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Synergistic extraction of U(VI) and Th(IV) from nitric acid media with HBMPPT and TBP in toluene

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Abstract The synergistic extraction of U(VI) and Th(IV) from nitric acid solution by HBMPPT (4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione) and TBP (tributylphosphate) in toluene was studied. The extraction ability of HBMPPT for U(VI) and Th(IV) was not so high, but when a little TBP was added in, the ability to extract U(VI) and Th(IV) was improved. The extracted complexes may be presented as $UO_2NO_3 \cdot BMPPT \cdot TBP$ and $UO_2(BMPPT)_2 \cdot TBP$ for U(VI), and $Th(NO_3)_3 \cdot BMPPT \cdot TBP$ and $Th(NO_3)_2 (BMPPT)_2 \cdot TBP$ for Th(IV), respectively, in the synergistic extraction system. The synergistic effect of HBMPPT and TBP makes the separation coefficient of U(VI) /Th(IV) or U(VI)/Eu(III) reach a high value.

Keywords U/Th separation, Synergistic extraction

1 Introduction

The extraction of An(III) and Ln(III) from aqueous solution with HBMPPT and TOPO were studied by some authors.[1~5] Under certain conditions, the synergistic effect between HBMPPT and TOPO is able to make An(III) and Ln(III) reach a high separation coefficient. As far as the extraction of Lanthanide and Actinide is concerned, HBMPPT is a very useful extraction agent. The synergistic extraction of U(VI) and Th(IV) from aqueous solution with HBMPPT and TBP has not been studied as yet, so we here report the synergistic extraction of U(VI) and Th(IV) in nitric acid media with HBMPPT and TBP in toluene.

2 Experimental

2.1 Materials

Uranyl nitrate solution and thorium nitrate solution were obtained by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ and $Th(NO_3)_4 \cdot 6H_2O$ (AR grade) in nitric acid solution and were standardized by the volumetric analysis. The synthesis and properties of HBMPPT were described in a previous paper.[6] TBP, toluene and other reagents adopted are all of analytical reagent grade.

2.2 Distribution determination

The extraction procedures were as follows: 5 mL of the aqueous phase containing a certain amount of U(VI) or Th(IV) and HNO_3 was shaken for 15 min with 1 mL of the organic phase containing a given concentration of HBMPPT and TBP. The diluent was toluene. Sample of aqueous phase was analyzed immediately after the phase separation by means of the arsenazo(III) spectro-photometric method, and the concentration of U(VI) or Th(IV) in organic phase was obtained by calculating $[M]_{a,i}$-$[M]_{a,e}$ ($[M]_{a,i}$ is the initial concentration of U(VI) or Th(IV) in the aqueous solution, and $[M]_{a,e}$ is concentration of U(VI) or Th(IV) in the aqueous solution after equilibrium). The distribution ratio was calculated.[6,7] The pH of the aqueous solution was measured after equilibrium. The

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experimental temperature was controlled at 25±2°C.

3 Results and discussion

3.1 Extraction of U(VI) and Th(IV) with HBMPPT or TBP

The extraction of U(VI) and Th(IV) with TBP was described by some authors[8], and the extraction complexes was presented as $UO_2(NO_3)_2 2TBP$ or $Th(NO_3)_4 2TBP$. From our previous paper[6,7], the extraction complexes of UO_2^{2+} (or Th^{4+}) with HBMPPT were presented as $UO_2NO_3 \cdot BMPPT$ and $UO_2(BMPPT)_2$ for U(VI), and $Th(NO_3)_3 \cdot BMPPT$ and $Th(NO_3)_2(BMPPT)_2$ for Th(IV), respectively.

3.2 Synergistic figure of U(VI) with HBMPPT and TBP

The initial acidity in aqueous solution was pH=2.04 and a constant ion-strength of 0.1mol/L was maintained by adding NH_4NO_3. The synergistic figure is shown in Fig.1. Under this condition, a little TBP makes the extraction ability of HBMPPT to be improved rapidly. From the experimental result, 0.01-0.03 mol/L TBP makes the ability of HBMPPT to extract U(VI) reach the highest. In this experiment, we chose $[TBP]_{(o)}=0.01$mol/L as the synergistic reagent.

Under the experimental conditions, it has no extraction ability of U(VI) and Th(IV) when HBMPPT or TBP was used alone($D_1=0$, $D_2=0$). Hence, the determined distribution ratio of Th(IV) is the synergistic extraction distribution ratio($D = D_{12} + D_1 + D_2 = D_{12}$).

