (29), and Gd^{3+} ($4f^7$) is in such a stable state that it is difficult to react with a ligand (15).

As can be seen in Fig. 3, it is evident that the extraction increases linearly with an increasing NO_3^- ion concentration under the higher $LiNO_3$ concentration, but departs from the linearity at the lower $LiNO_3$ concentration for middle-heavy rare earth (Gd, Yb and Y), which can be concluded that the extraction mechanism of middle-heavy rare earths changes with the increasing

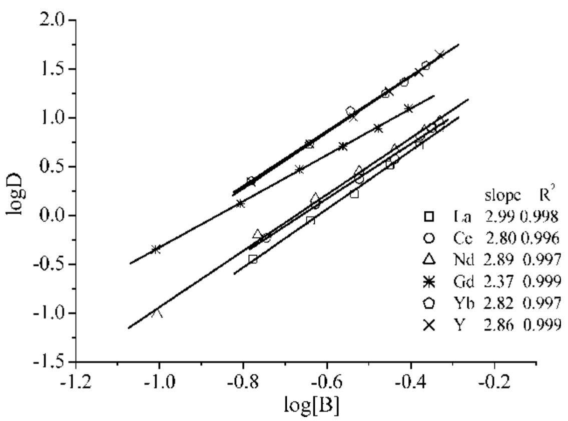


Figure 2. The effect of DEHEHP - heptane concentration on logD of La, Ce, Nd, Gd, Yb and Y, $pH_e = 3.00$, $LiNO_3 = 3.48$ mol/L, $RE^{3+} = 1.0 \times 10^{-3}$ mol/L.

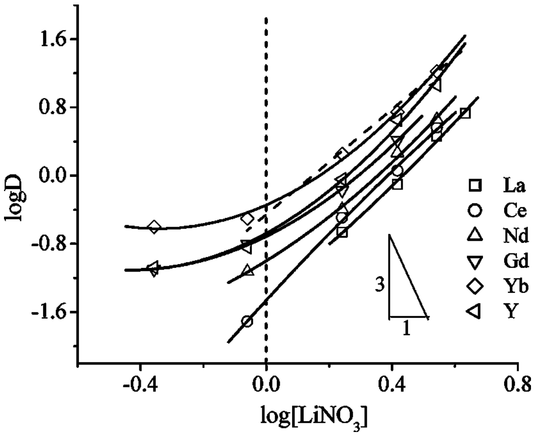


Figure 3. The effect of LiNO$_3$ concentration on logD of RE(III). pH$_e$ = 2.00, RE^{3+} = 1.0 × 10^{-3} mol/L, DEHEHP (in heptane) = 0.42 mol/L.

concentration of NO_3^-. However, this uncertain mechanism for middle-heavy rare earths (such as Gd, Yb, and Y) at a lower concentration of NO_3^- (<1 mol/L) needs to be further investigated in more detail. The linearity part shows a slope value of around 3.

Based on the above discussion, the extracted species of RE (La, Ce, Nd, Y, and Yb), can be formulated as $RE(NO_3)_3 \cdot 3B$ under higher LiNO$_3$

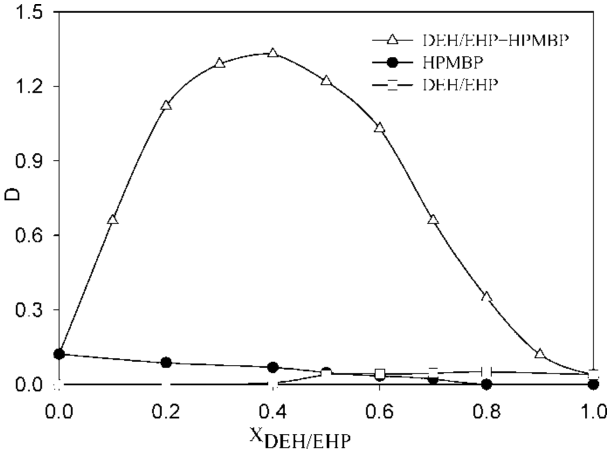


Figure 4. Synergistic extraction of Y^{3+} by HPMBP and DEHEHP in benzene. [Y^{3+}] = 9.469 × 10^{-4} mol/L, μ = 1.0 mol/L, pH$_e$ = 2.00 [HPMBP + DEHEHP]$_{(o)}$ = 0.05 mol/L.

