# The dodecyltolylsulfoxide extraction of uranium(VI)*

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**Abstract** The liquid-liquid extraction behavior of uranium(VI) from aqueous nitric acid media with dodecyltolylsulfoxide (DTSO) has been studied over a wide range of conditions. The extracted species appear to be $UO_2(NO_3)_2 \cdot 2DTSO$. It was found that the extraction was increased with increasing nitric acid concentration up to 5 mol/L $HNO_3$ and then decreased, and the extraction of uranium(VI) decreased with increasing temperature. So it can be deduced that the process of extraction is exothermic and the enthalpy of the extraction obtained is $\Delta H = -16.3\,\text{kJ/mol}$.

**Keywords** Dodecyltolylsulfoxide, Solvent extraction, Uranium(VI)

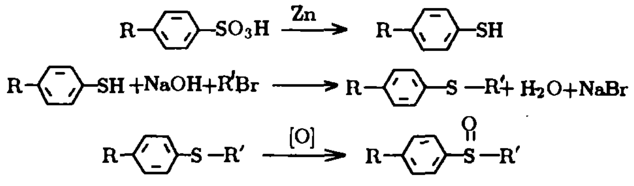
## 1 Introduction

Tri-*n*-butyl phosphate (TBP) has been used for several decades as the most successful extractant for recovery of uranium from spent nuclear fuel (c.f. Purex process). However, there exist two serious disadvantages: (1) the selectivity is not high, and (2) radiolytic degradations of TBP give rise to mono and dibutyl phosphates, which increase the extraction of fission products resulting in a decrease in the overall decontamination factors obtained.[1] Therefore, it's necessary to search and develop some new extractants instead of TBP. Sulfoxides contain the S═O group, and have many advantages, such as thermal stability, low toxicity, potentially enomous and economical supply, noncorrosivity, nonvolatility and good coordination ability. So sulfoxides have been considered as potential extractants for use in nuclear applications for many years.[2~8] In this paper, we will report our results on the extraction of uranyl nitrate from nitric acid with dodecyltolylsulfoxide (DTSO) in toluene.

## 2 Experimental

### 2.1 Synthesis of sulfoxides

The sulfoxide used in this study was not commercially available, it was synthesized and purified in our laboratory:



where R, R′ are alkyl radicals. The final products were purified by recrystallization and distillation under vacuum. The purity of products is checked by elemental analysis, IR spectrometry and NMR spectrometry. The purity of dodecyltolylsulfoxides is $\geq 96\%$.

### 2.2 Instruments and reagents

Vibrator (made by Yancheng Science Instrument Factory, Jiangsu Province, vibration frequency is about 4.58 Hz), temperature controller (precision: ±1 K), 752 type UV grating spectrometer (Shanghai Third Analysis Instrument Factory).

Toluene (AR, made by Reagent Factory, Qilu Petrochemistry Company Research Institute), uranyl nitrate (AR, made in China), nitric acid (industry super purity, Shanghai First Reagent Factory).

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### 2.3 Experimental methods

Except temperature experiment, the experimental temperature was controlled in 298±1 K. Apart from acidity experiment, the experimental acidity is controlled in 2.0 mol/L.

Distribution experiment: extraction coefficients were determined through shaking two phases with the same volume up to equilibrium. In all cases, two phases were shaken mechanically for 15 min to ensure the equilibrium. Uranium (VI) concentration in aqueous solution was assayed with photo spectrometer[9], and uranium (VI) concentration in organic solution was calculated from the difference between total quantity and that in aqueous solution. Distribution coefficients ($D$) of the uranium(VI) is defined as

$$D=\frac{\textit{total concentration of the uranium(VI) in the organic phase}}{\textit{total concentration of the uranium(VI) in the aqueous phase}}$$

## 3 Results and discussion

### 3.1 Influence of nitric acid concentration

In order to examine the variation of $D_{\mathrm{U}}$ as a function of aqueous nitric acid concentration, the extractability of U(VI) in toluene was systematically examined by changing $HNO_3$ concentration from 1 to 7 mol/L in 0.25 mol/L DTSO (see Fig.1). It can be seen from Fig.1 that with increasing aqueous nitric acid molarity, the extraction of U(VI) first increased up to a maximum at about 5 mol/L and then decreased. The initial increase of $D_{\mathrm{U}}$ may be caused by the salting-out effect of nitric aid. With further increasing nitric acid molarity, the concentration of free extractant decreased as a result of coextraction nitric acid. The decrease of $D_{\mathrm{U}}$ at higher acid molarities may also be attributed to the formation of the less extractable complex anion, such as $[UO_2(NO_3)_3]^-$. Further extraction studies were conducted in 2 mol/L $HNO_3$ aqueous medium.

### 3.2 Influence of salting-out agent

The results are indicated in Table 1. It shows that the distribution ratio of uranium (VI) increases rapidly as ammonium nitrate concentration in aqueous solution increases.

**Table 1** The effect of salting-out agent concentration on uranium distribution ratio

| Ammonium nitrate/mol·L$^{-1}$ | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| $D_{\mathrm{U}}$ | 1.10 | 2.51 | 3.65 | 3.97 | 6.29 |

$C^0_{\mathrm{DTSO}}$ = 0.25 mol/L; $C^0_{[UO_2]^{2+}}$ = 4.00 × $10^{-3}$ mol/L; $C^0_{HNO_3}$ = 2.00 mol/L; $T$ = 298±1 K

### 3.3 Influence of complex anion

The results are presented in Table 2. It shows that the distribution ratio of extraction uranium(VI) with DTSO cuts down rapidly as strong complex anion ($C_2O_4^{2-}$) concentration in aqueous solution raises in extraction system. This is because the complex anion ($C_2O_4^{2-}$) and uranium(VI) form hydrophilic complex which may make distribution ratio of uranium(VI) decrease.

