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Abstract: In this paper, the extractabilities of Cyanex 302 and purified Cyanex 302 (hereafter HBTMPTP or HA) in heptane have been compared by extracting the scandium, yttrium, lanthanum, and gadolinium from hydrochloric acid solutions. The roles of the different components in Cyanex 302 on lanthanum extraction have been analyzed. The result demonstrates that the Cyanex 302 has a higher extractability than HBTMPTP, which perhaps originates from the interaction among the components in Cyanex 302. Especially for R_3PO, obviously synergistic effect can be observed in the lower pH range and extraction mechanism of lanthanum using the mixture of HBTMPTP and TOPO has been deduced to be:

$$La(OH)^{2+} + (HA)_2 + B \Leftrightarrow La(OH)A_2 \cdot B + 2H^+$$

where $(HA)_2$ and B denote the dimeric form of HBTMPTP and TOPO, respectively. At the same time, the separation abilities of Cyanex 302 and HBTMPTP on the rare earth

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elements have been compared. Also, the effect of temperature on the extraction with Cyaenx 302, HBTMPTP and the mixture of HBTMPTP and TOPO has also been discussed with thermodynamic functions ΔH, ΔS, and ΔG calculated.

Keywords: Cyanex 302, HBTMPTP, TOPO, synergistic extraction, rare earths, separation

INTRODUCTION

Cyanex 302, a monothio analogues of Cyanex 272, is developed by CYTEC Canada Inc (1). It has been reported that this reagent was significantly more resistant toward decomposition by hydrolysis than its phosphoro analogues (2). Its commercial availability since the 1990s results in a lot of investigations into the solvent extraction of cadmium, zinc, cobalt, nickel, titanium(III), and other heavy metals (3–6). Moreover, some studies on rare earths show that Cyanex 302 has excellent extraction and separation properties (7–9). For example, its high pKa value (5.63) makes the stripping of rare earth ions easier, taking place at lower aqueous acidity than with D2EHPA (pKa = 2.79)or EHE/EHP (pKa = 3.24). Its higher average separation coefficients for heavy rare earth elements($\beta^{z+1/z}$ $_{\text{Gd-Lu}} = 3.44$)(8) in chloride media than Cyanax 272($\beta^{z+1/z}$ $_{\text{Gd-Lu}} = 2.44$)(10) demonstrate that Cyanex 302 would be a better extractant for extracting and separating rare earths than other organophosphorus extractants (6).

According to Sole et al. (11), Cyanex 302 consists of bis (2, 4, 4-trimethylpenty) monothiophosphinic acid (i.e. purified Cyanex 302, abbr. HBTMPTP: 78–80%), tris-alkylphosphine oxide(abbr. R_3PO:10–12%), bis (2,4,4-trimethylpentyl) phosphinic acid (i.e. Cyanex 272, abbr. HBTMPP:2–3%), bis (2,4,4-trimetylpentyl) dithiphosphinic acid(i.e. Cyanex 301: 1–2%), and other unknown components (8%). Therefore, there are possibilities that the extraction characters of HBTMPTP are different from that of Cyanex 302 and minor organophosphinic species in Cyanex 302 also may be operate on the extraction. The similar phenomenon has been reported by Freiser et al. (12) that the extractability of purified Di(2-ethylhexyl)dithiophosphoric(HDEHDTP) for Eu(III) is much lower than that of unpurified HDEHDTP, which is due to the effect of impurity (HDEHP). Furthermore, the synergistic effect of R_3PO and HBTMPTP on the Sc(III) extraction from sulfuric acid solutions has been investigated in earlier work (13). However, no information is available for the roles of minor organophosphinic species on the lanthanide extraction from chloride media with Cyanex 302. Therefore, it is of great significance to not only to contrast the extractabilities between Cyanex 302 and HBTMPTP,but also to analyze the function of different components of Cyanex302, further exploring the existence of a synergist helping to the enhancement of extractability, and to investigate the nature of the complexes extracted into the organic phase.

In this work, the extraction ability between Cyanex 302 and HBTMPTP for lanthanide in chloride media has been compared and the roles of different compounds in Cyanex 302 have been analyzed. Also, the extraction mechanism of lanthanide(take lanthanum as an example) with the mixture of HBTMPTP and R_3PO and the separation selectivity among the rare earth elements with Cyanex 302 or HBTMPTP have been studied.

