Solvent extraction of nitric acid, uranium(VI) and thorium(IV) by N,N,N′,N′-tetrahexylsuccinylamide

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Abstract A new kind of diamide N,N,N′,N′-tetrahexylsuccinylamide (THSA) was synthesized, characterized and used for the extraction of HNO_3, U(VI) and Th(IV) in a diluent composed of 0.5 volume fraction 1,2,4-trimethy benzene(TMB) and 0.5 volume fraction kerosene(OK). Extraction distribution coefficients of U(VI) and Th(IV) as functions of aqueous nitric acid concentration, extractant concentration, temperature and salting-out agent ($LiNO_3$) have been studied, and it is found that THSA as an extractant is superior to TBP for extraction of U(VI) and Th(IV). Back extraction was also studied. At low acidity, the main adduct of THSA and HNO_3 is $HNO_3\cdot$THSA. THSA$\cdot(HNO_3)_2$ and THSA$\cdot(HNO_3)_3$ are also found at high acidity. The compositions of extracted species, apparent equilibrium constants and enthalpies of extraction reactions have also been calculated.

Keywords N,N,N′,N′-tetrahexylsuccinylamide, Nitric acid, Uranium(VI), Thorium(IV), Back extraction, Salting-out agent

1 Introduction

Up to the present, many different extractants have been studied and exploited for a series of elements extraction and recovery since tri-n-butyl phosphate(TBP) was used in nuclear fuel reprocessing.[1] Recently, the new extractants of diamide type have been paied attention from the viewpoint that they can extract a host of tri, tetra and hexavalent actinides from nitric acid solutions[2~11], such as Am(III), Pu(IV) and U(VI), particularly for decontaminating high level radioactive wastes.[2,3] Some research work about the diamides for extraction of HNO_3, U(VI) and Th(IV) have also been reported.[4~11] The advantages of these extractants and their innocuous radiolytic products make them as worthy candidates for further investigations in nuclear waste management.

The extractions of HNO_3, U(VI) and Th(IV) ions were discussed systematically along with the results in this paper. The extracting data indicate that THSA is better than TBP for the extraction of U(VI) and Th(IV) from nitric acid medium. The extraction mechanisms of U(VI) and Th(IV) by THSA and thermodynamic parameters are also presented.

2 Experimental

2.1 Preparation of extractant

THSA was obtained by the reaction of di-n-hexylamine with succinyl chloride in ethylene hloride medium.[12]

$$(CH_2COCl)_2 + 2NH(C_6H_{13})_2 \xrightarrow{CH_2Cl_2} (CH_2CO-N(C_6H_{13})_2)_2 \tag{1}$$

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

2.2 Procedure and apparatus

0.5 mL of the aqueous phase which contains a certain amount of U(VI) or Th(IV) and HNO_3 is mixed with 1 mL of the organic phase

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containing a given concentration of THSA and shaken for 10 min. The diluent composed of 0.5 volume fraction 1,2,4-trimethyl benzene(TMB) and 0.5 volume fraction kerosene (OK). Samples are of both phases are analyzed immediately after the phase separation. The concentration of U(VI) is determined by the Arsenazo-III spectrophotometric method. The concentration of Th(IV) is measured by chlorophosphonazo-mA spectrophotometric method, and then the distribution coefficients of U(VI) and Th(IV) are calculated.

0.1~1.0 mol/L THSA was equilibrated with 1.0 mol/L and 3.0 mol/L HNO_3 for 10 min. After the phase separation, the aqueous phase is titrated with 0.05 mol/L NaOH solution to determine the nitric acid concentration.

For the back extraction studies, first the organic phase containing certain amounts of U(VI) and Th(IV) is prepared, and then dilute nitric acid is mixed with an equal volume of the above organic phase and shaken for about 10 min.

IR spectra are recorded by a FT Nicolet 5DXC spectrometer with KBr window cells. Singls of 96 scans at resolution of $4\,\mathrm{cm}^{-1}$ were averaged before Fourier transformation, the IR spectra covered the range of $400\sim4000\,\mathrm{cm}^{-1}$.

