Extraction of uranium(VI) with di-(2-ethylhexyl) sulfoxide in toluene*

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Abstract The mechanism of extraction uranium(VI) with di(2-ethylhexyl) sulfoxide (DEHSO) from aqueous nitric acid media has been studied. The influence of the concentrations of nitric acid, extractant, salting-out agent, temperature and complex anions ($C_2O_4^{2-}$) on the distribution ratio was studied.

Keywords Di(2-ethylhexyl) sulfoxide, Solvent extraction, Uranium(VI)

1 Introduction

The solvent extraction method was one of the important techniques in condensing and purification of uranium. Since 1950s, the Purex process in which TBP was used as extractant has been applied widely in nuclear fuel treatment for its better stability, no toxicity, good extraction and selectivity, but there are some drawbacks, such as the chemical decomposing of TBP in using and the explosion of uranyl nitrate solution containing TBP in denitrate process.[1] In order to overcome these drawbacks, developing some new extractants instead of TBP is necessary. Now scientists are very interested in extractant of sulfoxide type, because it contains the S=O group which has stronger coordination ability to metal ions. Besides better heat stability, it has low toxicity and harmless radiolytic degradation products. And it has been demonstrated that sulfoxides had great superiority in nuclear industry utilization.[2~7] But, so far it has not been reported about uranium extraction with DEHSO in toluene. In this paper, the influence of some factors, such as concentration of nitric acid, extractant, salting-out agent, complex anion and temperature on uranium extraction with DEHSO is studied.

2 Experimental

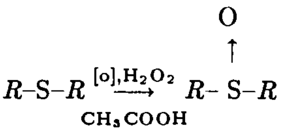
2.1 Synthesis of sulfoxides

Sulfoxides were synthesized in laboratory as it is not available in the market. The synthesis path is as follows:

First, synthesizing mercaptan

$$2R\mathrm{Br} + \mathrm{Na_2S} \longrightarrow R\text{-S-}R$$

Then, synthesizing sulfoxides



$$R\text{-S-}R \xrightarrow[\mathrm{CH_3COOH}]{[\mathrm{o}],\mathrm{H_2O_2}} R\text{-}\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}\text{-}R$$

where R is alkyl radical. The most important step is controlling oxidation in synthesis process. The purity of product is checked by elemental analysis, IR spectrometry and NMR spectrometry. The purity of di(2-ethylhexyl) sulfoxide is more than 96%.

2.2 Instruments and reagents

Vibrator (made by Yancheng Science Instrument Factory, Jiangsu Province), vibration frequency is about 4.5 Hz, controlling temperature precision: ±1 K; 752 type UV grating spectrometer (Shanghai Third Analysis Instrument Factory).

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

2.3 Experimental methods

Except temperature experiment, the temperature is controlled within 298± 1K. Except acidity experiment, the experimental acidity is controlled within 2.0 mol/L.

Distribution experiment: extraction coefficients were determined by shaking up equal volumes of two phases to equilibrium. In all

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cases, to ensure the equilibrium two phases were shaken mechanically for 15 min. Uranium(VI) concentration in aqueous solution was measured by spectrophtometetermeter[8], and uranium(VI) concentration in organic solution was calculated from the difference between total quantity and its quantity in aqueous solution.

3 Results and discussion

3.1 Effect of HNO_3 concentration on U(VI) extraction

Data on the extraction of uranium at different concentrations of nitric acid with 0.25 mol/L DEHSO in toluene are presented in Fig.1. The data in Fig.1 shows that the distribution ratios of uranium are increased as concentration of nitric acid increases; after getting peak value, then decreased. This was because, in the condition of higher nitric acid concentration, some complex anion such as $[UO_2(NO_3)_3]^-$ can be formed which made uranium extraction more difficult. The peak value of uranium distribution ratio appeared at nitric acid concentration about 2 mol/L.

3.2 Effect of extractant concentration

The effect of extractant concentration on extraction equilibrium was investigated under uranium(VI) concentration of 4.00×10^{-3} mol/L and nitric acid concentration 2.00 mol/L in aqueous solution (see Fig.2).