EXPERIMENTAL

Reagents

The extractants, Cyanex 272(HBTMPP), Cyanex 301, Cyanex 302, TOPO (purity $> 97\%$), Cyanex 923, and Cyanex 925, were kindly supplied by CYTEC Canada Inc. Cyanex 272 and Cyanex 302 were purified by precipitation of copper salt (12) and cobalt salt (14), respectively. The purified Cyanex 302(99%) and Cyanex 272(99%) are a clear, viscous liquid. Cyanex 301, Cyanex 923, and Cyanex 925 were used without purification. According to the composition of Cyanex 302, n-heptane solution of R_3PO (TOPO, a pure tri-n-octylphosphinic oxide, Cyanex 923, a straight chain trialkylphosphinic oxide and a branched trialkylphosphinic oxide, Cyanex 925), HBTMPTP and HBTMPP, or mixed solutions of HBTMPTP with either R_3PO or HBTMPP, were prepared. N-heptane is of analytical grade.

The stock solutions of rare earth ions(III) were prepared by dissolving their oxide ($>99.9\%$) in hydrochloric acid and standardized by EDTA titration using xylenol orange as an indicator. The working solutions were made by appropriate dilution of the stock solutions.

Apparatus

A Shimadzu Model UV-365 spectrophotometer was adopted for measuring the concentration of rare earth ions(III) in the aqueous phase. A Model pHs-3C pH meter calibrated daily with 4.01 and 6.86 standard buffer solution was employed for measuring pH value in aqueous phase.

Methods

Equilibrium extraction experiments were performed as described previously (15). The ion strength μ in the aqueous phase had been maintained at $1.0\,\text{mol}\,l^{-1}$ by the addition of sodium chloride. Aqueous acidity had been adjusted by acetic acid – sodium acetate buffer solution. The concentration of rare earth ions(III) in the aqueous phase was determined by Arsenazo(III) method on spectrometer. The concentration of the rare earth ions(III) in the organic phase was obtained by mass balance. The distribution ratio, ***D***, was taken as the ratio of the concentration of rare earth ions(III) in the organic phase to that in the aqueous phase.

RESULTS AND DISCUSSION

The Comparisons of Extractability for Rare Earths in Cyanex 302 or HBTMPTP System

The comparison of extractability can be achieved by discussing the effect of aqueous pH and extractant concentration on the extraction. The effect of pH on the extraction illustrated in Fig.1 demonstrates that the extractability of Cyanex 302 is much higher than that of HBTMPTP for Sc, Y, La, and Gd(III). At constant pH value of 5.11, the effect of extractant concentration on the La(III) extraction is presented in Table 1. Also, it can be found that the Cyanex 302 has a higher extractability than HBTMPTP.

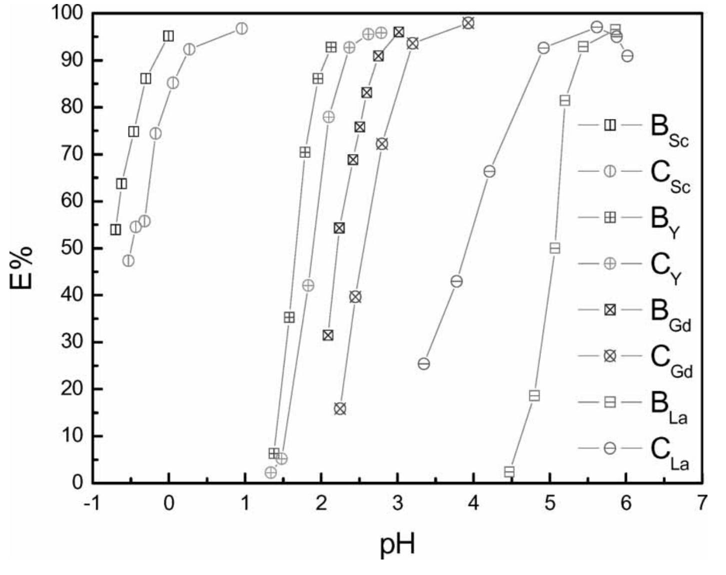

Figure 1. The effect of aqueous pH on the Sc, Y, La, and Gd(III) extraction with Cyanex 302 or HBTMPTP. $\mu = 1.0\,\text{mol l}^{-1}$. B_{Sc}.0.048M Cyanex 302, Sc(III) = 6.37×10^{-4}; B_Y.0.048M Cyanex 302, Y(III) = 3×10^{-4}M; B_{Gd}.0.048M Cyanex 302, Gd(III) = 3×10^{-4}M; B_{La}.0.048M Cyanex 302, La(III) = 3×10^{-4}M; C_{Sc}. 0.048M HBTMPTP, Sc(III) = 6.37×10^{-4}M; C_{Yc}. 0.048M HBTMPTP, Y(III) = 3×10^{-4}M; C_{Gd}. 0.048M HBTMPTP, Gd(III) = 3×10^{-4}M; C_{La}. 0.048M HBTMPTP, La(III) = 3×10^{-4}M.