concentration. The corresponding extraction reaction equation can be written as follows:

$$RE^{3+} + 3NO_3^- + 3B \xleftrightarrow{k_2} RE(NO_3)_3 \cdot 3B \tag{2}$$

Extraction of RE^{3+} by Mixtures of HPMBP and DEHEHP in Benzene

Taking Y^{3+} as an example, the extraction mechanism has been systematically studied. Figure 4 shows the extraction behaviors of Y^{3+} by mixtures of HPMBP and DEHEHP in benzene and the results show that there is an evident synergistic effect. The largest synergistic extraction distribution ratio was observed when X_B is close to 0.4. The synergistic enhancement coefficient, $R = D_{max}/(D_B + D_{HA})$, is calculated according to Xu et al. (30) to be listed in Table 2. It can be concluded that R_{max} is 17.82 under the present experimental condition.

If the synergistic extraction of Y^{3+} by the mixture of DEHEHP and HPMBP from the nitrate medium is expressed as:

$$Y^{3+}_{(a)} + 3NO^-_{3(a)} + xHA_{(O)} + yB_{(O)} \xleftrightarrow{k_{12}} Y(NO_3)_{3-z} \cdot A_t \cdot (HA)_{x-z} \cdot yB_{(O)} + zHNO_{3(a)} \tag{3}$$

Then the relationship between the distribution ratio D_{12} and the equilibrium constant K_{12} of the synergistic extraction reaction should be:

$$K_{12} = \frac{[Y(NO_3)_{3-z} \cdot A_z \cdot (HA)_{x-z} \cdot yB]_{(o)}[H^+]^z_{(a)}}{[Y^{3+}]_{(a)} \cdot [NO_3^-]^{3-z}_{(a)} \cdot [HA]^x_{(o)} \cdot [B]^y_{(o)}} = \frac{D_{12} \cdot [H^+]^z_{(a)}}{[NO_3^-]^{3-z}_{(a)} \cdot [HA]^x_{(o)} \cdot [B]^y_{(o)}} \tag{4}$$

Rearranging equation (4) in the logarithmic form:

$$\log D_{12} = x \log[HA]_{(o)} + y \log[B]_{(o)} + zpH_e + \log K_{12} + (3 - z) \times \log[NO_3^-]_{(a)} \tag{5}$$

Table 2. Synergistic enhancement coefficients of Y^{3+} at pHe = 2.00

X_{DEHEHP}	0	0.2	0.4	0.5	0.6	0.7	0.8	1
R	1	12.85	17.82	14.13	13.53	9.83	7.00	1

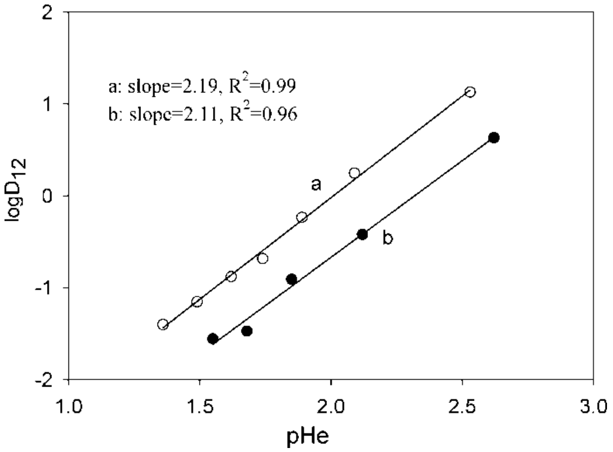


Figure 5. Distribution ratio for Y^{3+} as a function of equilibrium pH in benzene. $[Y^{3+}] = 9.469 \times 10^{-4}$ mol/L, $\mu = 1.0$ mol/L, $[HPMBP + DEHEHP]_{(o)} = 0.05$ mol/L a: C_{DEHEHP}:C_{HPMBP} = 2:3 b: C_{DEHEHP}:C_{HPMBP} = 4:1.