3 Results and discussion

3.1 Extraction of nitric acid

THSA is found to extract nitric acid into the organic phase. The nature of the extracted species and the apparent equilibrium constant (K_{H^+}) are presented for the following reaction:[3]

$$\mathrm{H}^+_{(\mathrm{a})} + \mathrm{NO}^-_{3(\mathrm{a})} + n\mathrm{THSA}_{(\mathrm{o})} \longrightarrow \mathrm{HNO_3} \cdot n\mathrm{THSA}_{(\mathrm{o})} \qquad (2)$$

The aspect equilibrium constant (K_{H^+}) of the Eq.(2) can be written as follows:

$$K_{\mathrm{H}^+} = \frac{[\mathrm{HNO_3} \cdot n\mathrm{THSA}]_{(\mathrm{o})}}{[\mathrm{H}^+]_{(\mathrm{a})}[\mathrm{NO}_3^+]_{(\mathrm{a})}[\mathrm{THSA}]^n_{(\mathrm{o})}} \qquad (3)$$

The concentration of the diamide and HNO_3 are restricted to no more than 1.0 mol/L, molar concentrations instead of activities are employed in all the calculations.

Rewriting the above equation in logarithmic form:

$$\mathrm{lg}[\mathrm{H}^+]_{(\mathrm{o})} - 2\mathrm{lg}[\mathrm{H}^+]_{(\mathrm{a})} = \mathrm{lg}K_{\mathrm{H}^+} + n\mathrm{lg}[\mathrm{THSA}]_{(\mathrm{o})} \qquad (4)$$

where $[\mathrm{H}^+]_{(\mathrm{o})} = [\mathrm{HNO_3} \cdot n\mathrm{THSA}]_{(\mathrm{o})}$ and $[\mathrm{H}^+]_{(\mathrm{a})} = [\mathrm{NO}_3^-]_{(\mathrm{a})}$

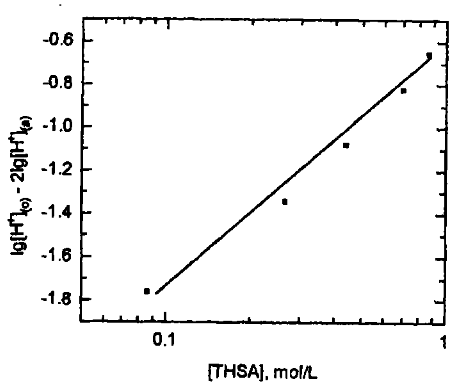

Fig.1 Distribution coefficients of HNO_3 as a function of THSA concentration at 25°C, $[HNO_3]$=1.0 mol/L

By plotting the left side of Eq.(4) against $\mathrm{lg}[\mathrm{THSA}]_{(\mathrm{o})}$, a straight line with a slope equaling to n and an intercept equaling to $\mathrm{lg}K_{\mathrm{H}^+}$ are obtained. The result (n =1.1) indicating that only one HNO_3 molecule is attached to each THSA molecule (see Fig.1). The value of K_{H^+} calculated from the intercept is 0.23.

Fig.2 shows the effect of the initinal THSA concentration on the extraction of HNO_3 (the slope is 1.1). The result is similar to the study on N,N′-dimethyl-N,N′-dioctylmalonamide[12] and N,N,N′,N′-tetrabutylglutaramide reported by Musikas.[13] In any case, the plots of lg[diamide] give a straight line with the slope of about 1.1 in the medium of 3~4 mol/L nitric acid. As a result of the detailed IR spectra studies, the formations of THSA-HNO_3 adducts, for example, $(\mathrm{THSA})_2 \cdot \mathrm{HNO_3}$

(1646 cm^{-1}), THSA·HNO_3 (1575 cm^{-1}) and THSA·$(HNO_3)_2$ (1540 cm^{-1}), are responsible for such the phenomenon (the slope is 1.1).