Table 1. The effect of extractant concentration on the extraction of lanthanum

Extractant concentration ($mol\ l^{-1}$)	% Extraction (E)		Distribution coefficient (D)	
	Cyanex 302	[HBTMPTP]	Cyanex 302	[HBTMPTP]
0.013	11.3	0	0.3	0
0.024	39.8	7.6	0.66	0.077
0.034	66.3	21.6	2.18	0.199
0.044	79.0	31.6	3.70	0.43
0.056	85.2	48.4	6.05	0.89
0.08	92.4	72.8	17.52	2.65
0.12	98.0	90.2	37.7	9.2

La(III) $= 3 \times 10^{-4}$mol l^{-1}; $\mu = 1.0$ mol l^{-1}; pH = 5.11; t = 25°C.

Roles of the Different Components in Cyanex 302 for Lanthanum Extraction

According to the composition of Cyanex 302 (78–80% HBTMPTP, 10–12% R_3PO, 2–3% HBTMPP, 2% Cyanex301 and 8% unknown component), a series of solutions were prepared for discussing the effect of compounds in Cyanex 302 on the La(III) extraction.

The Effect of R_3PO on the La(III) Extraction

The effect of R_3PO on the lanthanum extraction can be observed in Fig 2. It can be shown that the extractability of R_3PO is very weak and nearly cannot extract lanthanum in the pH value less than 5.20 ranges. However, adulating it into HBTMPTP, it can be seen that the extraction percent has a significant enhancement, especially for TOPO. Therefore, we take TOPO as an example for the following studies on synergistic extraction.

Not only TOPO with HBTMPTP, but also TOPO in the presence of the mixture of HBTMPP and HBTMPTP, an improvement in extractability for lanthanum also can be observed. Defining the synergistic enhancement coefficient, *Q*, which is equal to $D_{123}/D_1 + D_2 + D_3$ (16), Table 2 clearly indicates that the TOPO together with HBTMPP and HBTMPTP has a higher synergistic effect on the lanthanum extraction, especially in the lower pH range and higher concentration of TOPO, which is mainly due to synergistic effect of TOPO with HBTMPTP.

The Effect of HBTMPP on the Lanthanum Extraction

Table 3 gives the values of synergistic enhancement coefficient for HBTMPP +HBTMPTP or HBTMPP +TOPO system. It can be seen that the mixture of