A series of experiments were carried out to determine the values of x, y, and z. As shown in Fig. 5, the plots of logD$_{12}$ versus pH$_e$ give a straight line with a slope of about 2.0 keeping the other conditions as constants. So z equals to 2.

Similarly, at an invariable aqueous acidity and concentration of the other extractant, the plots shown in Fig. 6 are linear with slopes of about 3 and 1 for logD$_{12}$-2pHe vs. log[HPMBP] and log[DEHEHP], respectively. So x equals to 3 and y is 1, and the extracted species can thus be determined.

Therefore, the synergistic extraction reaction, Eq. (3), can be rewritten as:

$$Y^{3+}_{(a)} + 3NO^-_{3(a)} + 3HA_{(O)} + B_{(O)} \overset{k_{12}}{\longleftrightarrow} Y(NO_3) \cdot A_2 \cdot HA \cdot B_{(O)} + 2HNO_{3(a)} \qquad (6)$$

Then the relationship between the distribution ratio D$_{12}$ and the equilibrium constant K$_{12}$ of the synergistic extraction reaction should be:

$$K_{12} = \frac{D_{12} \cdot [H^+]^2_{(a)}}{[NO_3^-]_{(a)} \cdot [HA]^3_{(o)} \cdot [B]_{(o)}} \qquad (7)$$

Rearranging equation (7) in the logarithmic form:

$$\log D_{12} = 3\log[HA]_{(o)} + \log[B]_{(o)} + 2pH_e + \log K_{12} + \log[NO_3^-]_{(a)}$$

The calculated synergistic extraction equilibirum constants for Y^{3+} at different acidities are represented in Table 3.

The synergistic reaction in the nitrate medium belongs to the combination of a cation exchange mechanism and a solvate complexation mechanism. That

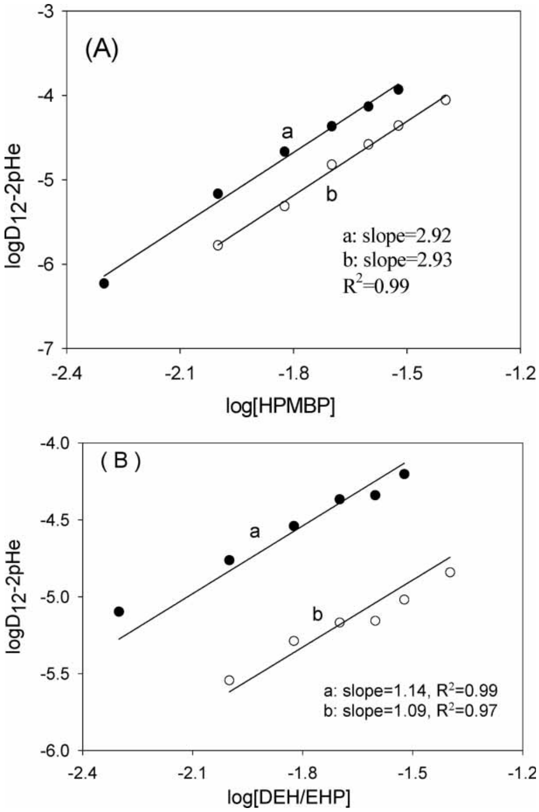


Figure 6. Relationship between distribution ratio D_{12} and equilibrium concentration of DEHEHP or HPMBP in benzene, $\mu = 1.0$ mol/L, $pH_e = 2.00$. (A) $[Y^{3+}] = 9.469 \times 10^{-4}$ mol/L, a: DEHEHP = 0.02 mol/L, b: DEHEHP = 0.01 mol/L (B) $[Y^{3+}] = 9.571 \times 10^{-4}$ mol/L, a: HPMBP = 0.02 mol/L, b: HPMBP = 0.01 mol/L.

