

N,N,N',N'-tetrabutylsuccinylamide as a new extractant in n-dodecane for extraction of uranium(VI) and thorium(IV) ions

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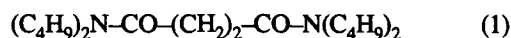
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N,N,N',N'-tetrabutylsuccinylamide (TBSA) was synthesized, characterised and used for the extraction of U(VI) and Th(IV) from nitric acid solutions into n-dodecane. Extraction distribution coefficients of U(VI) and Th(IV) as a function of aqueous nitric acid concentration, extractant concentration and temperature have been measured and found that n-dodecane as diluent was superior to 50% 1,2,4-trimethyl benzene (TMB) and 50% kerosene (OK) system for extraction of U(VI) and Th(IV). The compositions of extracted species, equilibrium constants and enthalpies of extraction reactions have also been calculated. The formation of the 1 : 2 : 1 complex of uranyl(II) ion or the 1 : 4 : 1 complex of thorium(IV) ion, nitrate ion and TBSA and extracted species was further confirmed by the IR spectra of saturated extract of U(VI) and Th(IV).

Introduction

During the past twenty years, bidentate ligands as extractants have come to occupy an important field in the solvent extraction of metals. The special features of these extractants are that they are more selective and exhibit higher efficiency.¹ These characteristics are partly due to their ability to form chelate complexes. These extractants are successfully applied in different areas, such as for extraction of the actinides and lanthanides. There is a particular class of bifunctional ligands namely the multisubstituted alkylamides which have been researched since SIDDALL III first suggested the substituted alkylamides as promising extractants for the actinides in the early 1960's. The diamides useful tri-, tetra- and hexavalent actinides such as Am(III), Pu(IV) and U(VI) have excellent extractability from highly acidic waste solutions for decontaminating high level radioactive wastes.^{3,4} We have also done some research work about the diamides for extraction of U(VI) and Th(IV) ions from nitric acid solutions. The main advantages of these extractants are their innocuous radiolytic products and easy incinerability, these attractive features making them worthy candidates for further investigations in nuclear waste management.

One molecule was synthesized and selected: N,N,N',N'-tetrabutylsuccinylamide (TBSA).



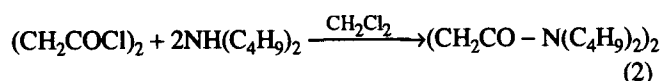
We have studied extraction of U(VI) and Th(IV) with TBSA in the diluent composed of 50% 1,2,4-trimethyl benzene (TMB) and 50% kerosene (OK) and found that TBSA was the best one of the extractants which we studied,^{6,7} we plan to do further research about the extraction functions of TBSA in order to gain more information about it.

In this paper, extraction conditions such as (1) nitric acid concentration (2) extractant concentration and (3) temperature have systematically been studied from the nitric acid solutions into n-dodecane. The extraction mechanisms of U(VI) and Th(IV) by TBSA and thermodynamic parameters are also presented.

Experimental

Preparation of extractant

TBSA was obtained by the reaction of di-n-butylamine with succinyl chloride in methylene chloride medium.⁸



After alkali, acid and water washing, TBSA was purified by distillation under vacuum. The final distilled TBSA was checked by element analysis (found: N = 8.041%, C = 70.45% and H = 11.86%; calculated for $\text{C}_{20}\text{H}_{40}\text{N}_2\text{O}_2$: N = 8.221%, C = 70.47% and H = 11.74%), IR spectrometry and NMR spectrometry.

Procedure and apparatus

0.5 ml of the aqueous phase which contained a certain amount of U(VI) or Th(IV) and HNO_3 was shaken for 10 min with 1 ml of the organic phase containing a given concentration of TBSA. The diluent was composed by 50% 1,2,4-trimethyl benzene (TMB) and 50% 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. The concentration of Th(IV) was measured by chlorophosphonazo-mA spectrophotometric method and

then the distribution coefficients of U(VI) and Th(IV) were calculated.

IR spectra were recorded with a FT Nicolet 5DXC spectrometer, using KBr window cells. Signals of 96 scans at a resolution of 4 cm^{-1} were averaged before Fourier transformation, the spectra covered the range of $400\text{--}4000\text{ cm}^{-1}$.

