The n-Octyldodecylsulfoxide(ODSO)-carbon tetrachloride extracting uranium(VI)

YANG Yan-Zhao, YANG Yong-Hui, SUN Si-Xiu
(*Department of Chemisty, Shandong University, Jinan 250100*)

BAO Bo-Rong
(*Shanghai Institute of Nuclear Research,the Chinese Academy of Sciences, Shanghai 201800*)

Abstract The liquid-liquid extraction behavior of uranium(VI) from nitric acid aqueous solution with n-octyldodecylsulfoxide(ODSO) has been studied over a wide range of conditions. The extracted species appear to be $UO_2(NO_3)_2 \cdot 2ODSO$. It was found that the extraction was increased with increasing sodium nitrate concentration. Extracting also increases with increasing extractant concentration. The influence of temperature and nitric acid concentration on extraction equilibrium was also investigated and the enthalpy of the extraction reaction was obtained.

Keywords *n-Octyldodecylsulfoxide, Solvent extraction, Uranium(VI).*

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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 (cf. Purex Process). However, there are two major 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 is necessary to search and develp some new extractants instead of TBP. Sulfoxides contain the S=O group , and have many advantages, such as good thermal stability, low toxicity,potentially enormous and economical supply, noncorrosivity, nonvolatility and good coordination ability. So sulfoxides have been considered as potential extratants for use in nuclear applications for many years.[2~8] In this paper , the influence of some factors, such as concentration of nitric acid, extractant, salting-out and temperature on uranium extraction with octyldodecylsulfoxide (ODSO)- carbon tetrachloride is studied.

2 EXPERIMENTAL

2.1 Synthesis of sulfoxides

The sulfoxide used in our investigation was not commercially available. It was synthesized and purified in our laboratory using the following reactions:

$$RSH + NaOH + R'Br \xrightarrow[\text{Reflux}]{5\%(C_4H_9)_4NBr} RSR' + NaBr + H_2O$$

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$$R\text{-}S\text{-}R' \xrightarrow[25^0C,\ 48h]{H_2O_2,CH_3COOH} R\text{-}\overset{\overset{O}{\|}}{S}\text{-}R' \qquad R = \text{-n-}C_{12}H_{25}, \quad R' = \text{-n-}C_8H_{17}.$$

The solvent was evaporated in vacuum and the solid residue recrystallized from ethanol. The final product was obtained. Its purity was checked by elemental analysis, IR spectrometry and NMR spectrometry. The purity of n-octyldodecylsulfoxide(ODSO) is≥96%, and its melting point is 78°C.

2.2 Instruments and reagents

Vibrator(made by Yancheng Science Instrument Factory, Jiangsu Province), vibration frequency 275±5times/min, controlling temperature precision: ±1K; Type 752 UV grating spectrometer (Shanghai Third Analysis Instrument Factory).

Carbon tetrachloride (AR, made by Jinan Chemical Industry 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 303±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 cases, to ensure the equilibrium two phases were shaken mechanically for 15min. 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 its quantity in aqueous solution. In the paper, the accuracy of all experiment data is the same.

3 RESULTS AND DISCUSSION

3.1 Influence of extractant concentration

The extractability of uranium(VI) from 2.0mol/L nitric acid aqueous medium by ODSO (0.05 to 0.25mol/L) increases with increasing extractant concentration (Fig.1).

$C^0_{UO_2^{2+}}$, and $[UO_2^{2+}]$ refer to the original and equilibrium concentrations of UO_2^{2+}, respectively. The same applies to C^0_{ODSO} and [ODSO].

If the extraction reaction is presented as follows:

$$UO_2^{2+} + 2NO_3^- + nODSO_{(o)} \overset{Kex}{=\!=} UO_2(NO_3)_2 \cdot nODSO_{(o)} \tag{1}$$

Equilibrium constant

$$K_{ex} = \frac{[UO_2(NO_3)_2 \cdot nODSO]_{(o)}}{[UO_2^{2+}][NO_3^-]^2[ODSO]^n_{(o)}} \tag{2}$$

Distribution ratio

$$D = K_{ex}[NO_3^-]^2[ODSO]^n_{(o)} \tag{3}$$

The effect of ODSO concentration on D is shown in Fig.1. The plots of lg$D$ vs lg$[ODSO]_{(o)}$ give a slope of 1.92 which is close to 2, so the extracted compound should be $UO_2(NO_3)_2 \cdot 2ODSO$.

