Solvent extraction of uranium(VI) and thorium(IV) in nitric acid solution by N,N,N',N'-tetrabutyladipicamide*

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Abstract N,N,N'N'-tetrabutyladipicamide(TBAA) has been synthesized, and applied to the extraction of U(VI) and Th(IV) from nitric acid solutions in a diluent composed of 0.50 volume fraction 1,2,4-trimethyl benzene(TMB) and 0.50 volume fraction kerosene(OK). The effects of the aqueous nitric acid concentration, extractant concentration, salting-out agent (LiNO₃) and temperature on extraction ability of TBAA for U(VI) and Th(IV) have been studied. Back extraction of U(VI) and Th(IV) from organic phases were performed by dilute nitric acid. The compositions of extracted complexes, equilibrium constants and enthalpies of extraction reactions have also been estimated. The IR spectra of extraction of U(VI) and Th(IV) have been studied.

Keywords N,N,N',N'-tetrabutyladipicamide(TBAA), Solvent extraction, Uranium(VI), Thorium(IV), Back-extraction, Salting-out effect, IR spectra

1 Introduction

Numerous multisubstituted alkyl diamides have been reported to be powerful extractants for a host of tri, tetra and hexavalent actinides since Siddall suggested the substituted alkylamide as a promising extractant for actinides and lanthanides in the early 1960's^[1~4]. The diamides have an excellent extracting ability for the actinides such as Am(III), Pu(IV)and U(VI) from highly acidic waste solutions, particularly for decontaminating high level radioactive wastes^[2~3]. These compounds contain strongly polar C=O groups. Their chelating ability for metallic cations is similar to that for the extractants containing phosphorus. The compounds containing no phosphorus atoms are important, they do not produce new solid waste because of being completely incinerable. The radiolytic and hydrolytic degradation products (such as carboxylic acids and amines) are not harmful to the process. They are considered as potential extractants for the reprocessing of nuclear fuel.

We have synthesized and studied ten kinds of N,N,N',N'-tetraalkyl diamides in our preliminary study^[5], one among them is N,N,N',N'tetrabutyladipicamide (TBAA).

$$(C_4H_9)_2N-CO-(CH_2)_4-CO-N(C_4H_9)_2$$
 (1)

In this paper the effects of the concentrations of HNO_3 , TBAA and salting-out agent(LiNO₃) as well as the extraction temperature on the extracting ability of TBAA for U(VI) and Th(IV) are tested, and the back extraction is also studied in the dilute nitric acid medium. The results show that TBAA is a better extractant for the extraction of U(VI) and Th(IV) from nitric acid medium than TBP.

2 Experimental

2.1 Preparation of extractant

TBAA can be obtained by the reaction of di-n-butylamine with adipic chloride in methylene chloride medium.^[5]

$$(C_2H_4COCl)_2 + 2NH(C_4H_9)_2 \xrightarrow{CH_2Cl_2} (C_2H_4CO - N(C_4H_9)_2)_2$$
(2)

1.11

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After alkali and acid washing, TBAA was purified by distillation under vacuum. The final distilled TBAA was checked by element analysis, IR spectrometry and NMR spectrometry. The purity of the product was higher than 98%. 2.2 Procedure and apparatus.

Containing a certain amount of U(VI) or Th(IV) and HNO₃, 0.5 ml of the aqueous solution was shaken for 10 min with 1 ml of the organic phase containing a given concentration of TBAA, which was preequilibrated with a suitable nitric acid solution. The diluent was composed of 0.50 volume fraction 1,2,4trimethyl benzene(TMB) and 0.50 volume fraction kerosene(OK). Samples of both phases were analyzed immediately after the phase separation.

The concentration of U(VI) was determined by the arsenazo-III spectrophotometric method, but Th(IV) by chlorophosphonazo-mA spectrophotometric method, then the distribution coefficients of U(VI) and Th(IV) were calculated.