Table 3. Synergistic extraction equilibrium constants for Y^{3+} at 298K. $[Y^{3+}] = 9.469 \times 10^{-4}$ mol/L, $[NO_3^-] = 1.0$ mol/L, $[HPMBP + DEHEHP]_{(o)} = 0.05$ mol/L

C_B/C_{HA}	pHe	$Y^{3+}_{(a)} \times 10^4$	$Y^{3+}_{(o)} \times 10^4$	$[HA]_{(o)}$	$[B]_{(o)}$	$\log K_{12}$	Avg. $\log K_{12}$
2:3	2.53	0.6506	8.818	0.02735	0.01912	2.48	2.26 ± 0.11
	2.09	3.435	6.034	0.02819	0.01940	2.43	
	1.89	5.986	3.483	0.02896	0.01965	2.31	
	1.74	7.808	1.662	0.02950	0.01983	2.13	
	1.62	8.338	1.131	0.02966	0.01989	2.16	
	1.49	8.849	0.620	0.02981	0.01994	2.14	
	1.36	9.109	0.3603	0.02989	0.01996	2.15	

is, the extraction mechanism of the acidic chelating extractant usually belongs to the former and that of the neutral organophosphate belongs to the latter (28). The extraction of Y^{3+} by HPMBP or DEHEHP alone was repeated under the current experimental conditions to obtain the extraction constant $\log K_1$ and $\log K_2$, which were calculated to be -3.98 ± 0.07 and -5.02 ± 0.02, respectively. The following reaction can describe the hypothetical formation combined with Eqs. (1), (2), and (6):

$$YA_{3(o)} + B_{(o)} + HNO_{3(a)} \overset{\beta_1}{\longleftrightarrow} Y(NO_3)A_2 \cdot HA \cdot B_{(o)} \tag{8}$$

$$Y(NO_3)_3 \cdot 3B_{(o)} + 3HA_{(o)} \overset{\beta_2}{\longleftrightarrow} Y(NO_3)A_2 \cdot HA \cdot B_{(o)} + 2HNO_{3(a)} + 2B_{(o)} \tag{9}$$

$$\frac{1}{2}Y(NO_3)_3 \cdot 3B_{(o)} + \frac{1}{2}YA_{3(o)} + \frac{3}{2}HA_{(o)} \overset{\beta_3}{\longleftrightarrow} Y(NO_3)A_2 \cdot HA \cdot B_{(o)} + \frac{1}{2}B_{(o)} + \frac{1}{2}HNO_{3(a)} \tag{10}$$

where β_1, β_2 and β_3 are the formation constants which can be expressed as:

$$\begin{aligned}
\log\beta_1 &= \log K_{12} - \log K_1 = 2.26 - (-3.98) = 6.24 \\
\log\beta_2 &= \log K_{12} - \log K_2 = 2.26 - (-5.02) = 7.28 \\
\log\beta_3 &= \log K_{12} - \frac{1}{2}\log K_1 - \frac{1}{2}\log K_2 = 2.26 \\
&\quad - \frac{1}{2} \times (-3.98) - \frac{1}{2} \times (-5.02) = 6.76
\end{aligned}$$

From the values of β_1, β_2, and β_3, Eqs. (8), (9), and (10) all are in favor of forming the synergistic extracted species $Y(NO_3)A_2 \cdot HA \cdot B$. However, Eq. (9) contributes more. Just because of $\beta 2 > \beta 3 > \beta 1 > K12 \gg K2 > K1$, we can suppose that the synergistic extracted species $Y(NO_3)A_2 \cdot HA \cdot B$ should be more stable or hydrophobic.

The Effect of Temperature

Figure 7 shows the effect of temperatures (288–323K) on the distribution ratios D_{12} with a slope of 1.26 ± 0.04.