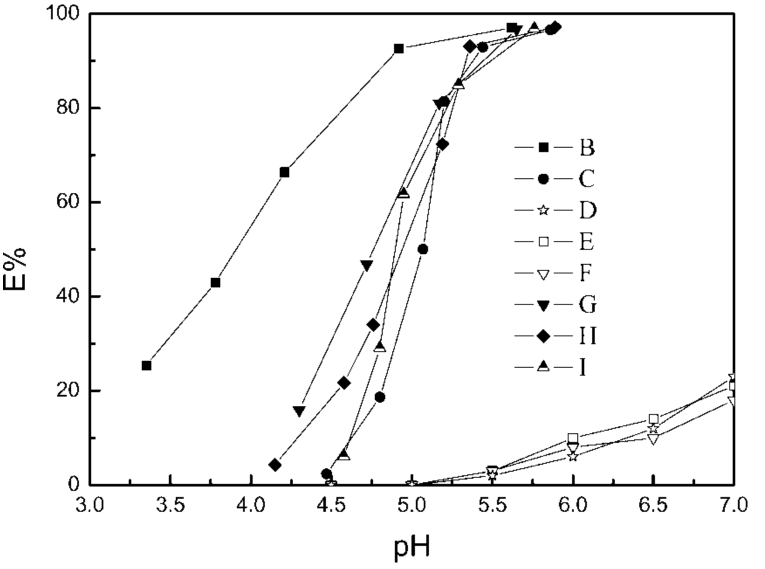

Figure 2. The effect of TOPO, Cyanex 923 and Cyanex 925 on the extraction. *B*. 0.048M Cyanex 302; *C*. 0.048M HBTMPTP; *D*. 0.0048M TOPO; *E*. 0.0048M Cyanex 925; *F*. 0.0048M Cyanex 923; *G*. 0.048M HBTMPTP + 0.0048M TOPO; *H*. 0.048M HBTMPTP + 0.0048M Cyanex 925; *I*. 0.048M HBTMPTP + 0.0048M Cyanex 923. $\mu = 1.0\,\text{mol l}^{-1}$; La(III) $= 3 \times 10^{-4}$M; t $= 25°$C.

HBTMPTP and HBTMPP has weak synergistic ability compared with the mixture of HBTMPTP and TOPO system. For the mixture system of HBTMPP and TOPO, there is no obviously synergistic effect on the lanthanum extraction, the similar phenomena has been reported by Saleh that the synergistic effect of TOPO with Cyanex 272 is found only at higher TOPO concentration and there is no synergistic effect of TOPO at lower concentration (17).

The Effect of Cyanex 301 and Unknown Compounds on the Extraction

Figure 3 presents the results that the extractability of Cyanex 301 is very weak and nearly cannot extract lanthanum alone in the selective concentration (0.001M). Putting the Cyanex 301 into the mixture of HBTMPTP, HBTMPP and TOPO, the extractability of lanthanum has no obvious change, which means the effect of Cyanex 301 on the extraction is very slight. At the same time, it can be found that the extractability of the mixture of HBTMPTP, HBTMPP, TOPO, and Cyanex 301 for lanthanum extraction is weaker than Cyanex 302, therefore, we can draw a conclusion

Table 2. The effect of the mixture of TOPO, HBTMPP, and HBTMPTP on the extraction equilibrium

pH	4.3	4.5	4.75	5.0	5.25	5.5
D_1(HBTMPTP)	0.011	0.03	0.22	1.06	2.84	14.4
D_2(HBTMPP)	0.0	0.0	0.0	0.29	1.45	2.82
D_3(TOPO)^a	0.0	0.0	0.0	0.0	0.0	0.03
D_3(TOPO)^b	0.008	0.07	0.11	0.15	0.2	0.29
D_{123}(HBTMPTP + HBTMPP + TOPO)^a	0.19	0.42	1.74	4.26	12.6	22.3
D_{123}(HBTMPTP + HBTMPP + TOPO)^b	0.48	1.98	3.30	6.64	16.8	35.6
$Q = D_{123(a)}/(D_1 + D_2 + D_3)$	17.3	14.0	7.91	3.16	2.94	1.29
$Q = D_{123(b)}/(D_1 + D_2 + D_3)$	25.3	19.8	11.0	4.42	3.74	2.06

[HBTMPTP] = 0.048M, [HBTMPP] = 0.0014M, $TOPO^a = 0.005\ mol\ l^{-1}$; $TOPO^b = 0.014\ mol\ l^{-1}$; $La(III) = 3 \times 10^{-4}\ mol\ l^{-1}$; $\mu = 1.0\ mol\ l^{-1}$.

that unknown compounds in Cyanex 302 also may be operating on the extraction process.

In short, in the process of lanthanum extraction from chloride media with Cyanex 302, the synergistic effect of R_3PO is the most prominent and minor organophosphinic acid also operates on the extraction.

Synergistic Extraction of La(III) with Mixture of HBTMPTP and TOPO

In order to further understand the synergistic effect of the HBTMPTP with R_3PO, we choose TOPO to study the synergistic extraction mechanism because the TOPO is a pure trialkylphosphine oxide. Taking into account there are only two kinds of anions in the aqueous phase, it can be deduced

Table 3. The effect of the mixture of HBTMPP and HBTMPTP on the extraction equilibrium

pH	4.5	4.75	5.0	5.13	5.5	5.75	6.0
D_1(HBTMPP)	0.0	0.0	0.29	0.48	2.82	9.55	30.2
D_2(HBTMPTP)	0.03	0.22	1.06	2.51	14.4	23.98	33.1
D_2(TOPO)	0.0	0.0	0.0	0.0	0.03	0.07	0.13
D_{12}(HBTMPP + HBTMPTP)	0.14	0.62	1.95	3.89	16.3	31.6	33.1
Q(HBTMPP + HBTMPTP)	4.67	2.82	1.44	1.30	0.95	0.74	0.52
D_{12}(HBTMPP + TOPO)	0.0	0.0	0.27	0.46	2.38	10.0	33.1
Q(HBTMPP + TOPO)	—	—	0.93	0.96	0.84	1.04	1.09

[HBTMPTP] = 0.048M, [HBTMPP] = 0.0014M, [TOPO] = 0.005M, $La(III) = 3 \times 10^{-4}\ mol\ l^{-1}$; $\mu = 1.0\ mol\ l^{-1}$.