For the back extraction, the organic phase containing certain amount of U(VI) and Th(IV) was prepared, and then was shaken with an

equal volume of dilute nitric acid for about 10 min.

IR spectra were recorded with a Nicolet FT spectrometer using KBr window cells. Signals of 96 scans at a resolution of 4 cm^{-1} were averaged before Fourier transformation, the IR spectra covered the range of $400 \sim 4000 \text{ cm}^{-1}$.

3 Results and discussion

3.1 Effect of HNO₃ concentration

It can be seen from Fig.1 that the distribution coefficient of U(VI) increases with the increase in the concentration of HNO₃ until a maximum which is due to the competition of U(VI) and HNO_3 for the coordination sites of TBAA, and the distribution coefficient of Th(IV) always increases in the region of the study. Results in Table 1 indicate that a better U-Th separation could be reached for TBAA as the extraction is carried out at medium acidity (for instance, 1-2 mol/L HNO₃), and also indicate that a better coextraction between U(VI)and Th(IV) could be obtained when the HNO₃ concentration surpasses 4 mol/L. The extraction data show that TBAA is better for the extraction of U(VI) and Th(IV) than $TBP^{[5]}$.

Table 1 The separation factors $\alpha (= D_U/D_{Th})$ at different [HNO₃]_{ag}

[HNO ₃]	1	2	3	4	5	6	7
D_{U}	3.340	8.935	13.87	17.89	21.01	19.60	10.86
D_{Th}	0.0092	0.2599	1.745	5.995	10.97	20.74	39.82
α	363.0	34.38	7.948	2.984	1.915	0.9450	0.3218

3.2 Effect of extractant concentration

As shown in Fig.2, the plots of $\lg D$ vs \lg [TBAA] are linear with slopes of 1.0 and 0.91 for U(VI) and Th(IV), respectively. These values indicate that the compositions of extracted species are UO_2^{2+} ·TBAA and Th⁴⁺·TBAA. From the data, the extraction constants are also calculated to be 3.33 and 0.0528, for U(VI) and Th(IV), respectively.

3.3 IR spectra of extraction of U(VI) and Th(IV)

In order to gain insight into the structure of complexes of U(VI) and Th(IV) with TBAA, we measured the IR spectra of saturated extraction of U(VI) and Th(IV). The free C=O stretching vibration is at 1640 cm⁻¹. When the concentration of U(VI) or Th(IV) in organic phase is equal to the concentration of TBAA, the free C=O stretching vibration would vanish and the new bands would appear. The coordination bands of U(VI) with TBAA were at 1602, 1574 cm^{-1} ; the coordination bands of Th(IV) with TBAA were at 1616, 1588 cm^{-1} . These features suggest that TBAA are bidentate ligands in the extracted complexes.

3.4 Temperature effect

It can be seen from Fig.3 that D values decrease with the increase in temperature for the extraction reactions of U(VI) and Th(IV). This implies that the extraction reactions of U(VI) and Th(IV) are exothermic. It is similar to TBP.^[6] The relationship of lgD to 1/T is a straightline. According to the thermodynamic equation

$$\left[\frac{\partial \lg D}{\partial (1/T)}\right]_{\rm p} = -\frac{\Delta H}{2.303R} \tag{3}$$

the enthalpies of extraction reactions of U(VI)and Th(IV) can be calculated

$$\Delta H_{\rm UO_2^{2+}} = -14.18 \, \rm kJ/mol$$
 (4)

$$\Delta H_{\mathrm{Th}^{4+}} = -15.89 \,\mathrm{kJ/mol} \tag{5}$$







Fig.3 Distribution coefficients of U(VI) and Th(IV) as a function of temperature $[U(VI)] = [Th(IV)] = 5.0 \times 10^{-3} \text{ mol/L},$ $[TBAA] = 0.5 \text{ mol/L}, [HNO_3] = 3 \text{ mol/L}$