Results and discussion

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

Figure 1 shows the effect of the initial concentration of HNO_3 on the distribution coefficients of U(VI) and Th(IV). The distribution coefficient of U(VI) or Th(IV)

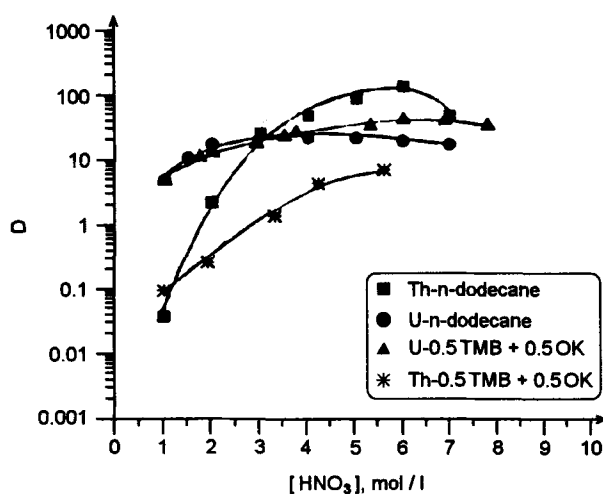


Fig. 1. Distribution coefficients of U(VI) and Th(IV) as a function of initial aqueous HNO_3 concentration at $25\text{ }^\circ\text{C}$; $[\text{U(VI)}] = [\text{Th(IV)}] = 5.0 \cdot 10^{-3}\text{ mol/l}$, $[\text{TBSA}] = 0.5\text{ mol/l}$

increases with the increase in the concentration of HNO_3 , until a maximum which is due to the competition of U(VI) or Th(IV) and HNO_3 for the coordination sites of TBSA is reached. Results in Table 1 indicate that a better U-Th separation could be reached with TBSA if the extraction is carried out at medium acidity (for instance, $< 1.5\text{ mol/l HNO}_3$) and also indicate that a satisfactory coextraction both of U(VI) and Th(IV) could be obtained when the HNO_3 concentration surpassed 3 mol/l . The extraction data shows that TBSA

yields better extraction of U(VI) and Th(IV) than in 50% TMB and 50% OK system.

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

The results are shown in Figure 2. It is seen that in the case of $[\text{HNO}_3] = 3\text{ mol/l}$ ($[\text{NO}_3^-] = 2.82\text{ mol/l}$)⁹ and $[\text{U(VI)}] = [\text{Th(IV)}] = 5.0 \cdot 10^{-3}\text{ mol/l}$, the plots $\log D$ vs. $\log [\text{TBSA}]$ are straight lines with slopes of 0.87 and 0.98

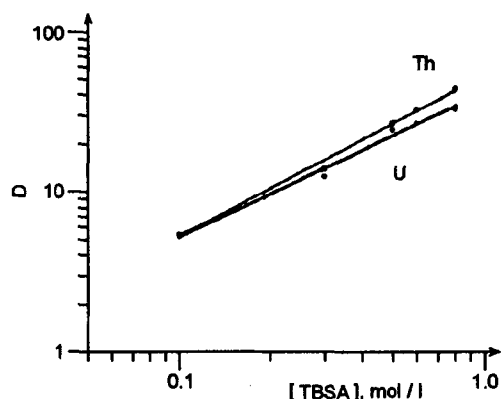


Fig. 2. Distribution coefficients of U(VI) and Th(IV) as a function of initial TBSA concentration at $25\text{ }^\circ\text{C}$; $[\text{U(VI)}] = [\text{Th(IV)}] = 5.0 \cdot 10^{-3}\text{ mol/l}$, $[\text{HNO}_3] = 3.0\text{ mol/l}$

for U(VI) and Th(IV), respectively. These values indicate that the compositions of extracted species are $\text{UO}_2^{2+} \cdot \text{TBSA}$ and $\text{Th}^{4+} \cdot \text{TBSA}$. The apparent extraction constants are also calculated to be 4.74 ± 0.05 and 0.766 ± 0.006 for U(VI) and Th(IV), respectively.

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

In order to gain insight into the structures of TBSA with U(VI) and Th(IV) complexes, the IR spectra of extracts of U(VI) and Th(IV) were investigated. The free C=O stretching vibration is at 1645 cm^{-1} . If the concentration of U(VI) or Th(IV) in organic phase is equal to the concentration of TBSA, the free C=O stretching vibration vanishes and new bands appear. The coordination bands of U(VI) were at 1600 and 1579 cm^{-1} and the coordination bands of Th(IV) were at 1616 cm^{-1} and 1581 cm^{-1} . These features suggest that TBSA is bid in extracted complexes.

