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THE EXTRACTION OF Fe^{3+} AND La^{3+} BY SYNERGETIC EFFECTS OF TBP AND *p*-*TERT*-BUTYLCALIX[8]ARENE OCTACARBOXYLIC ACID

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ABSTRACT

The extraction of Fe^{3+} and La^{3+} with *p*-*tert*-butylcalix[8]arene octacarboxylic acid (H_8L) and tributyl phosphate (TBP) was studied at 30 ± 1°C and ionic strength of 0.1. Fe^{3+} and La^{3+} are highly extractible with H_8L; $Fe^{3+} > La^{3+}$. The results showed that TBP had a significant synergetic effect on the extraction of Fe^{3+} by H_8L. By the slope method, the extraction mechanism is given as $Fe^{3+} + H_8L_{(O)} + 2TBP_{(O)} = (TBP)_2Fe\ H_5L_{(O)} + 3H^+$. The equilibrium constant of the extraction reaction was $\log K\text{ex}_{(s)} = 4.68 \pm 0.12$. However, TBP showed no synergetic effect on the extraction of La^{3+} with H_8L.

Key Words: Synergetic extraction; TBP; Calixarene; Iron; Lanthanum

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INTRODUCTION

Due to their special properties, calixarenes can form host-guest complexes with both neutral guest molecules and ions (1). As a relatively new generation of macrocyclic compounds (compared with cyclodextrins and crown ethers), calixarenes will play an important role in the fields of ion transportation, chemical sensors, separation and analysis of noble and rare metals, selective ion electrodes, molecule inclusion and recognition, molecular catalysis, and enzyme simulation (2–5). The coordination chemistry of calixarenes (6–9) has been rapidly developed in recent years. A great deal of attention has been paid to the extraction studies of transition metals and lanthanides with calixarenes (10–15). The recent research may provide new methods of separation and purification for the rare earth elements and information on supramolecular chemistry. In contrast to a number of reports on the solvent extraction of metal ions with calixarenes, reports on the synergetic effect between calixarenes and other extractants have been very limited. We studied the synergetic extraction of Fe^{3+} and La^{3+} with *p-tert*-butylcalix[8]arene octacarboxylic acid (H_8L) and tributyl phosphate (TBP) for the high-efficiency separation of lanthanum from various impurities.

EXPERIMENTAL

Figure 1 illustrates the formula of *p-tert*-butylcalix[8]arene octacarboxylic acid (H_8L). H_8L was synthesized according to procedures outlined in the literature. The characteristics of H_8L are as follows: The melting point is 255–256°C; the infrared (IR) spectra (KBr) peaks are located at 1737 cm^{-1} and (Br, OH) 2700–3600 cm^{-1}; ^1H NMR δ [$(CD_3)_2SOCDCl_3$] values are 6.96 (16H, s, ArH), 2.87–4.07 (32H, Br, $ArCH_2Ar$, CH_2COOH), and 1.15 (72H, s, CMe_3). These data are in good agreement with the results cited in the literature (16). IR spectra were recorded on a Nicolet-170 SXFT spectrometer and ^1H NMR spectra were determined on a Bruker AM500 (MHz) spectrometer.

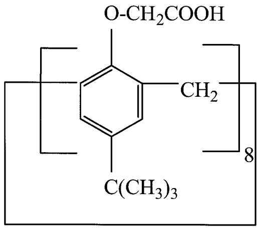

Figure 1. The formula of *p-tert*-butylcalix[8]arene octacarboxylic acid (H_8L).

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Table 1. Extractabilities of Fe^{3+} with H_8L

pH	3.15	3.31	3.55	3.76
E(%)	70.8	76.4	80.9	83.8

$C^0_{H_8L} = 1.11 \times 10^{-4}$ mol/L; $C^0_{Fe} = 1.196 \times 10^{-4}$ mol/L; $\mu = 0.1$; 30°C for 1 hour

The extractor solution was prepared by dissolving H_8L in chloroform at refluxing temperature. Chloroform was purified by distillation before use. Ion exchanged and redistilled water was used for the aqueous solution of $Fe(NO_3)_3$ and $La(NO_3)_3$. The pH of the aqueous solution was buffered with CH_3COONa/CH_3COOH, and ionic strength (μ) was adjusted to 0.1 with KNO_3. At equal phase volumes of 10 mL, the extraction experiments were carried out in stopped flasks at 30 ± 1°C and $\mu = 0.1$. The flasks containing the 2 phase system were subsequently placed on a shaker and shaken until the extractability was not affected by further shaking, indicating that equilibrium had been attained. The concentrations of metal cations in aqueous solution were determined by the spectrophotometric method on a UV/VIS Spectrometer Lambda Bio 40 (Perkin Elmer Co). Arsenazo III was used as a color reagent for La^{3+} ($\lambda_{max} = 650$ nm) and *o*-phenanthroline for Fe^{3+} ($\lambda_{max} = 510$ nm). The extractabilities (Ex%) were determined from the decrease of metal concentration in the aqueous phase after the extraction.