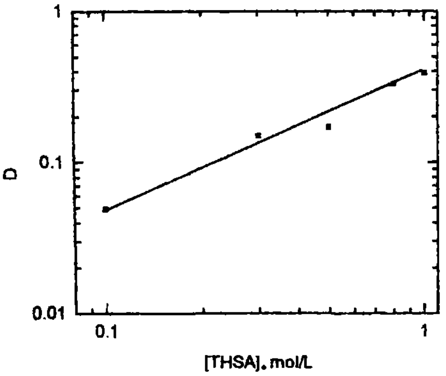

Fig.2 Distribution coefficients of HNO_3 as a function of initial THSA concentration at 25°C, $[HNO_3]$=3.0 mol/L

3.2 Extraction of uranium(VI) and thorium (IV)

3.2.1 Distribution coefficients of U(VI) and Th(IV) as a function of aqueous HNO_3 concentration

Fig.3 shows the effect of the concentration of HNO_3 on the distribution coefficients of U(VI) and Th(IV) in the two phases. The distribution coefficient of U(VI) or Th(IV) increases with the increases of the concentration of HNO_3 up to the maximum which is due to the competition of U(VI) or Th(IV) and HNO_3 for the coordination sites of THSA. Results in Table 1 indicate that a better U-Th separation can be reached for THSA if the extraction is carried out at medium acidity (for instance, $1\sim2$ mol/L HNO_3), and indicate that a better coextraction between U(VI) and Th(IV) can also be obtained when the HNO_3 concentration surpassed to 4 mol/L. The extraction data show that THSA is better than TBP for the extraction of U(VI) and Th(IV).

Table 1 U-Th separation factor $\alpha = D_U/D_{Th}$ at different acidities

$[HNO_3]$	1	2	3	4	5	6	7
D_U	3.056	7.946	13.86	12.00	14.04	16.63	12.39
D_{Th}	0.0530	0.1649	0.9100	5.863	23.54	65.29	56.97
α	57.66	48.19	15.23	2.047	0.5964	0.2534	0.2175

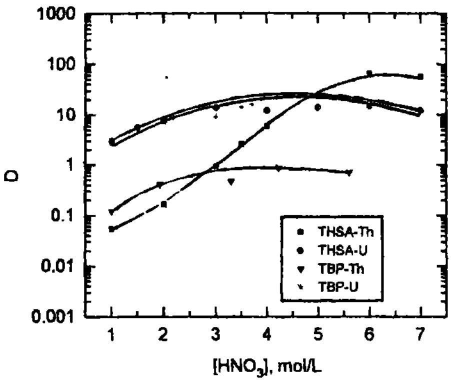

Fig.3 Distribution coefficients of U(VI) and Th(IV) as a function of aqueous HNO_3 concentration at 25°C, [U(VI)]=[Th(IV)]=5.0×10^{-3} mol/L, [THSA]=0.5 mol/L

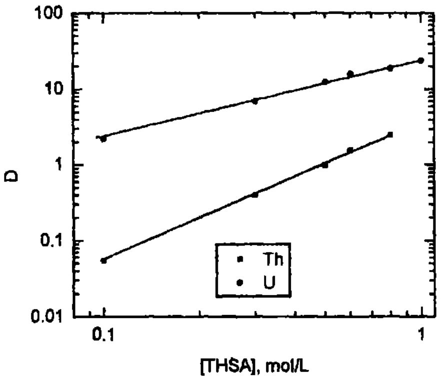

Fig.4 Distribution coefficients of U(VI) and Th(IV) as a function of THSA concentration at 25°C, [U(VI)]=[Th(IV)]=5.0×10^{-3} mol/L, [THSA]=3.0 mol/L

3.2.2 Distribution coefficients of U(VI) and Th(IV) as a function of extractant concentration

The results are shown in Fig.4, the plots of lg*D* vs. lg[THSA] are straight lines with slopes of 1.00 and 1.84, for U(VI) and Th(IV), respectively. The results suggest that the 1:2:1 complex for U(VI) or 1:4:2 complex for Th(IV), NO_3

and THSA is extracted into the organic phase. Thus, the extraction reactions of the present system can be expressed as follows.