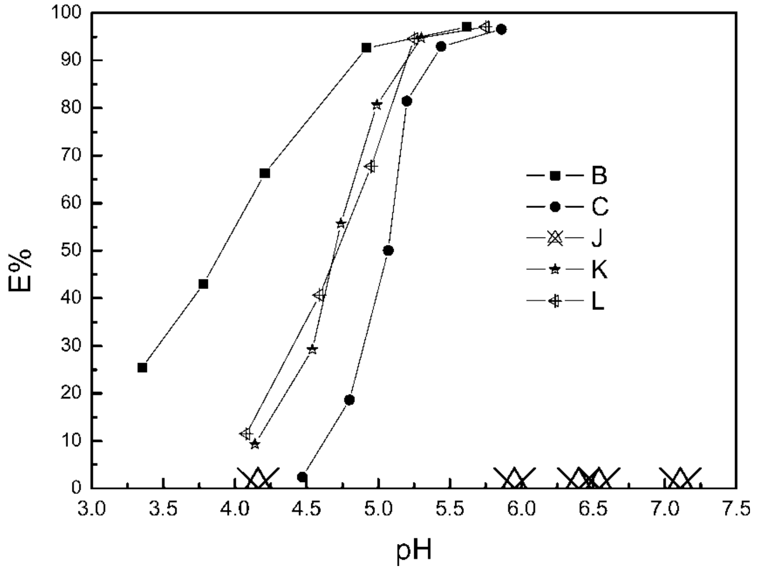

Figure 3. The effect of pH on the extraction for different components of Cyanex 302 La(III) $= 3 \times 10^{-4}$ M; $\mu = 1.0\,\mathrm{mol\,l^{-1}}$, t = 25°C. *B*. 0.048M Cyanex 302; *C*. 0.048M HBTMPTP; *J*. 0.001M Cyanex 301; *K*. 0.048M HBTMPTP + 0.0014M HBTMPP + 0.005M TOPO; *L*. 0.048M HBTMPTP + 0.0014M HBTMPP + 0.005M TOPO + 0.001M Cyanex 301.

that La^{3+} exists in the form of $LaCl_x^{(3-x)+}$ or $La(OH)_x^{(3-x)+}$ and the extraction of La^{3+} can be expressed as:

$$LaL_{x(a)}^{(3-x)+} + m(H_2A_2)_{(O)} + nB_{(O)} \xleftrightarrow{K_{12}} LaL_xA_{2m}B_{n(O)} + (3-x)H^+_{(a)} \quad (1)$$

where HA is

and $[(H_2A_2)]$ refers to the dimeric form of HBTMPTP (10), L denotes the OH^- or Cl^- and $LaL_x^{(3-x)+}$ is the hydroxyl or chloride complex of La (III) existed in aqueous solution. The subscript *(a)* and *(o)* denote aqueous phase and organic phase, respectively. K_{12} is the extraction equilibrium constant. When the temperature and ionic strength in the aqueous phase have been kept constant, the distribution ratio (D_{12}) of the mixed system should be:

$$\log D_{12} = \log K_{12} + (3-x)pH + m\log[(H_2A_2)] + n\log B \quad (2)$$

There is a relationship between the values of "x" and "m" as follows:

$$x = 3 - 2m \tag{3}$$

The dependences of the distribution ratio on the aqueous pH with the different concentration ratio of HBTMPTP and TOPO were given in Fig. 4. It presents the results that the distribution ratio increases with increasing pH and the slopes of the $\log D_{12}$ against pH plots trend to 2.0 in certain pH ranges, and this apparently indicates that two hydrogen ions are librated in forming the complex for the extraction system and the value of "x" is equal to 1. The dependence of the distribution ratio on the extractant concentration given as plots of $\log D_{12} - 2pH$ vs. $\log[H_2A_2]$ or log[TOPO] at constant aqueous pH in Fig. 5 indicates that 1 H_2A_2 and 1 TOPO molecule are attached to the synergistic species extracted into the organic phase, which means that at the mole fraction $X_{HA} = 0.5$ the maximal synergistic enhancement can be obtained and the value of "m" equal to 1.0 is consistent with the Eq.(3). According to the stability constant of La^{3+} with OH^- or Cl^-, it can be considered that OH^- is prone to take part in the extraction and Cl^- is barely extracted into organic phase, which has been confirmed by Wu et al (15). Thus, the

