Vol.7 No.4 NUCLEAR SCIENCE AND TECHNIQUES November 1996

Solvent extraction of U(VI) and Th(IV) ions with N,N,N',N'-tetrabutylsuccinylamide from nitric acid solutions*

Wang You-Shao (王友绍), Bao Bo-Rong(包伯荣), Xie De-Feng(谢德峰)
(Shanghai Institute of Nuclear Research, the Chinese Academy of Sciences, Shanghai 201800)
Sun Si-Xiu (孙思修)
(Department of Chemistry, Shandong University, Jinan 250100)
and Cao Wei-Guo (曹卫国)
(Department of Chemistry, Shanghai University,Shanghai 201800)

Abstract The solvent extraction of U(VI) and Th(IV) from nitric acid medium by N,N,N',N'-tetrabutylsuccinylamide(TBSA) in a diluent composed of 0.5 volume fraction trimethyl benzene(TMB) and 0.5 volume fraction kerosene(OK) has been studied. The distribution ratios of U(VI) and Th(IV) as a function of aqueous HNO_3 concentration, extractant concentration and temperature have been measured. From the data, the composition of extracted species, equilibrium constants and enthalpies of extraction reaction are also calculated.

Keywords N,N,N',N'-tetrabutylsuccinylamide, Uranium, Thorium, Solvent extraction

1 Introduction

The extraction behavior of the substituted alkylamide has been extensively studied since Siddal first suggested the substituted alkylamide as a promising extractant for actinides in the early 1960's.[1-4] These compounds contain strongly polar C=O groups. Their chelating ability for metallic cations is similar to those of the extractants containing phosphorus. The compounds without phosphorus atoms are critical. They do not produce new solid waste because of being completely incinerable. The radiolytic and hydrolytic degradation products (carboxylic acids and amines) all are not harmful to the process. They are considered as potential extractants for the reprocessing of nuclear fuel.

We have synthesized and studied ten N,N,N',N'-tetraalkyl diamides. After the preliminary study, another molecule N,N,N',N'-tetrabutylsuccinylamide (TBSA)[5] was selected. Its molecular formula is as follows:

$$(C_4H_9)_2N - CO - CH_2CH_2 - CO - N(C_4H_9)_2 \tag{1}$$

This paper discusses systematically the extraction of U(VI) and Th(IV) by TBSA. The extracting data indicate that TBSA is better for the extraction of U(VI) and Th(IV) from nitric acid medium compared with TBP. The extraction mechanisms of U(VI) and Th(IV) by TBSA and thermodynamic parameters are also presented.

2 Experimental

2.1 Preparation of extractant

N,N,N',N'- tetraalkyldiamides used in our investigation are not commercially available. They were synthesized and purified in our laboratory.[5] TBSA was obtained by the reaction of di-n-butylamine with succinyl chloride in methylene chloride medium:[6]

$$-[CH_2CO - Cl]_2 + 2NH(C_4H_9)_2 \xrightarrow{CH_2Cl_2} -[CH_2 - CO - N(C_4H_9)_2]_2 \tag{2}$$

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*The Project Supported by National Natural Science Foundation of China
Manuscript received date: 1996-05-20

After alkali and acid washing, TBSA was purified by distilling under vacuum. The final distilled TBSA was checked by element analysis, IR spectrometry and NMR spectrometry. The purity of the product was higher than 0.98.

2.2 Determination of distribution ratio of U(VI) and Th(IV)

A typical extraction procedure was as follows: 0.5 ml of the aqueous phase containing a certain amount of U(VI) or Th(IV) and HNO_3 was shaken with 1 ml of the organic phase containing a given concentration of TBSA for 10 min, which was preequilibrated with a suitable nitric acid solution. The diluent was composed of 0.50 volume fraction trimethyl benzene(TMB) and 0.50 volume fraction kerosene(OK). Samples of both phases were analyzed immediately after the phase separation.

2.3 Analytical methods

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

3 Results and discussion

3.1 Distribution ratios of U(VI) and Th(IV) as a function of aqueous HNO_3 concentration

Fig.1 shows that with the increase in the concentration of HNO_3 the distribution ratios of U(VI) and Th(IV) increase in the range

Table 1 Separation factor $\alpha = D_U/D_{Th}$ in different acidities

$[HNO_3]$	1.0	1.92	3.3	4.22	5.6
α	50.75	44.70	15.00	6.306	5.114

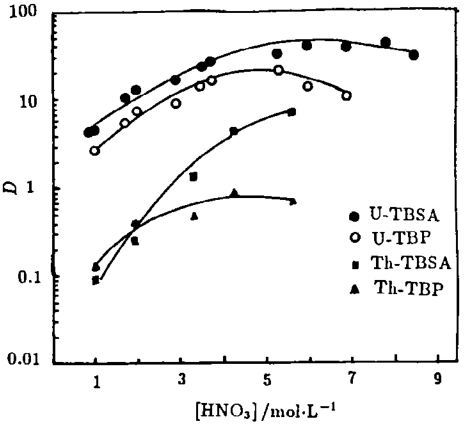

Fig.1 Distribution ratios of U(VI) and Th(IV) as a function of aqueous HNO_3 concentration at 25°C, $[U(VI)]_{(a)} = [Th(IV)]_{(a)} = 5.0\times10^{-3}$ mol/L, $[TBSA]_{(o)}$=0.5 mol/L