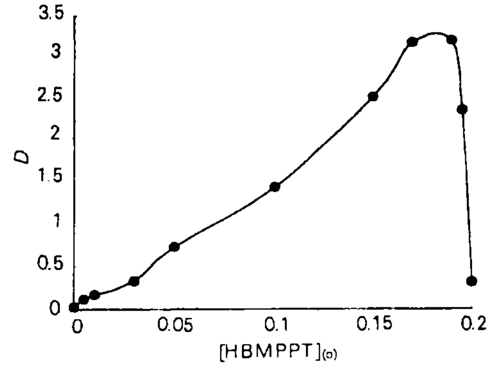

Fig.1 Distribution ratio of U(VI) as a function of the extractant concentration ($[BMPPT]_{(O)}+[TBP]_{(O)}=0.20$ mol/L) in toluene at 25°C; $[UO_2^{2+}]_{(a)}=5.48\times10^{-4}$ mol/L, pH=2.04, $[NH_4NO_3]_{(a)}=0.1$ mol/L

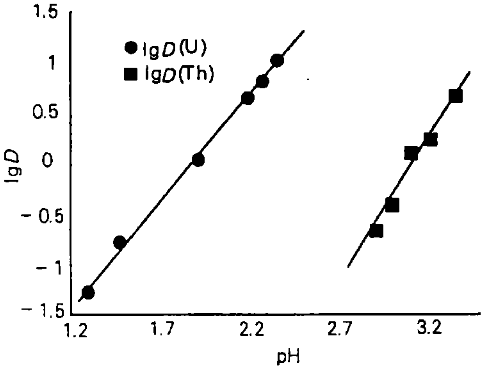

Fig.2 Distribution ratios of U(VI) and Th(IV) as function of aqueous pH at 25°C, $[UO_2^{2+}]_{(a)}=5.48\times10^{-4}$mol/L, $[Th^{4+}]_{(a)}=5.68\times10^{-4}$mol/L, $[BMPPT]_{(O)}=0.10$ mol/L, $[TBP]_{(O)}=0.01$ mol/L, $[NH_4NO_3]_{(a)}=0.1$ mol/L

3.3 Synergistic extraction of U(VI) and Th(IV) with HBMPPT and TBP

3.3.1 Effect of pH on the distribution ratio of U(VI) and Th(IV). The dependence of distribution ratio of U(VI) and Th(IV) on pH in aqueous solution with HBMPPT and TBP in toluene is shown in Fig.2. The distribution ratios of U(VI) and Th(IV) increase with the increase of pH. The relationship of lgD_U-pH and lgD_{Th}-pH is linear with the slopes of 1.52 and 1.53.

3.3.2 Effect of TBP concentration on the distribution ratio. The distribution ratios of U(VI) and Th(IV) increase with the increase of TBP concentration (Fig.3). The relationship of lg$D$ *vs* lg$[\mathrm{TBP}]_{(o)}$ is linear with the slope of 0.25 and 0.28 for U(VI) and Th(IV), respectively. This result suggests that the extracted complexes may contains 0 or 1 TBP molecule, which means that only part of U(VI) and Th(IV) form the synergistic extraction complex with HBMPPT and TBP under the experimental condition.

3.3.3 Effect of HBMPPT concentration on the distribution ratio. The dependence of lgD *vs* lg$[\mathrm{HBMPPT}]_{(o)}$ is plotted in Fig.4. The distribution ratios of U(VI) and Th(IV) increase with the increase of HBMPPT concentration. The relationship of lg$D$-lg$[\mathrm{HBMPPT}]_{(o)}$ is linear with the slopes of 1.62 and 1.50 for U(VI) and Th(IV), respectively.

From the slope of lg$D$ *vs* pH, the extraction mechanism seems complexes. Under normal condition, the slope is a whole number. If there are more than 2 complexes in the organic phase, the slope will not be a whole number. Smith *et al.* have discussed this question in his paper[1].

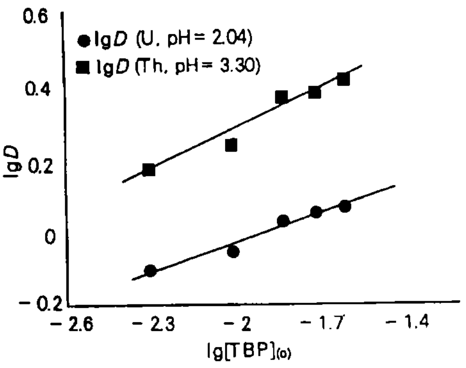

Fig.3 Distribution ratios of U(VI) and Th(IV) as a function of lg[TBP] at 25°C, $[\mathrm{UO_2^{2+}}]_{(a)}=5.48\times10^{-4}$ mol/L, $[\mathrm{Th^{4+}}]_{(a)}=5.68\times10^{-4}$ mol/L, $[\mathrm{HBMPPT}]_{(O)}=0.10$ mol/L, $[\mathrm{NH_4NO_3}]_{(a)}=0.1$ mol/L