$$UO^{2+}_{2(a)} + 2NO^{-}_{3(a)} + THSA_{(0)} = UO_2(NO_3)_2 \cdot THSA_{(0)} \qquad (5)$$

$$Th^{4+}_{(a)} + NO^{-}_{3(a)} + 2THSA_{(0)} = Th(NO_3)_4 \cdot 2THSA_{(0)} \qquad (6)$$

Then, the aspect extraction constant K_{ex} can be defined as

$$K_{ex} = [M(NO_3)_m \cdot nTHSA]_{(0)}/[M^{m+}]_{(a)}[NO_3^-]^m_{(a)}[THSA]^n_{(0)} \qquad (7)$$

The values of the aspect extraction constants are also calculated to be 3.10 and 0.0598, for U(VI) and Th(IV), respectively.

3.2.3 Distribution coefficients of U(VI) and Th(IV) as a function of temperature

Results are shown in Fig.5. It is seen that D decreases with the increase of temperature for the extraction reaction of U(VI) and Th(IV). This means that the extraction reactions of U(VI) and Th(IV) are exothermic, and the case is similar to TBP.[14] The relationship lg$D$ vs. $1/T$ is a straight line. According to the thermodynamic formula:

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

the enthalpies of extraction reactions of U(VI) and Th(IV) can be calculated to be 15.19 kJ·mol^{-1} and -17.30 kJ mol^{-1} for U(VI) and Th(IV), respectively.

3.2.4 Back-extraction of U(VI) and Th(IV) from organic phases by dilute nitric acid

The back extraction of U(VI) and Th(IV) with concentrations of 0.01 mol/L and 0.001 mol/L dilute nitric acid are shown in Table 2. It can be seen that back extraction of U(VI) and Th(IV) from THSA-0.5 volume fraction in TMB-0.5 volume fraction OK was rather difficult than from TBP-0.5 volume fraction in TMB-0.5 volume fraction OK.

Table 2 Stripping of U(VI) and Th(IV) from 0.5 mol/L THSA and 0.5 mol/L TBP in 0.5 volume fraction TMB-0.5 volume fraction OK

Methal ion	[HNO$_3$] /mol·L^{-1}	THSA/% /Stripping	TBP/% /Stripping
U(VI)	0.01	65.28	95.21
	0.001	39.16	96.83
Th(IV)	0.01	59.84	99.81
	0.001	57.95	99.92

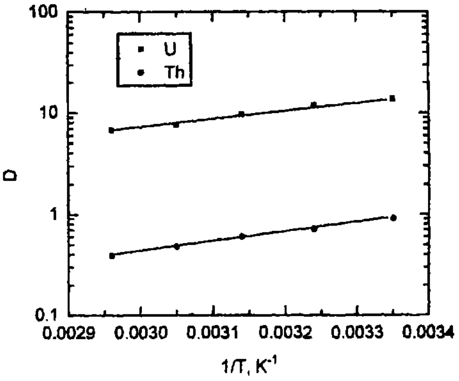

Fig.5 Distribution coefficients of U(VI) and Th(IV) as a function of temperature, [THSA]=0.5 mol/L, [U(VI)]=[Th(IV)]5.0×10^{-3} mol/L, [HNO$_3$]=3.0 mol/L

3.2.5 Effect of salting-out agent

It can be seen from Figs.6,7 that the salting-out agent is much beneficial to extraction of U(VI) and Th(IV) in the same HNO$_3$ concentration system. The salting-out agent (LiNO$_3$) with high water binding capacity will cause U(VI) and Th(IV) to be hydrated and will render the aqueous solution more deficient in free water.[15] This is why the salting-out agent may modify the extraction of U(VI) and Th(IV) with the aid of THSA.