RESULTS AND DISCUSSION

Comparison of the Extractabilities of Fe^{3+} and La^{3+} with H_8L

The extractabilities of Fe^{3+} and La^{3+} with H_8L under different pH values are listed in Tables 1 and 2. The results indicate that H_8L was a more efficient extractor of Fe^{3+} than La^{3+}, and equilibrium for the extraction of Fe^{3+} was reached more quickly than it was for La^{3+}. Furthermore, the extractabilities of both cations increased with increased pH in aqueous solution.

Table 2. Extractabilities of La^{3+} with H_8L

pH	3.40	3.61	3.93	4.23
E(%)	55.8	58.7	64.8	69.4

$C^0_{H_8L} = 1.11 \times 10^{-4}$ mol/L; $C^0_{La} = 1.214 \times 10^{-4}$ mol/L; $\mu = 0.1$; 30°C for 12 hours

Table 3. The Effect of TBP on the Extraction of Fe^{3+} with H_8L

C^0_{TBP} (10^{-4} mol/L)	0	1.60	2.41	3.21	4.01
D	0.706	0.782	0.986	1.30	1.78
D_s		0.076	0.28	0.594	1.07

$C^0_{H_8L} = 1.24 \times 10^{-4}$ mol/L; $C^0_{Fe} = 1.196 \times 10^{-4}$ mol/L; pH = 2.63; $\mu = 0.10$; 30°C for 1 hour

The Synergetic Effect of TBP on the Extraction of Fe^{3+} and La^{3+} with H_8L

Table 3 shows the distribution ratios of Fe^{3+} under different TBP concentrations and the fixed initial concentration of H_8L and the pH of the solution. $D_s = D - D_0$, where D represents the total distribution ratio and D_0 is the sum of distribution ratios of Fe^{3+} when either H_8L or TBP was used under the same experimental conditions. Table 4 shows the effect of TBP on the extraction of La^{3+} with H_8L.

The results of Tables 3 and 4 show that TBP had a significant synergetic effect on the extraction of Fe^{3+} with H_8L but not on La^{3+} extraction. Furthermore, TBP extracted nearly no Fe^{3+} when only TBP was used under the conditions listed in Table 3.

The Synergetic Mechanism of TBP on the Extraction of Fe^{3+} with H_8L

Theory

For further understanding the synergetic effect of TBP on the extraction of Fe^{3+} with H_8L, the following extraction reaction was considered (17)

$$M^{3+} + H_8L_{(O)} + k\,TBP_{(O)} = (TBP)_k\,M\,H_{8-m}L_{(O)} + mH^+ \tag{1}$$

and the conditional equilibrium constant K_s can be expressed as

$$K_s = \frac{[(TBP)_kMH_{8-m}L_{(O)}][H^+]^m}{[M^{3+}][H_8L_{(O)}][TBP_{(O)}]^k} \tag{2}$$

Table 4. The Effect of TBP on the Extraction of La^{3+} with H_8L

C^0_{TBP} (mol/L)	0	0.0010	0.0080	0.016	0.041
D	0.63	0.62	0.61	0.61	0.63

$C^0_{H_8L} = 6.54 \times 10^{-5}$ mol/L; $C^0_{La} = 1.214 \times 10^{-4}$ mol/L; 30°C for 12 hours

The distribution ratio of the synergetic extraction D_s is

$$D_s = \frac{[(\mathrm{TBP})_k\mathrm{MH}_{8-m}\mathrm{L}_{(O)}]}{[\mathrm{M}^{3+}]}$$

By substituting D_s into Eq. (2) and calculating the logarithm of each side of Eq. (2), one gets

$$\log K_s = \log D_s + m \log [\mathrm{H}^+] - \log [\mathrm{H_8L}]_{(O)} - k \log [\mathrm{TBP}]_{(O)} \quad (3)$$