3.2 Influence of nitric acid concentration

In order to examine the variation of D as a function of aqueous nitric acid concentration, the extractability of U(VI) from 1 to 8.5mol/L nitric acid into 0.25mol/L ODSO in toluene was systematically examined. (Fig.2). With aqueous nitric acid molarity increasing, the extraction of U(VI) first increased, passed through a maximum at about 3.5mol/L and then decreased. The initial increase of D may be caused by the salting-out effect of nitric acid. With further increasing of nitric acid molarity, the concentration of free extractant decreased as a result of coextraction nitric acid. The decrease of D at higher acid molarities may also be attributed to the formation of the less extractable complex anion, such as $[UO_2(NO)_3]^-$. Further extraction studies were conducted in 2.0 mol/L HNO_3 aqueous medium.

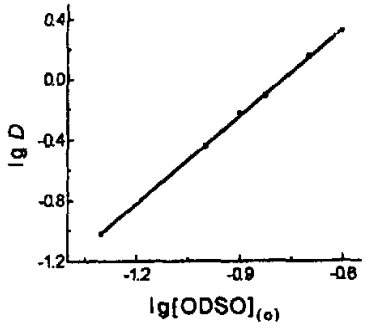

Fig.1 The effect of ODSO equilibrium concentration on distribution ratio ($C^0_{HNO_3}$=2.0mol/L, T=303±1K, $C^0_{UO_2^{2+}}$ =4.00×10^{-3}mol/L)

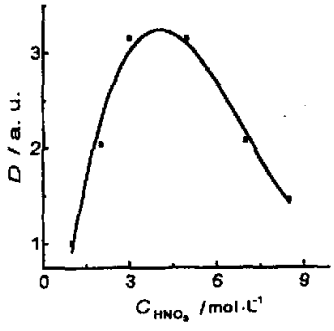

Fig.2 The effect of initial nitric acid concentration on distribution ratio (C^0_{ODSO}=0.25mol/L, T=303±1K, $C^0_{UO_2^{2+}}$=4.00×10^{-3}mol/L)

3.3 Influence of salting-out agent

Fig.3 shows that the distribution ratio of uranium(VI) increases rapidly as the sodium nitrate concentration in aqueous solution increases. D_0 is the distribution ratio without sodium nitrate. The salting-out effect is supposed to be due both to the increase in the thermodynamic activity of uranium(VI) in the aqueous phase (decrease in free water molecules owing to the strong hydration of Na^+ cation)[10] and to the increase in the NO_3^- concentration.

3.4 Effect of temperature

Fig.4 shows the plot of lgK_{ex} vs $1/T$ for 0.25 mol/L ODSO systems.
According to

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

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

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \tag{6}$$

we get

$$\Delta G^0 = -5.34\text{kJ/mol}$$

$$\Delta H^0 = -15.6\text{kJ/mol}$$

$$\Delta S^0 = -33.9\text{J/mol} \cdot \text{K}$$

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

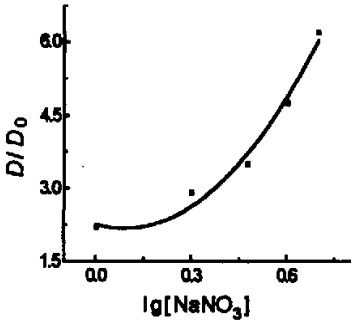

Fig.3 The effect of salting-out agent concentration on distribution ratio (C^0_{ODSO}=0.25mol/L, $C^0_{\text{HNO}_3}$=2.0mol/L, $C^0_{UO_2^{2+}}$=4.00×10^{-3}mol/L, T=303±1K)

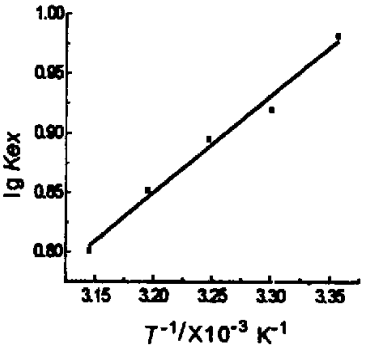

Fig.4 The effect of temperature on extraction equilibrium (C^0_{ODSO} =0.25mol/L, $C^0_{\text{HNO}_3}$=2.0mol/L, $C^0_{UO_2^{2+}}$=4.00×10^{-3}mol/L)

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