According to the following thermodynamic formula,

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

from the slope of the plots of $\log D_{12}$ vs. 1000/T combined with $R = 8.314\ J \cdot K^{-1} \cdot mol^{-1}$, the enthalpy increment of the extraction process

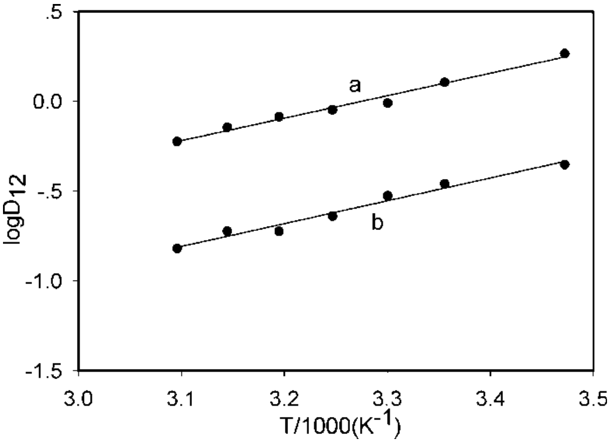


Figure 7. Relationship between synergistic distribution ratio D_{12} and temperature in benzene, $[Y^{3+}] = 9.469 \times 10^{-3}$ mol/L, $\mu = 1.0$ mol/L, $pH_e = 2.00$, $[HPMBP + DEHEHP]_{(o)} = 0.05$ mol/L. a: $C_{DEHEHP}:C_{HPMBP} = 2:3$ b: $C_{DEHEHP}:C_{HPMBP} = 4:1$.

was calculated to be $\Delta H = -24.12$ kJ/mol, which indicates that the synergistic extraction is an exothermic process.

When $C_{DEHEHP} = 0.02$ mol/L, $C_{HPMBP} = 0.03$ mol/L, ΔG and ΔS of the synergistic extraction system at room temperature (298K) can be calculated as:

$$\Delta G = -2.303RT \log K_{12} = -12.90 kJ \cdot mol^{-1}$$

$$\Delta S = (\Delta H - \Delta G)/T = -37.65 J \cdot K^{-1} \cdot mol^{-1} < 0$$

The synergistic extraction reaction of Y(III) is enthalpy driven, with the favorable enthalpic contribution being sufficient to overcome the unfavorable entropic contribution. The net enthalpy and entropy contributions of the extraction process are the results of several factors, such as the dehydration of the metal cation and metal coordination with the organic ligand, which lead to a large negative ΔG.

Extraction of HRE and Y by Mixtures of DEHEHP and HPMBP

The extraction of Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}, and Y^{3+} from nitrate solutions by HPMBP and DEHEHP had been investigated at similar conditions (shown in Fig. 8).

Under the present experimental conditions, the results show that there is negligible extraction when DEHEHP is used as a single extractant because of the lower aqueous phase ionic strength, while the extraction by HPMBP alone shows a certain extractability. However, the mixtures of DEHEHP and HPMBP can enhance the extractability for all of the extracted metal ions.

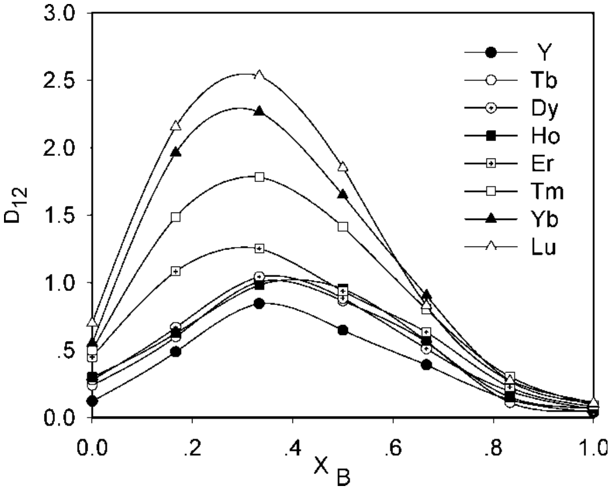


Figure 8. Synergistic extraction of HRE and Y by mixtures of DEHEHP and HPMBP in benzene, $[M^{3+}] = 8.0 \times 10^{-4}$ mol/L, $\mu = 1.0$ mol/L, $pH_e = 1.88$, $[HPMBP + DEHEHP]_{(o)} = 0.05$ mol/L.