The relationships between the equilibrium concentration $[\mathrm{H_8L}]_{(O)}$, $[\mathrm{TBP}]_{(O)}$, and the initial concentrations $C^0_{\mathrm{H_8L}}$, C^0_{TBP}, and C^0_{Fe} are

$$[\mathrm{H_8L}]_{(O)} = C^0_{\mathrm{H_8L}} - \frac{D}{D+1} C^0_{\mathrm{Fe}} \quad (4)$$

$$[\mathrm{TBP}]_{(O)} = C^0_{\mathrm{TBP}} - \frac{D}{D+1} kC^0_{\mathrm{Fe}} \quad (5)$$

Due to the influence of subsidiary reaction coefficients on D_s, the actual equilibrium distribution ratio D_{ex} becomes $D_s\alpha$. Here, α denotes the subsidiary reaction coefficients and is related to the subsidiary reactions caused by the anions OH^- and Ac^-. When the values of $C^0_{\mathrm{H_8L}}$ and pH are fixed, $\log \alpha$ will remain constant. D_0 did not change under different C^0_{TBP}. So the actual equilibrium constant $K\mathrm{ex}_{(S)}$ and the corresponding $\log \mathrm{Kex}_{(S)}$ can be expressed as

$$\log K\mathrm{ex}_{(S)} = \log D\mathrm{ex}_{(S)} + m \log [\mathrm{H}^+] - \log [\mathrm{H_8L}]_{(O)} - k \log [\mathrm{TBP}]_{(O)} \quad (6)$$

A linear relationship exists in the plot of $\log D\mathrm{ex}_{(S)}$ vs. $\log [\mathrm{TBP}]_{(O)}$. Because the concentration difference between $C^0_{\mathrm{H_8L}}$ and $\mathrm{C}^0_{\mathrm{Fe}}$ was not big enough, $D\mathrm{ex}_{(S)}$ was rectified. The equation

$$D'\mathrm{ex}_{(s)} = \frac{C^0_{\mathrm{H_8L}}}{[\mathrm{H_8L}]_{(O)}} \times D_s \times \alpha$$

was used to plot $\log \mathrm{D}'\mathrm{ex}_{(S)}$ vs. $\log [\mathrm{TBP}]_{(O)}$.

The relationship of $\log D'\mathrm{ex}_{(S)}$ vs. $\log [\mathrm{H_8L}]_{(O)}$ is described by the equation

$$D'\mathrm{ex}_{(s)} = \left[\frac{C^0_{\mathrm{TBP}}}{[\mathrm{TBP}]_{(O)}}\right]^k \times D_s \times \alpha$$

which was used to plot $\log D'\mathrm{ex}_{(S)}$ vs. $\log [\mathrm{H_8L}]_{(O)}$. α will remain constant while pH is fixed. Through the use of

$$D'_s = \frac{C^0_{\mathrm{H_8L}}}{[\mathrm{H_8L}]_{(O)}} \times D_s$$

and

$$D'_s = \left[\frac{C^0_{\mathrm{TBP}}}{[\mathrm{TBP}]_{(O)}}\right]^k \times D_s$$

Table 5. The H_8L and TBP Synergetic Extraction of Fe^{3+} at Different TBP Concentrations

C^0_{TBP} (10^{-4} mol/L)	0	1.60	2.41	3.21	4.01
D	0.706	0.782	0.986	1.30	1.78
D_s		0.076	0.28	0.594	1.07
$\log D'_s$		−0.880	−0.270	0.115	0.447
$\log\,[TBP]_{(O)}$		−4.26	−3.91	−3.73	−3.61

$C^0_{TBP} = 1.24 \times 10^{-4}$ mol/L; $C^0_{Fe} = 1.196 \times 10^{-4}$ mol/L; pH = 2.63; $\mu = 0.10$; 30°C for 1 hour

instead of $D'\mathrm{ex}_{(s)}$, the plots of $\log D'_s$ vs. $\log\,[TBP]_{(O)}$ and $\log D'_s$ vs. $\log[H_8L]_{(O)}$ can be obtained. Through the equation

$$D'\mathrm{ex}_{(s)} = \left[\frac{C^0_{H_8L}}{[H_8L]_{(O)}}\right] \times \left[\frac{C^0_{TBP}}{[TBP]_{(O)}}\right]^k \times D_s \times \alpha$$

The relationship of $\log D'\mathrm{ex}_{(s)}$ vs. pH can be obtained by the plot of $\log D'\mathrm{ex}_{(s)}$ vs. pH. The equilibrium constants of the synergetic extraction can be calculated from Eq. (6).