**Table 2** The effect of complex anion concentration on uranium distribution ratio

| Sodium oxalate/mol·L$^{-1}$ | 0 | 0.1 | 0.2 | 0.3 | 0.5 |
|---|---|---|---|---|---|
| $D_{\mathrm{U}}$ | 1.10 | 0.818 | 0.724 | 0.629 | 0.190 |

$C^0_{\mathrm{DTSO}}$=0.25 mol/L; $C^0_{[UO_2]^{2+}}$ = 4.00 × $10^{-3}$mol/L; $C^0_{HNO_3}$ = 2.00 mol/L; $T$ = 298±1 K

### 3.4 Variation with extractant concentration

If extraction reaction is supposed as follows:

$$UO_2^{2+} + 2NO_3^- + n\mathrm{DTSO}_{(o)} \overset{K_{ex}}{\rightleftharpoons} UO_2(NO_3)_2\cdot n\mathrm{DTSO}_{(o)} \qquad (1)$$

Equilibrium constant

$$K_{\mathrm{ex}}=\frac{[UO_2(NO_3)_2\cdot n\mathrm{DTSO}]_{(o)}}{[UO_2^{2+}][NO_3^-]^2[\mathrm{DTSO}]^n_{(o)}} \qquad (2)$$

Distribution ratio

$$D=K_{\mathrm{ex}}[NO_3^-]^2[\mathrm{DTSO}]^n_{(o)} \qquad (3)$$

The effect of DTSO concentration on $D_{\mathrm{U}}$ is shown in Fig.2. The plots of lg$D_{\mathrm{U}}$ *vs* lg$[\mathrm{DTSO}]_{(o)}$ give a slope of 1.82 which is close to 2, so the extracted compound should be $UO_2(NO_3)_2\cdot 2\mathrm{DTSO}$.

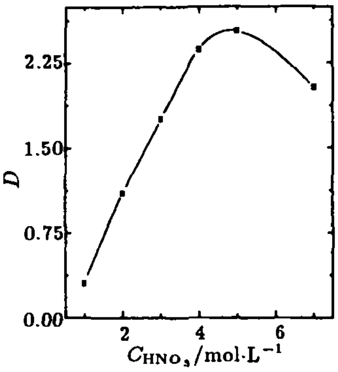

**Fig.1** The effect of nitric acid concentration on distribution ratio

$C^0_{DTSO}$=0.25 mol/L; $T$=298±1 K; $C^0_{[UO_2]^{2+}}$ = 4.00 × $10^{-3}$ mol/L

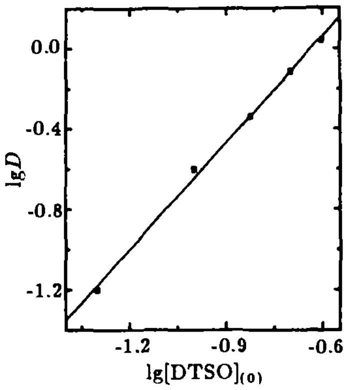

**Fig.2** The effect of DTSO concentration on distribution ratio

$C^0_{HNO_3}$=2.00 mol/L; $T$=298±1 K; $C^0_{[UO_2]^{2+}}$ = 4.00×$10^{-3}$mol/L

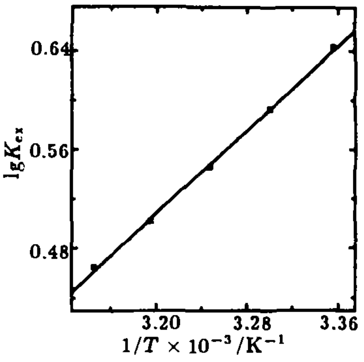

**Fig.3** The effect of temperature on extraction equilibrium

$C^0_{DTSO}$=0.25 mol/L; $C^0_{HNO_3}$=2.00 mol/L; $C^0_{[UO_2]^{2+}}$=4.00×$10^{-3}$mol/L

### 3.5 Effect of temperature

Fig.3 shows the plots of lg$K_{ex}$ *vs* $1/T$ for 0.25 mol/L DTSO systems. According to thermodynamic equations as follows

$$\lg K_{ex} = -\frac{\Delta H^0}{2.303RT} + C \qquad (4)$$

$$\Delta G^0 = -RT\ln K_{ex} \qquad (5)$$

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \qquad (6)$$

we get

$$\Delta G^0 = -3.67\text{kJ/mol}$$

$$\Delta H^0 = -16.3\text{kJ/mol}$$

$$\Delta S^0 = -42.4\text{J/(mol} \cdot \text{K)}$$

The result shows that the reaction of uranium(VI) extraction with DTSO is an exothermic reaction, low temperature is beneficial to extraction reaction, thus uranium can be obtained by distillatory method.

### 3.6 IR spectrum

To study the bond characteristic of the extracted compound, we detected the different IR spectrums of the organic phase before and after extraction with DTSO-toluene. The characteristic absorption peak value of S=O group before extraction is 1045.788cm$^{-1}$, but it decreased to 1028.857 cm$^{-1}$ after extraction. This indicates that the oxygen atom in DTSO can directly form a coordinate bond with U(VI), which may reduce the characteristic extending vibration of S=O group. Furthermore, it is verified that the extracted compound exists in organic phase.

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