As can be seen in Fig. 8, it is apparent that the extraction of rare earth ions follows the order of the atomic number and the extraction of Y^{3+} is lowest whether for HPMBP system or for HPMBP + DEHEHP system. The order of extraction ability can also be explained by HSAB theory (31). Lewis base, a nucleophilic reagent or ligand, can be divided into two categories, those that are polarizable, or "soft" and those that are nonpolarizable or "hard." For example, the atoms F, O, and N are hardest in groups V, VI, and VII. For these extractants, whether HPMBP, DEHEHP, or HPMBP + DEHEHP, complex metal ions through O atom. So all of them can be regarded as a hard base. While rare earth ions are hard acids because of their most stable complexes with O atom according to the classification of metal ions as acids by Ahrland, Chatt, and Davies (32). And the smaller is the ionic radius, the "harder" is the rare earth ion, which results in the increasing extraction ability by HPMBP + DEHEHP with decreasing ionic radii of the lanthanide ions. Usually, Y^{3+} is an exception due to its particularity.

The largest synergistic extraction distribution ratios were also observed when X_B is close to 0.4. The corresponding separation factors between Y and the other rare earth elements ($SF_{RE/Y}$) are calculated and listed in Table 4. In addition, $SF_{RE/Y}$ of the single system by HPMBP or DEHEHP is also shown in Table 4 as a comparison.

Although an appropriate proportion of the two extractants can enhance the extraction efficiency, the synergistic extraction system does not embody better separation selectivity than the single HPMBP system. However, the separation selectivity of the synergistic extraction system is superior to

Table 4. The separation factors $SF_{RE/Y}$ in different systems

	system	Y	Tb	Dy	Ho	Er	Tm	Yb	Lu
$SF_{RE/Y}$	HA	—	1.97	2.30	2.46	3.69	4.10	4.51	5.74
	B^a	—	0.81	1.27	1.39	1.39	1.77	1.46	1.95
	HA + B	—	1.19	1.23	1.20	1.48	2.11	2.68	3.00

[a] B = 0.42 mol/L, LiNO3 = 2.61 mol/L, [RE3 +] = 1.0E-3 mol/L.

single DEHEHP system, especially for heavy rare earths Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}. As far as DEHEHP, a possible industrialized extractant, is concerned, this embodies a more practical significance. In fact, the synergistic extraction system can be considered to separate Y^{3+} from Tm^{3+}, Yb^{3+} and Lu^{3+} which is difficult to be realized by DEHEHP alone.

CONCLUSIONS

The extraction of trivalent rare earths (RE) from nitrate solutions with DEHEHP and synergistic extraction with mixtures of DEHEHP and HPMBP were systematically investigated. In the single DEHEHP system, the extraction distribution ratios of rare earths are found to be demonstrated a distinct "tetra effect" and Y lies between Tb and Dy. Meanwhile, the extracted species has been formulated as $RE(NO_3)_3 \cdot 3B$ under higher $LiNO_3$ concentration. From the corresponding separation factors (SF_{12}) for adjacent pairs of rare earths, it can be predicted that DEHEHP could be employed for the separation of La from the other rare earths, and Y from light rare earths.

The investigation of the synergistic extraction with mixtures of DEHEHP and HPMBP shows that the binary system has an evident synergistic effect for RE(III). Taking Y(III) as an example, the enhancement of extraction in the binary system can be explained in terms of the species $Y(NO_3) \cdot A_2 \cdot HA \cdot B$ formed. The synergistic enhancement coefficients R_{max} is calculated to be 17.82 for Y^{3+} under the present experimental condition. The synergistic reaction is an exothermic process. In addition, the extraction of Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+} and Y^{3+} at the same conditions shows that the synergistic extraction distribution ratios follow the order:

$$Y^{3+} < Tb^{3+} \approx Dy^{3+} \approx Ho^{3+} < Er^{3+} < Tm^{3+} < Yb^{3+} < Lu^{3+}$$

The separation factors ($SF_{RE/Y}$) between Y and the other metal ions show that synergistic extraction system is superior to single DEHEHP system especially for heavy rare earths Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}, but does not embody better separation selectivity than the HPMBP system.