Mechanism of Synergetic Extraction

Table 5 and Fig. 2 show the results of the synergetic extraction of Fe^{3+} by H_8L at different TBP concentrations when $C^0_{H_8L}$ and pH were fixed. The plot of $\log D'_s$ vs. $\log\,[TBP]_{(O)}$ is a straight line with a slope of 2, and a correlation coefficient of $R^2 = 0.991$, indicating that the ratio of Fe^{3+} to TBP in the extract is 1:2.

Table 6 and Fig. 3 show the results of the synergetic extraction of Fe^{3+} by H_8L at different H_8L concentrations when C^0_{TBP} and pH were fixed. The plot of

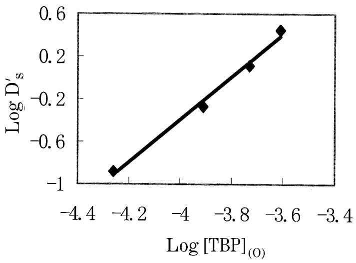

Figure 2. H_8L and TBP synergetic extraction of Fe^{3+} at different TBP concentrations.

Table 6. The H_8L and TBP Synergetic Extraction of Fe^{3+} at Different H_8L Concentrations

$C^0_{H_8L}$ (10^{-4} mol/L)	0.896	1.24	1.79	2.69
D	1.19	1.73	2.86	4.35
D_0	0.487	0.706	1.16	1.87
D_s	0.703	1.02	1.70	2.48
log D'_S	0.188	0.412	0.737	0.971
log $[H_8L]_{(O)}$	−4.61	−4.32	−4.04	−3.76

$C^0_{TBP} = 4.01 \times 10^{-4}$ mol/L; $C^0_{Fe} = 1.196 \times 10^{-4}$ mol/L; pH = 2.63; $\mu = 0.10$; 30°C for 1 hour. D_0 is the distribution ratio when no TBP exists in the organic phase under the same conditions as when it is present.

log D'_s vs. log $[H_8L]_{(O)}$ is a straight line with a slope of 1 and correlation coefficient of $R^2 = 0.994$, indicating that the ratio of Fe^{3+} to H_8L in the extract is 1:1.

Table 7 and Fig. 4 show the results of the synergetic extraction of Fe^{3+} with H_8L and TBP at different pH values when C^0_{TBP} and $C^0_{H_8L}$ were fixed.

The plot of log $D'ex_{(s)}$ vs. pH is a straight line with a slope of 3 and correlation coefficient of $R^2 = 0.988$, suggesting that 3 H^+ were displaced from H_8L by Fe^{3+}.

According to the above results, the synergetic extraction equation can be expressed as

$$Fe^{3+} + H_8L_{(O)} + 2\ TBP_{(O)} = (TBP)_2\ Fe\ H_5L_{(O)} + 3H^+ \qquad (7)$$

The corresponding equilibrium constants of the synergetic extraction were obtained from Eq. (7) and Table 5 and are listed in Table 8.

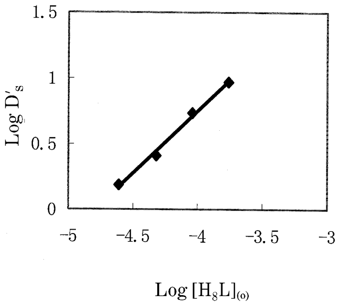

Figure 3. The synergetic H_8L and TBP extraction of Fe^{3+} at different H_8L concentrations.

Table 7. H_8L and TBP Synergetic Extraction of Fe^{3+} at Different pH Values

pH	2.58	2.80	2.97	3.15
D	1.75	2.59	4.04	4.58
D_0	0.695	1.36	1.86	2.53
D_s	1.06	1.23	2.18	2.05
log α	0.683	0.999	1.20	1.51
log $D'ex_{(S)}$	1.53	2.09	2.74	3.09

$C^0_{TBP} = 4.01 \times 10^{-4}$ mol/L; $C^0_{H_8L} = 1.24 \times 10^{-4}$ mol/L; $C^0_{Fe} = 1.196 \times 10^{-4}$ mol/L; $\mu = 0.10$; 30°C for 1 hour. D_0 is the distribution ratio when no TBP exists in the organic phase under the same other conditions as when it is present.