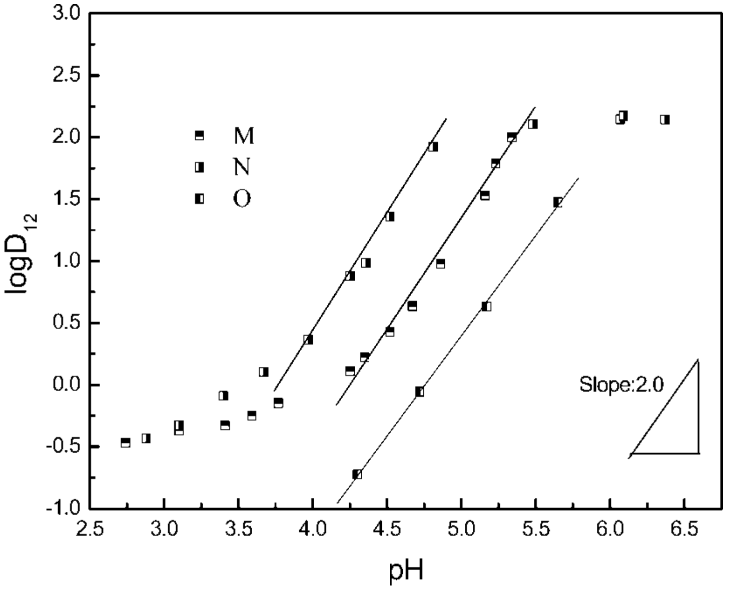

Figure 4. The effect of equilibrium pH on the extraction of La(III) with mixtures of TOPO and HBTMPTP. *M.* 0.01M TOPO + 0.04M HBTMPTP; *N.* 0.04M TOPO + 0.01M HBTMPTP; *O.* 0.005M TOPO + 0.05M HBTMPTP; La(III) = 3.0×10^{-4}M; $\mu = 1.0\,\mathrm{mol\,l^{-1}}$, t = 25°C.

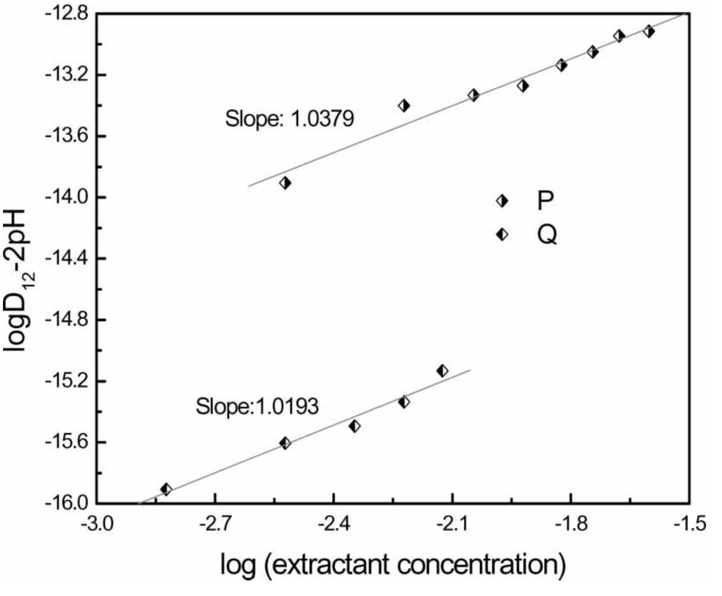

Figure 5. The effect of equilibrium extractant concentration on the extraction of La(III) with mixtures of HBTMPTP and TOPO. *P*. For HBTMPTP-La: [TOPO] $= 0.025\,\mathrm{mol/L}$, pH $= 4.91$, $\mu = 1.0\,\mathrm{mol\ l^{-1}}$, La (III) $= 3.0 \times 10^{-4}$M. *Q*. For TOPO-La: [HBTMPTP] $= 0.025\,\mathrm{mol/L}$, pH $= 4.91$, $\mu = 1.0\,\mathrm{mol\ l^{-1}}$, La (III) $= 3.0 \times 10^{-4}$M

extraction mechanism can be rewritten as:

$$La(OH)^{2+} + H_2A_2 + B \xleftrightarrow{K_{12}} La(OH)A_2 \cdot B + 2H^+ \qquad (4)$$

The equilibrium constant ($\log K_{ex}$) is calculated to be -9.4 ± 0.03 (Figs. 4 and 5).