Therefore, the binary extraction system can be considered to separate Y^{3+} from Tm^{3+}, Yb^{3+} and Lu^{3+}.

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REFERENCES

1. Sabot, J.L., Maestro, P., and Recherches, R.P. (1996) Lanthanides. *Encyclopedia of Chemical Technology*; Kroschwitz, J.I. and Howe-Grant, M. (eds.), Wiley: New York; Vol. 14, 1091.
2. Xu, G.X. and Yuan, Ch.Y. (1987) *Solvent Extraction of Rare Earths*; 1st Ed.; Science Press: Beijing, 89.
3. Zahir, H. and Masuda, Y. (1997) Extractive separation of trivalent lanthanide metals with a combination of di(2-ethylhexyl)phosphoric acid and 1,10-phenanthroline. *Talanta*, 44 (3): 365.
4. Dai, L.M., Minh, D.V., and Hai, P.V. (2000) Solvent Extraction of Lanthanides with Triisoamylphosphate and Di-(2-ethylhexyl)phosphoric Acid from Trichloroacetic Acid and Nitric Acid Solutions. *J. Alloy. Compd.*, 311 (1): 46.
5. Reddy, M.L.P., Bosco Bharathi, J.R., Peter, S., and Ramamohan, T.R. (1999) Synergistic extraction of rare earths with bis(2,4,4-trimethyl pentyl) dithiophosphinic acid and trialkylphosphine oxide. *Talanta*, 50 (1): 79.
6. Krea, M. and Khalaf, H. (2000) Liquid–liquid extraction of uranium and lanthanides from phosphoric acid using a synergistic DOPPA–TOPO mixture. *Hydrometallurgy*, 58 (3): 215.
7. Sun, X.B., Zhao, J.M., Meng, Sh.L., and Li, D.Q. (2005) Synergistic extraction and separation of yttrium from heavy rare earths using mixture of sec-octylphenoxy acetic acid and bis(2,4,4-trimethylpentyl)phosphinic acid. *Anal. Chim. Acta*, 533 (1): 83.
8. Kitatsuji, Y., Meguro, Y., Yoshida, Z., Yamamato, T., and Nishizawa, K. (1995) Synergistic Ion-pair Extraction of Lanthanide(III) with thenoyltrifluoroacetone and crown ether into 1,2-Dichloroethane. *Solvent Extr. Ion Exch.*, 13 (2): 289.
9. Reddy, M.L.P., Sujatha, S., and Varma, R.L. (1997) Mixed-ligand chelate extraction of trivalent lanthanides with 4,4,4-trifluoro-1-phenyl-1,3-butanedione and neutral oxo – donors. *Talanta*, 44 (1): 97.
10. Marcus, Y. and Kertes, A.S. (1969) *Ion Exchange and Solvent Extraction of Metal Complexes*; Wiley-Interscience: London.
11. Sekine, T. and Hasegawa, Y. (1977) *Solvent Extraction Chemistry*. Marcel Dekker: New York.
12. Rydberg, J., Musikas, C., and Choppin, G.R. (1992) *Principles and Practices of Solvent Extraction*; Rydberg, J., Musikas, C. and Choppin, G.R. (eds.), Marcel Dekker: New York.