The Difference of Synergetic Effect of TBP and H_8L on Lanthanum and Iron Ions

As a host, H_8L usually can provide 8 possible coordination sites to guest ions. The size of the cavity formed by the upper rim of H_8L, the part containing carboxyl groups, has a close correlation with the coordination numbers of the related complexes. The lanthanum ion with a radius of 0.115 nm is much bigger than the iron ion with a 0.064-nm diameter. Lanthanum might be included in the coordination space of the upper rim of H_8L to satisfy the 8 coordinating sites, which results in the inability of TBP to take part in the synergetic extraction of lanthanum ions with H_8L.

Fe^{3+}, with a relatively smaller size of radius, usually has a coordination number of 6 and cannot combine with all the possible coordination carboxyl groups of H_8L. Some H_8L carboxyl groups may be close to Fe^{3+} and form coordination bonds, while other carboxyl groups may be distant from Fe^{3+} and left

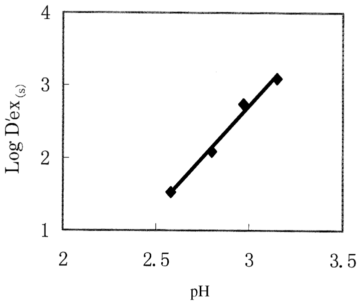

Figure 4. The H_8L and TBP synergetic extraction of Fe^{3+} at different pH values.

Table 8. Equilibrium Constants of the Synergetic Extraction

log D_s	0.447	0.115	−0.270	−0.88
log α	0.690	0.690	0.690	0.690
pH	2.63	2.63	2.63	2.63
log $[H_8L]_{(O)}$	−4.32	−4.25	−4.19	−4.15
log $[TBP]_{(O)}$	−3.61	−3.73	−3.91	−4.26
log $Kex_{(S)}$	4.78	4.62	4.56	4.59

log $Kex_{(S)} = 4.68 \pm 0.12$

in an uncoordinated state. Three carboxyl groups of H_8L may replace the coordination water molecules in the hydrated iron ion, and TBP may also occupy 2 coordination sites, displacing water molecules, but the last coordination site of the iron ion may still be satisfied with a water molecule. Because TBP has relatively low polarity and a higher solubility in the organic phase, the synergistically applied TBP and H_8L will effectively increase the total extractability of Fe^{3+}.

Size is not the only factor to affect the stability of the complexes. Because Fe^{3+} has a higher charge/radius ratio than does La^{3+}, it usually showed a stronger tendency to form a stable complex when the coordination space of the extractant species is sufficient for complexation. H_8L has sufficient space to include La^{3+} or Fe^{3+} ions and the charge/radius ratio was the main factor affecting complex stability. The cavity size of H_8L might become an important factor for metal ion extraction. The relatively bigger size cavity of H_8L for Fe^{3+} ions may allow TBP molecules to participate in the synergetic extraction, but La^{3+} may be excluded from the complex.

CONCLUSIONS

The conclusion can be summarized in 3 points. First, *p-tert*-butylcalix[8]arene octacarboxylic acid (H_8L) can effectively extract both Fe^{3+} and La^{3+} into the organic phase from acidic aqueous solution, and the extractability of Fe^{3+} is significantly higher than it is for La^{3+}. Second, TBP has a significant synergetic effect on the extraction of Fe^{3+} with H_8L but not of La^{3+}. Finally, the mechanism of synergetic extraction can be given as

$$Fe^{3+} + H_8L_{(O)} + 2\ TBP_{(O)} = (TBP)_2\ Fe\ H_5L_{(O)} + 3H^+$$

The corresponding equilibrium constant of this synergetic extraction is log $Kex_{(S)} = 4.68 \pm 0.12$ under 30 ± 1°C and $\mu = 0.1$.

NOMENCLATURE

Symbols

E	extractability
D	total distribution ratio, i.e., the total concentration of metal ions in the organic phase to that in aqueous phase
D_0	blank distribution ratio (amount extracted by TBP plus amount extracted by H_8L)
D_s	distribution ratio due to the synergetic extraction
$C^0_{H_8L}$, C^0_{TBP}, and C^0_{Fe}	the initial concentrations of H_8L, TBP, and Fe^{3+}
K_s	conditional equilibrium constant of the synergetic extraction
$K\mathrm{ex}_{(s)}$	the actual equilibrium constant that accounts for the effect of the subsidiary reaction
$D\mathrm{ex}_{(s)}$	the actual distribution ratio that results from the effect of the subsidiary reaction

Greek Letters

μ	ionic strength
α	subsidiary reaction coefficient

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