Table 1. U-Th separation factors $\alpha = D_{\text{U}}/D_{\text{Th}}$ at different acidities in n-dodecane system

$[\text{HNO}_3]$, mol/l	1	2	3	4	5	6	7
D_{U}	4.98	17.2	23.8	22.4	21.8	19.8	17.6
D_{Th}	0.0365	2.21	25.0	46.6	85.4	131	48.0
α	137	7.8	0.95	0.48	0.26	0.15	0.37

Table 2. The temperature dependence of distribution coefficients of U(VI) and Th(IV) and their separation factors

Temperature, °C	D_U	D_{Th}	α
20	22.6	25.1	0.90
30	17.6	18.0	0.98
40	13.9	13.5	1.03
50	10.5	11.0	0.98
60	8.24	7.72	1.07

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

Results are shown in Table 2 and Fig. 3. It can be seen that D decreases with the increase in temperature for the extraction of U(VI) and Th(IV). This means that the extraction reactions of U(VI) and Th(IV) are exothermic. The relationship $\log D$ vs. $1/T$ is a straight line. According to the thermodynamic formula:

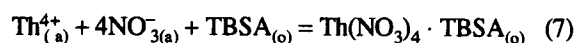
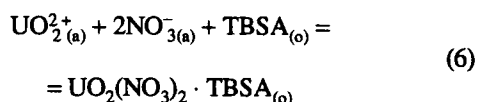
$$\left[\frac{\partial \log D}{\partial (1/T)} \right]_p = - \frac{\Delta H}{2.302R} \quad (3)$$

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

$$\Delta H_{UO_2^{2+}} = -21.08 \text{ kJ/mol} \quad (4)$$

$$\Delta H_{Th^{4+}} = -21.37 \text{ kJ/mol} \quad (5)$$

In these extraction studies, the concentrations of TBSA were in a large excess compared with those of U(VI) and Th(IV). The results suggest that the 1 : 2 : 1 complex U(VI) or 1 : 4 : 1 complex of Th(IV), NO_3^- and TBSA was extracted into the organic phase. Thus, the extraction reactions of the present system can be expressed as follows:



Conclusions

The extraction of U(VI) and Th(IV) by TBSA from nitric acid medium into *n*-dodecane phase is more efficient than into 50% TMB and 50% OK phase. At low acidity (< 1.5 mol/l HNO_3), a good U-Th separation can be reached. An efficient coextraction both of U(VI) and Th(IV) can be obtained if the HNO_3 concentration exceeds

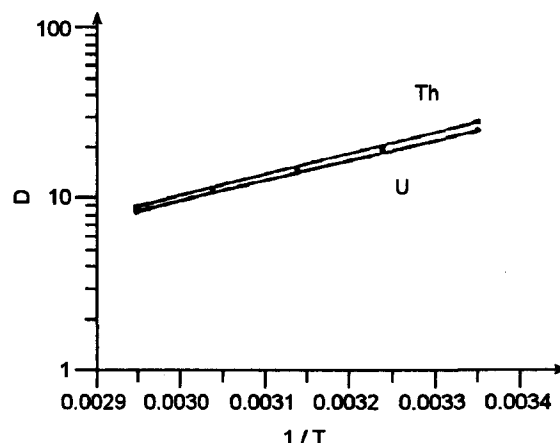


Fig. 3. Distribution coefficients of U(VI) and Th(IV) as a function of temperature; [TBSA] = 0.5 mol/l, [U(VI)] = [Th(IV)] = $5.0 \cdot 10^{-3}$ mol/l, $[HNO_3] = 3.0$ mol/l

3 mol/l. The extraction reactions for U(VI) and Th(IV) are exothermic and the compositions of extracted species are $UO_2(NO_3)_2 \cdot TBSA$ and $Th(NO_3)_4 \cdot TBSA$, respectively. TBSA behaves as a bid in the extracted complexes.

The distinct advantage of TBSA compared with TBP is complete incinerability and harmless radiolytic and hydrolytic degradation products. This is very important for practical applications in the separation of radioelements. TBSA is a promising extractant that might be used in extraction process for reprocessing of U-Th fuel.

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