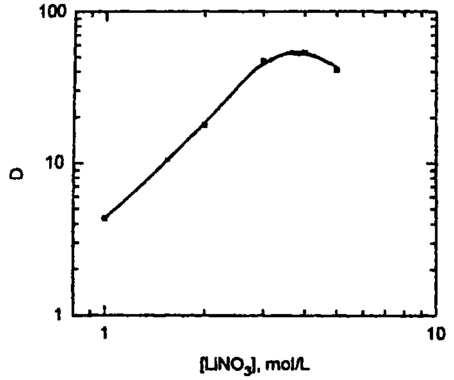

Fig.6 Distribution coefficients of U(VI) as a function of $LiNO_3$ concentration at 25°C, [THSA]=0.5 mol/L, [U(VI)]=[Th(IV)]5.0×10^{-3} mol/L, [HNO_3]=3.0 mol/L

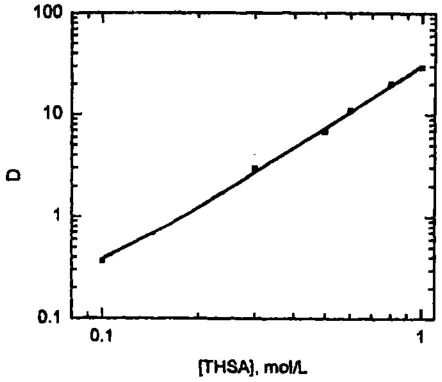

Fig.7 Distribution coefficients of Th(IV) as a function of THSA concentration at 25°C [Th(IV)=5.0×10^{-3} mol/L, [HNO_3]=0.075 mol/L, [$LiNO_3$]=4.0 mol/L

4 Conclusions

The THSA for extraction of U(VI) and Th(IV) from nitric acid medium is superior to TBP. At low acidity (1~2 mol/L HNO_3), a better U-Th separation can be reached. A better coextraction between U(VI) and Th(IV) could be obtained when the HNO_3 concentration exceeds 4 mol/L. The main adduct of THSA and HNO_3 is $HNO_3\cdot THSA$ at low acidity, $THSA\cdot(HNO_3)_2$ and $THSA\cdot(HNO_3)_3$ are also found at high acidity. The extraction reactions for U(VI) and Th(IV) are exothermic, and compositions of extracted species are $UO_2(NO_3)_2\cdot THSA$ and $Th(NO_3)_4\cdot 2THSA$. Back extraction of U(VI) and Th(IV) from THSA-0.5 volume fraction TMB-0.5 volume fraction OK was rather difficult than from TBP-0.5 volume fraction TMB-0.5 volume fraction OK, and the salting-out agent $LiNO_3$ may modify the extraction of U(VI) and Th(IV) with the aid of THSA

References

1 SHEN C H, BAO B R, J Nucl Radiochem (in Chinese), 1993, **15**(4):243~

2 Musikas C, Sep Sci Technol, 1988, **23**(12/130):121

3 Nair G M, Prabhu D R, Mahajan G R*et al.* Sol Extr Ion Exch, 1993,**11**(5):813

4 WANG Y S, SHEN C H, ZHU J K *et al.* J Radioanal Nucl Chem Let, 1996, **212**(2):101

5 WANG Y S, SUN G X, XIE D F *et al.* J Radioanal Nucl Chem Let, 1996, **214**(2):67

6 WANG Y S, SUN S X, YANG Y Z *et al.* J Radioanal Nucl Chem Let, 1997, **218**(1):123

7 WANG Y S, SUN G X, BAO B R *et al.* J Radioanal Nucl Chem Let, 1997, **219**(1):119

8 WANG Y S, BAO B R, CAO W G *et al.* J Radioanal Nucl Chem Let, 1997, **222**(1):279

9 WANG Y S, SUN G X, BAO B R *et al.* J Radioanal Nucl Chem Let, 1997, **224**(1~2):151

10 WANG Y S, CAI Q F, TAN X F *et al.* J Radioanal Nucl Chem Let, 1998, **226**(1~2)(in press)

11 Stanley R S, Wolf K, Organnic founctional group prepartions, Vol 1. New York:Academic Press, 1968, 277

12 Musikas C, Hubert H. Sol Extr Ion Exch, 1987, **5**(1):151

13 Charonnel M C, Musikas C. Sol Extr Ion Exch, 1988, **6**(3):461

14 BAO B R, BAO Y Z, SHEN C H *et al.* J Radioanal Nucl Chem Let, 1992, **162**(2):391

15 Tian Q Z, Hughes M A. Proceedings of ISEC'93, Vol.1 London and New York: Published for SCI Elsevier Applies Science, 1993, 404