3.5 Effect of salting-out agent

It can be seen from Figs.4,5 that the salting-out agent was much beneficial to extraction of U(VI) and Th(IV) in the same HNO₃

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Fig.2 Distribution coefficients of U(VI) and Th(IV) as a function of TBAA concentration at $25^{\circ}C$ $[U(VI)] = [Th(IV)] = 5.0 \times 10^{-3} \text{ mol/L},$

$$[HNO_3]=3 \text{ mol/L}$$



Fig.4 Distribution coefficients of U(VI) as a function of LiNO₃ concentration at 25°C $[U(VI)] = 5.0 \times 10^{-3} \text{ mol/L}, [TBAA]=0.5 \text{ mol/L},$ $[HNO_3]=0.01 \text{ mol/L}$

concentration system. The salting-out agent $(LiNO_3)$ with high water binding capacity will cause U(VI) and Th(IV) to be less hydrated and will render the aqueous solution more deficient

No.2

in free water. This is why the salting-out agent may modify the extraction of U(VI) and Th(IV) with the aid of TBAA.

3.6 Back-extraction

The back extraction results of U(VI) and Th(IV) with 0.01 mol/L and 0.001 mol/L dilute nitric acid solutions are shown in Table 2. It can be seen that back extraction of U(VI) and Th(IV) from TBAA-50%TMB-50%OK (volume fraction) was rather more difficult than those from TBP-50%TMB-50% OK(volume fraction).

In these extraction experiments, the concentrations of TBAA in organic phase were in a large excess compared with those of U(VI)and Th(IV) in the aqueous phase. The results suggest that the 1:2:1 complex U(VI) or 1:4:1

Table 2 Stripping of U(VI) and Th(IV) from 0.5 mol/L TBAA and 0.5 mol/L TBP in 50% TMB-50% OK

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Metal	[HNO ₃]	TBAA	TBP
ions*	mol/L	% Stripping	%Stripping
U(VI)	0.01	48.42	95.21
	0.001	42.39	96.83
Th(IV)	0.01	53.49	99.81
	0.001	49.92	99.9 2

*All the organic phases were made in 3.0 mol/LHNO₃ solutions

complex of Th(IV), NO_3^- and TBAA was extracted into the organic phase. Thus, the extraction reactions can be expressed as follows:

$$UO_{2(\mathbf{a})}^{2+} + 2NO_{3(\mathbf{a})}^{-} + TBAA_{(\mathbf{o})} = UO_2(NO_3)_2 \cdot TBAA_{(\mathbf{o})}$$
(6)

$$\operatorname{Th}_{(\mathbf{a})}^{4+} + 4\operatorname{NO}_{3(\mathbf{a})}^{-} + \operatorname{TBAA}_{(\mathbf{o})} = \operatorname{Th}(\operatorname{NO}_3)_4 \cdot \operatorname{TBAA}_{(\mathbf{o})}$$
(7)



Fig.5 Distribution coefficients of Th(IV) as a function of TBAA concentration at 25°C [Th(IV)] = 5.0×10^{-3} mol/L, [HNO₃] = 0.075 mol/L, [LiNO₃]=4.0mol/L

4 Conclusions

The extractions of U(VI) and $Th(\mathbf{k})$ from nitric acid medium by TBAA are better than by TBP. At low acidity, a better U-Th separation can be reached. A better coextraction between U(VI) and Th(IV) could be obtained when the HNO₃ concentration exceeds 4 mol/L. The extraction reactions for U(VI) and Th(IV) are exothermic, and compositions of extracted complexes are UO₂(NO₃)₂·TBAA and the Th(NO₃)₄·TBAA. LiNO₃ may modify the extraction of U(VI) and Th(IV) through TBAA. Back extraction of U(VI) and Th(IV) from TBAA-50%TMB-50%OK was much more difficult than from TBP-50%TMB-50%OK.

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