The Comparison of Separation Selectivity among the Rare Earths with Cyanex 302 or HBTMPTP as an Extractant

If the values of $pH_{1/2}$ are used to compare the extraction ability and $\Delta pH_{1/2}$ for the separation selectivity, defining the separation factors, $\log\beta = 3\Delta pH_{1/2}$ (18), Table 4 clearly projects the results that the extractabilities increase with increasing aqueous pH and the order of extractabilities for Sc, Y, Gd and La(III) is Sc(III) $\gg$ Y(III) $>$ Gd(III) $\gg$ La(III) no matter with Cyanex 302 and with HBTMPTP as an extractant. More important, the separation factors(β) between these trivalent rare earths with HBTMPTP system is obviously higher than that of Cyanex 302 system, which means that separation selectivity of HBTMPTP is much superior to that of Cyanex 302. The β values

Table 4. The values of $pH_{1/2}$ and separation factors for rare earth ion extraction

Extractants	RE(III)	$pH_{1/2}$	$\Delta pH_{1/2(RE\text{-}Sc)}$	$\beta_{RE/Sc}$	$\Delta pH_{1/2(Re\text{-}Y)}$	$\beta_{RE/Y}$	$pH_{1/2(Gd\text{-}La)}$	$\beta_{Gd/La}$
Cyanex 302	Sc	−0.63	—	—	2.20	1.05E + 08	—	—
	Y	1.71	2.34	1.05E + 07	—	—	—	—
	Gd	2.23	2.86	3.8E + 08	0.52	36.3	1.64	8.32 E + 04
	La	3.87	4.5	3.16E + 13	2.16	3.02E + 07	—	—
HBTMPTP	Sc	−0.49	—	—	2.55	1.70E + 08	—	—
	Y	1.92	2.41	1.70E + 07	—	—	—	—
	Gd	2.59	3.08	1.74E + 09	0.67	102.3	2.44	2.09 E + 07
	La	5.03	5.52	3.63E + 16	3.11	2.14E + 09	—	—

Sc(III)= 6.37×10^{-4}, Y(III) = La(III) = Gd(III) = 3×10^{-4} M; $\mu = 1.0\,mol\,l^{-1}$; [Cyanex 302] = [HBTMPTP] = 0.048 M.