13. Maria, A. and Dukov, I.L. (2004) Synergistic solvent extraction and separation of trivalent lanthanide metals with mixtures of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one and aliquat 336. *Sep. Purif. Technol.*, 40 (2): 171.
14. Dukov, I.L. and Jordanov, V.M. (1998) Synergistic solvent extraction of lanthanides with mixtures of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and primary ammonium salts. *Hydrometallurgy*, 48 (2): 145.
15. Ma, G.X. and Li, D.Q. (1989) Synergistic extraction of rare earth ions (III) by HPMBP and primary amine N_{1923}. *J. Nucl. Radiochem.* (in Chinese) 11 (1): 36.
16. Li, D.Q. and Niu, W. (1990) Investigation of synergistic extraction mechanism of rare earth elements (III) with HEHEHP and PMBP. *J. Nucl. Radiochem.* (in Chinese) 12 (2): 92.
17. Kong, W., Li, D.Q., Zhang, X.Y., and Wang, C.M. (1997) Study of synergistic extraction of rare earth elements with HBTMPTP and HPMBP. *J. Nucl. Radiochem.* (in Chinese) 19 (3): 1.
18. Sun, J. and Li, D.Q. (1994) Study of synergistic extraction of rare earth elements (III) with BTMPPA and HPMBP. *Chinese J. Appl. Chem.* (in Chinese) 11 (3): 49.
19. Han, S.M. and Li, D.Q. (1991) Synergistic extraction of neodymium(III) from chloride medium by mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 and Di-(1-methylheptyl) methyl phosphonate. *Rare Metal.* (in Chinese) 3: 227.
20. Jia, Q., Shang, Q.K., and Zhou, W.H. (2004) Synergistic extraction of lanthanum(III) from a nitrate medium by mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 and triisobutylphosphine sulphide. *Ind. Eng. Chem. Res.*, 43 (21): 6703.
21. Zhao, J.M., Meng, Sh.L., and Li, D.Q. (2004) Liquid-liquid extraction of cerium(IV) from nitric acid media by di-(2-Ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP). *Solvent Extr. Ion Exc.*, 22 (3): 429.
22. Zhao, J.M., Zuo, Y., Li, D.Q., and Liu, Sh.Zh. (2004) Extraction and separation of cerium(IV) from nitric acid solutions containing thorium(IV) and rare earths(III) by DEHEHP. *J. Alloy. Compd.*, 374: 438.
23. Liao, W.P., Yu, G.H., and Li, D.Q. (2001) Solvent extraction of cerium(IV) and fluorine(I) from sulphuric acid leaching of bastnasite by cyanex923. *Solvent Extr. Ion Exc.*, 19 (2): 243.
24. Kassabov, G. and Al-Nimri, A.F. (1987) Influence of the temperature on the extraction of some lanthanides with 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5. *Monatsh. Chem.*, 118: 307.
25. Jordanov, V.M., Atanassova, M., and Dukov, I.L. (2002) Solvent Extraction of Lanthanides with 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5. *Sep. Sci. Technol.*, 37 (14): 3349.
26. Roy, A. and Nag, K. (1978) Solvent extraction behavior of rare earth ions with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone—II An examination of gadolinium break, tetrad effect, double-double effect and the relevance of "inclined-W" plot. *J. Inorg. Nucl. Chem.*, 40: 331.
27. Liu, J.M., Yang, R.D., and Ma, T.R. (1980) The reaction between 1-phenvl-3-methyl-4-benzoyl-pyrazalone-5 and Th(IV), rare earth elements (III) -studies of the extraction of rare earth elements and composition. *Chem. J. Chin. Univ.* (in Chinese) 1 (2): 23.
28. Li, D.Q., Ye, Zh.G., Ya, W.H., and Ou, H.F. (1995) *Rare Earths*; 2nd Ed.; Xu, G.X. (ed.), Metallurgy Industry Press: Beijing, 471.
29. Best, G.F., Hesford, E., and Mckay, H.A.C. (1959) Tri-n-butyl phosphate as an extracting agent for inorganic nitrates—VII: the trivalent actinide nitrates. *J. Inorg. Nucl. Chem.*, 12: 136.

30. Xu, G.X., Wang, W.Q., Wu, J.G., Li, B.L., Wu, G.B., and Shi, N. (1963) Extraction chemistry of nucleus fuel (I)—synergistic extraction of acidic chelate and nutral complexation. *Atom. Enge. Sci. Tech.* (in Chinese) 7: 487.
31. Pearson, R.G. (1963) Hard and soft acids and bases. *J. Am. Chem. Soc.*, 85 (22): 3533.
32. Ahrland, S., Chatt, J., and Davies, N.R. (1958) The relative affinities of ligand atoms for acceptor molecules and ions. *Quarl. Rev.*, 12: 265.