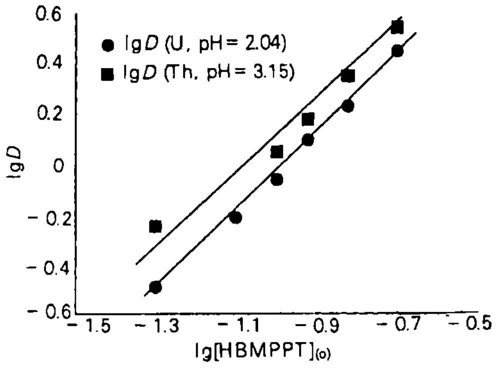

Fig.4 Distribution ratios of U(VI) and Th(IV) as a function of lg$[\mathrm{HBMPPT}]_{(o)}$ at 25°C, $[\mathrm{UO_2^{2+}}]_{(a)}=5.48\times10^{-4}$ mol/L, $[\mathrm{Th^{4+}}]_{(a)}=5.68\times10^{-4}$ mol/L, $[\mathrm{TBP}]_{(o)}=0.10$ mol/L, $[\mathrm{NH_4NO_3}]_{(a)}=0.1$ mol/L

Based on the values obtained, the extraction process may form the following synergistic extraction complexes presented as $\mathrm{UO_2NO_3{\cdot}BMPPT{\cdot}TBP}$ and $\mathrm{UO_2(BMPPT)_2{\cdot}TBP}$ for U(VI), and $\mathrm{Th(NO_3)_3{\cdot}BMPPT{\cdot}TBP}$ and $\mathrm{Th(NO_3)_2(BMPPT)_2{\cdot}TBP}$ for Th(IV), respectively, ($[\mathrm{HBMPPT}]_{(o)}=0.05\sim0.2$ mol/L). The synergistic extraction process may be described by the following equation:

$$\mathrm{UO_2^{2+}}_{(a)} + \mathrm{HBMPPT}_{(o)} + \mathrm{TBP}_{(o)} + \mathrm{NO_3^-}_{(a)} \longrightarrow \mathrm{UO_2NO_3 \cdot BMPPT \cdot TBP}_{(o)} + \mathrm{H}^+_{(a)}$$

$$\mathrm{UO_2^{2+}}_{(a)} + 2\mathrm{HBMPPT}_{(o)} + \mathrm{TBP}_{(o)} \longrightarrow \mathrm{UO_2(BMPPT)_2 \cdot TBP}_{(o)} + 2\mathrm{H}^+_{(a)}$$

$$\mathrm{Th}^{4+}_{(a)} + \mathrm{HBMPPT}_{(o)} + \mathrm{TBP}_{(o)} + 3\mathrm{NO}^{-}_{3\,(a)} \longrightarrow \mathrm{Th(NO_3)_3 \cdot BMPPT \cdot TBP}_{(o)} + \mathrm{H}^{+}_{(a)}$$

$$\mathrm{Th}^{4+}_{(a)} + 2\mathrm{HBMPPT}_{(o)} + \mathrm{TBP}_{(o)} + 2\mathrm{NO}^{-}_{3\,(a)} \longrightarrow \mathrm{Th(NO_3)_2(BMPPT)_2 \cdot TBP}_{(o)} + 2\mathrm{H}^{+}_{(a)}$$

where the subscripts (a) and (o) correspond to the aqueous phase and organic phase, respectively.

3.4 Separation of U(VI), Th(IV) and Eu(III)

The distribution ratios of U(VI), Th(IV) and Eu(III) under some conditions are shown in Table 1. A little amount of TBP greatly increases the ability of HBMPPT to extract U(VI), but less increases that for Th(IV) and Eu(III).

The extraction with HBMPPT alone basically cannot separate U(VI) and Th(IV). However, after adding a little TBP, it can make U(VI)/Th(IV) separation coefficient($\alpha_{\mathrm{U/Th}}$) reaches 363(pH=3.0), and it can more easily separate U(VI) from Eu(III) too.

Table 1 Separation coefficients for U(VI), Th(IV) and Eu(III)

Extract condition	D_{U}	D_{Th}	D_{Eu}	$\alpha_{\mathrm{U/Th}}$	$\alpha_{\mathrm{U/Eu}}$
0.10MHBMPPT	0.94	0.67	<0.15	1.4	>10
0.10MHBMPPT+0.01MTBP	316	0.87	<0.15	363	>2100

Notes: pH=3.0, $[\mathrm{UO}_2^{2+}]_{(a)}=5.48\times10^{-4}$ mol/L, $[\mathrm{Th}^{4+}]_{(a)}=5.68\times10^{-4}$ mol/L, $[\mathrm{NH_4NO_3}]_{(a)}=$ 0.1 mol/L, at 25°C

4 Summary

We have studied the synergistic effect of U(VI) and Th(IV) with HBMPPT and TBP for the first time. Based on the values obtained, the synergistic extracted complexes may be presented as $\mathrm{UO_2NO_3 \cdot BMPPT \cdot TBP}$ and $\mathrm{UO_2(BMPPT)_2 \cdot TBP}$ for U(VI), and $\mathrm{Th(NO_3)_3 \cdot BMPPT \cdot TBP}$ and $\mathrm{Th(NO_3)_2(BMPPT)_2 \cdot TBP}$ for Th(IV), respectively. The separation coefficient of U(VI) and Th(IV), $\alpha_{(\mathrm{U/Th})}$ is 363(pH=3.0), and the extraction system can more easily separate U(VI) from Eu(III) too.

Acknowledgements

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