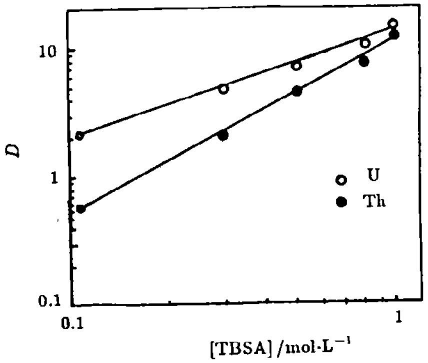

Fig.2 Distribution ratios of U(VI) and Th(IV) as a function of TBSA concentration at 25°C, $[U(VI)]_{(a)} = [Th(IV)]_{(a)} = 4.0 \times 10^{-3}$ mol/L, $[HNO_3]_{(a)}$=3.5 mol/L

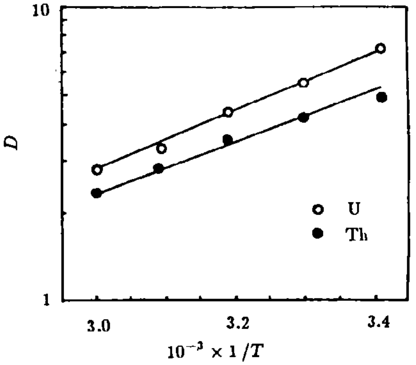

Fig.3 Distribution ratios of U(VI) and Th(IV) as a function of temperature; $[TBSA]_{(o)}$=0.5 mol/L, $[U(VI)]_{(a)}=[Th(IV)]_{(a)} = 4.0 \times 10^{-3}$ mol/L, $[HNO_3]_{(a)}$ = 3.5 mol/L

of 1~6 mol/L, because of competitive extraction between NO_3^- and U(VI) or Th(IV), the curve reached maximum value at about 6 mol/L HNO_3 and then decreased. If the extraction is carried out at medium acidity (for instance, 2~4 mol/L HNO_3), TBSA is better than TBP for extraction of U(VI) and Th(IV). The results indicate that better U-Th separation could be also reached by TBSA. (see Table 1)

3.2 Distribution ratios of U(VI) and Th(IV) as a function of extractant concentration

Fig.2 shows that in the case of $[HNO_3]_{(a)} = 3.5$ mol/L and $[U(VI)]_{(a)} = [Th(IV)]_{(a)} = 5.0\times10^{-3}$ mol/L, the plots $\lg D$ vs $\lg[TBSA]_{(o)}$ are straight lines with slopes 1.0 and 1.1 for U(VI) and Th(IV), respectively. These values indicate that the compositions of extracted species are $UO_2^{2+}\cdot TBSA$ and $Th^{4+}\cdot TBSA$. From the data, the extraction constants are also calculated to be 1.41±0.06 and 0.081±0.006 for U(VI) and Th(IV), respectively.

3.3 Distribution ratios of U(VI) and Th(IV) as a function of temperature

Table 2 and Fig.3 show that D decreases with the increase in temperature for the extraction reactions of U(VI) and Th(IV). This means that the extraction reactions of U(VI) and Th(IV) are exothermic. The case is similar to TBP.[7] The relationship $\lg D$ vs $1/T$ is a straight line. According to the thermodynamic formula:

Table 2 Distribution ratios of U(VI) and Th(IV) in different temperatures

Temperature/°C	$1/T/K^{-1}$	D_U	D_{Th}
20	3.41×10^{-3}	7.08	5.00
30	3.30×10^{-3}	5.52	4.20
40	3.19×10^{-3}	4.40	3.51
50	3.09×10^{-3}	3.33	2.80
60	3.00×10^{-3}	2.83	2.31

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

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

$$\Delta H_{UO_2^{2+}} = -18.63\text{kJ/mol} \qquad (4)$$

$$\Delta H_{Th^{4+}} = -17.56\text{kJ/mol} \qquad (5)$$

In these extraction studies, the concentrations of TBSA 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 for U(VI), NO_3^- and TBSA; and 1:4:1 complex for Th(IV), NO_3^- and TBSA were extracted into the organic phase. Thus, the extraction reactions of the present system can be expressed as follows

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

$$Th_{(a)}^{4+}+4NO_{3(a)}^{-}+TBSA_{(o)} = Th(NO_3)_4\cdot TBSA_{(o)} \qquad (7)$$

4 Conclusions

The extraction data show that TBSA is better for the extraction of U(VI) and Th(IV) than TBP. The extraction reactions for U(VI) and Th(IV) are exothermic, and compositions of extracted species are $UO_2(NO_3)_2\cdot TBSA$ and $Th(NO_3)_4\cdot TBSA$.

The distinct advantage of TBSA compared with TBP is completely incinerable and the radiolytic and hydrolytic degradation products are not harmful to the process. TBSA is a promising extractant for reprocessing of U-Th fuel.

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