If extraction reaction is as follows:

$$UO_2^{2+} + 2NO_3^- + n\text{DEHSO}_{(o)} \overset{K_{ex}}{\rightleftharpoons} UO_2(NO_3)_2\cdot n\text{DEHSO}_{(o)} \tag{1}$$

$$\text{Equilibrium constant } K_{ex} = \frac{[UO_2(NO_3)_2\cdot n[\text{DEHSO}]_{(o)}}{[UO_2^{2+}][NO_3^-]^2[\text{DEHSO}]^n_{(o)}} \tag{2}$$

$$\text{Distribution ratio } D_U = K_{ex}[NO_3^-]^2[\text{DEHSO}]^n_{(o)} \tag{3}$$

The effect of DEHSO concentration on D_U is shown in Fig.2. The plots of $\lg D_U$ vs $\lg[\text{DEHSO}]_{(o)}$ give a slope of 1.85, close to 2 which indicates that n=2, i.e. the extracted complex may be $UO_2(NO_3)_2\cdot 2\text{DEHSO}$.

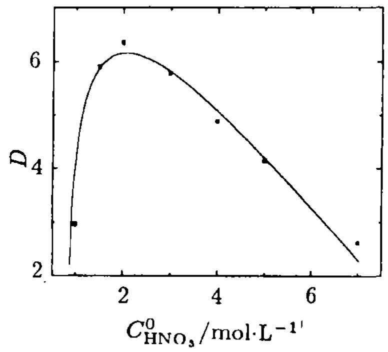

Fig.1 $[HNO_3]$ vs D_U
C^0_{DEHSO} = 0.25 mol/L; T = 298±1 K;
$C^0_{[UO_2]^{2+}} = 4.00\times10^{-3}$ mol/L

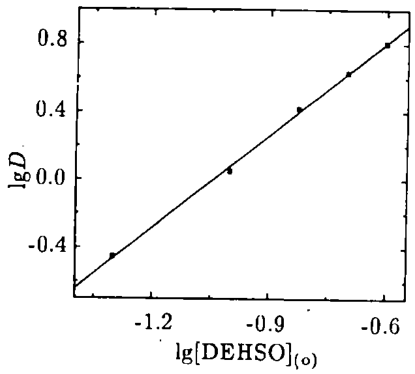

Fig.2 [DEHSO] vs D_U
$C^0_{HNO_3}$ = 2.00 mol/L; T = 298±1 K;
$C^0_{[UO_2]^{2+}} = 4.00\times10^{-3}$ mol/L

3.3 Effect of temperature

Extraction of uranium(VI) from 2 mol/L HNO_3 aqueous medium with 0.25 mol/L DEHSO was investigated at different temperatures. The data are given in Fig.3.

According to thermodynamic equations

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

$$\Delta G^0 = -RT\ln K_{ex} \tag{5}$$

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

By Fig.3 one can get

$$\Delta G^0 = -8.02\,\mathrm{kJ/mol}$$

$$\Delta H^0 = -22.5\,\mathrm{kJ/mol}$$

$$\Delta S^0 = -48.6\,\mathrm{J/(mol \cdot K)}$$

The results show that the reaction of uranium(VI) extraction with DEHSO is an exothermic reaction and low temperature is beneficial to extraction reaction.

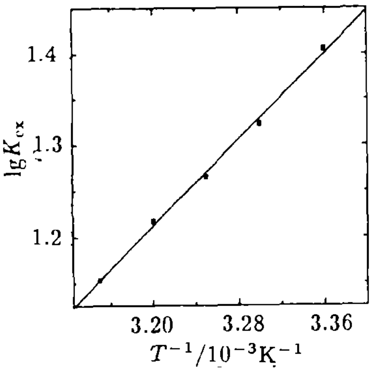

Fig.3 T vs K_{ex}

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

3.4 Effect of salting-out agent concentration

The results are presented in Table 1. The results show that the distribution ratio of uranium(VI) was increased rapidly as ammonium nitrate concentration in aqueous solution increased.

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

Ammonium nitrate/mol·L^{-1}	0	1	2	3	4
D_U	6.35	11.6	12.0	14.0	18.0

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

3.5 Effect of complex anion on uranium(VI) extraction

The results are shown in Table 2. The results show that the distribution ratio of extraction uranium(VI) with DEHSO is cut down rapidly as strong complex anion ($C_2O_4^{2-}$) concentration in aqueous solution is raised in extraction system. This is because complex anion ($C_2O_4^{2-}$) and uranium(VI) formed hydrophile complex which reduces distribution ratio of uranium(VI).

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_u	6.35	3.51	3.08	1.74	0.818

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

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