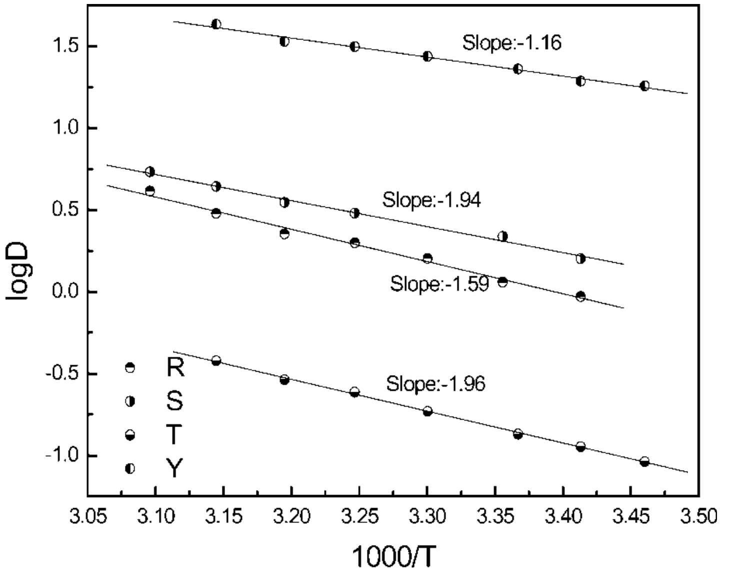

Figure 6. The effect of temperature on the extraction of La(III) with Cyanex 302, HBTMPTP and the mixture of HBTMPTP and TOPO. *R*. [Cyanex 302] = 0.048M, pH = 5.11, $La^{3+} = 3 \times 10^{-4}$M; $\mu = 1.0\,mol\ l^{-1}$; *S*. [HBTMPTP] = 0.035M, pH = 5.34, $La^{3+} = 3 \times 10^{-4}$M; $\mu = 1.0\,mol\ l^{-1}$; *T*. [HBTMPTP] = 0.025M, pH = 4.91,$La^{3+} = 3 \times 10^{-4}$M; $\mu = 1.0\,mol\,l^{-1}$; *Y*. [HBTMPTP] = [TOPO] = 0.025M, pH = 4.91, $La^{3+} = 3 \times 10^{-4}$M; $\mu = 1.0\,mol\ l^{-1}$.

of the Sc/Y, Y/Gd and Y/La pairs are also found to be comparable to the Cyanex 302 system. Therefore, it is possible that for all rare earth pairs the separation ability of HBTMPTP is better than that of Cyanex 302.

The Temperature Effect on the Lanthanum Extraction with Cyanex 302, HBTMPTP, and the Mixture of HBTMPTP and TOPO

The extractions of lanthanum from aqueous solution using Cyanex 302, HBTMPTP and the mixture of HBTMPTP and TOPO in heptane at varying temperatures between 288K and 323K were illustrated in Fig. 6. It has been found that the distribution coefficient increases with higher temperature in the all systems.

The enthalpy change(ΔH) of the extraction process was estimated from the temperature coefficient of extractability. This ΔH of extraction was obtained from the slope of the plot of $logD_{12}$ vs. 1000/T using Van't Hoff equation in the form:

$$logD_{12} = -\frac{\Delta H}{2.303R}\frac{1}{T} + C \qquad (5)$$

Table 5. Thermodynamic parameters in the different lanthanum extraction systems.

Extractant	ΔH(kJ/mol)	ΔG(kJ/mol)	ΔS(J/Kmol)
Cyanex 302[a]	31.0	93.6	−209.9
HBTMPTP[b]	37.3	58.8	−71.9
HBTMPTP + TOPO[c]	22.2	53.6	−105.4

La (III) = $3 \times 10^{-4}\,mol\,l^{-1}$; $\mu = 1.0\,mol\,l^{-1}$(a): pH = 5.11, [Cyanex 302] = 0.048 M; (b) pH = 5.34, [HBTMPTP] = 0.035 M (c) pH = 4.91, [TOPO]= [HBTMPTP] = 0.050 $mol\,l^{-1}$.

where R is the gas constant and C is a constant for a solution of constant ionic strength. The free energy change (ΔG) and the entropy change (ΔS) of the system are defined as follows:

$$\Delta G = -2.303RT\,\log K_{ex} \tag{6}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{7}$$

The thermodynamic values in the 289K to 323K temperature ranges are shown in Table 5. The positive values of ΔH mean that they are endothermic reactions. The positive values of free energy imply that reaction is nonspontaneous in the extraction of lanthanum. The less endothermic enthalpy for the synergistic extraction provides evidence of increased stabilization from enhanced covalency between the mixture of HBTMPTP and TOPO with La(III) in comparison with HBTMPTP alone. The negative values of ΔS shows that more order is introduced in the system upon metal extraction, that is, the disorder caused by metal ion dissociation is more than compensated for by the reduction of the number of particles brought about by the formation of the synergistic complex.

CONCLUSIONS

From the above mentioned, this study arrives at the following conclusions:

1. The extractability of Cyanex 302 for rare earth ions(III) has been weakened after purification. The elimination of R_3PO has been considered to be primary reason.
2. The mixture of HBTMPTP and TOPO has an obviously synergistic effect on lanthanum extraction. The largest synergistic enhancement can be obtained at mole fraction $X_{HBTMPTP} = 0.5$ and the corresponding extracted species in the organic phase are proposed to be $La(OH)A_2 \cdot B$.
3. The separation selectivity among the rare earth elements with HBTMPTP as an extractant is superior to that of Cyanex 302, which means that

HBTMPTP system would be of practical value for mutual separation of rare earths.

4. The temperature dependence of distribution coefficient gives apparent positive enthalpy change and free energy change, which means that the extraction reaction is endothermic and nonspontaneous. The negative values of ΔS shows that more order is introduced in the system upon metal extraction.

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