The synergic extraction of uranium (VI) with tri-n-butyl phosphate (TBP) and petroleum sulfoxides(PSO)/benzene

DONG Yan*, YANG Yan-Zhao, FAN Wei-Liu, SUN Si-Xiu**

(Department of Chemistry, Shandong University, Jinan 250100)

Abstract The synergistic extraction of uranium (VI) from nitric acid aqueous solution with a mixture of tri-n-butyl phosphate (TBP) and petroleum sulfoxides(PSO) in benzene was studied. It has been found that the maximum synergistic extraction effect occurs where the molar ratio of PSO to TBP is one to two. The composition of the complex of synergistic extraction is $UO_2(NO_3)_2 \cdot TBP \cdot PSO$. The formation constant of the complex K_{TP}=57.44.

Keywords Tri-n-butyl phosphate, Petroleum sulfoxides, Synergistic extraction, Uranium (VI)

CLC numbers O615.11, O625.62, TL283 A

1 INTRODUCTION

The solvent extraction method has been one of the important techniques for concentrating and purifying of uranium, tri-n-butyl phosphate (TBP) has been used for several decades as the most successful extractant for recovery of uranium from spent nuclear fuel. Sulfoxides have been considered as potential extractants for use in nuclear applications for many years.[1~5] Petroleum sulfoxides (PSO) obtained from petroleum refining are widely employed due to their good solubility, abundant and economical supply, nontoxicity, noncorrosivity and radiation stability.[6,7] In this paper, we will report our new results about the synergistic extraction of uranium(VI) with tri-n-butyl phosphate(TBP) and petroleum sulfoxides(PSO).

2 EXPERIMENTAL

2.1 Instruments and reagents

A self-made vibrator, the temperature was controlled with a precision: ±1K. 752 type UV grating spectrophotometer (Shanghai Third Analysis Instrument Factory). Tri-n-butyl phosphate (A.R. Hangzhou Shuanghuan Chemical Plant). Petroleum sulfoxides (the sulfur content in suifoxides was 8.88%, Jiang Han Petroleum Management Office

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Supported by the National Natural Science Foundation of China (20171029)

*Advanced visiting scholar from Dezhou College. **Author for correspondence(E-mail: ssx@sdu.edu.cn)

Manuscript received date: 2001-04-11

Petroleum Chemical Industry Factory). Uranyl nitrate (A.R., made in China). Nitric acid (A.R., Shanghai First Reagent Factory). Benzene (A.R., made in China)

2.2 Experimental methods

The experimental temperature was controlled at 298±1K, the experimental acidity was controlled at 2.0 mol/L. Distribution ratios were determined by mechanically shaking two phases with the same volume up to equilibrium for 20 minutes. The uranium (VI) concentration in aqueous solution was analyzed immediately by spectro-photometrical method[8] and the uranium(VI) concentration in the organic solution was calculated by mass balance.

3 RESULTS AND DISCUSSION

3.1 Extraction of uranium (VI) with TBP and PSO

The extraction of uranium (VI) from 2.0 mol/L nitric acid medium by TBP (0.02 to 0.1 mol/L) (Fig.1a) and PSO (0.02 to 0.1 mol/L) (Fig.1b) in benzene respectively, increases with extractant concentration.

If the extraction reaction is presented as follows:

$$UO_2^{2+} + 2NO_3^- + nTBP_{(o)} \overset{K_T}{\rightleftharpoons} UO_2(NO_3)_2 \cdot nTBP_{(o)} \tag{1}$$

Then the equilibrium constant

$$K_T = [UO_2(NO_3)_2 \cdot nTBP]_{(o)}/[UO_2^{2+}][NO_3^-]^2[TBP]^n_{(o)} \tag{2}$$

The distribution ratio

$$D_T = K_T[NO_3^-]^2[TBP]^n_{(o)} \tag{3}$$

Similarly, the equilibrium constant of PSO system is

$$K_P = [UO_2(NO_3)_2 \cdot nPSO]_{(o)}/[UO_2^{2+}][NO_3^-]^2[PSO]^n_{(o)} \tag{4}$$

and

$$D_P = K_P[NO_3^-]^2[PSO]^n_{(o)} \tag{5}$$

It can be seen from Fig.1a that the slope of the line is 1.99 which is close to 2, so the extracted compound should be $UO_2(NO_3)_2 \cdot 2TBP$. The plot of $\lg D_P$ vs $\lg[PSO]_{(o)}$ in Fig.1b gives a slope of 1.71 which is close to 2, so the extracted compound should be $UO_2[NO_3]_2 \cdot 2PSO$.

Therefore, Eqs.(3) and (5) can be expressed as

$$D_T = K_T[NO_3^-]^2[TBP]^2_{(o)} \tag{6}$$

$$D_P = K_P[NO_3]^2[PSO]^2_{(o)} \tag{7}$$

According to Eqs.(6), (7) and Fig.1a, Fig.1b

$$K_T = 19.03$$

$$K_P = 74.41$$

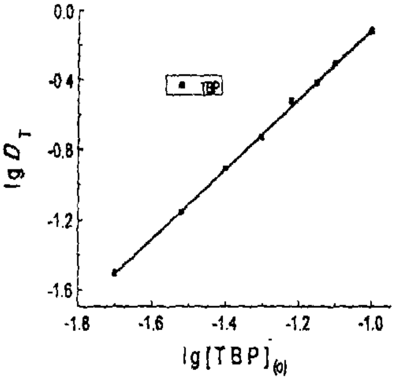

Fig.1a The effect of TBP equilibrium concentration on distribution ratio $C^0_{UO_2^{2+}}=1.0\times10^{-3}$ mol/L

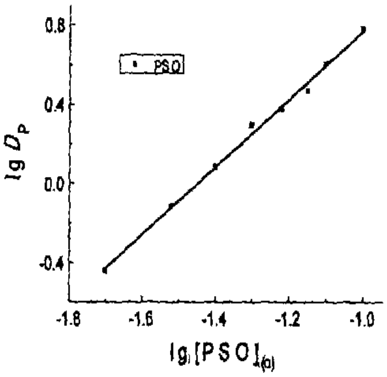

Fig.1b The effect of PSO equilibrium concentration on distribution ratio $C^0_{UO_2^{2+}}=1.0\times10^{-3}$mol/L

3.2 Synergistic extraction mechanism of uranium (VI) by a mixture of TBP and PSO

The distribution ratios of uranium (VI) between 2.0 mol/L aqueous nitric acid and TBP (0.02 to 0.1 mol/L) and 0.1 mol/L PSO in benzene increase with the increasing extractant concentration (Fig.2a). The extractability of uranium (VI) from 2.0 mol/L nitric acid aqueous medium by PSO (0.02 to 0.1 mol/L) and 0.1 mol/L TBP in benzene increases with extractant concentration (Fig.2b)

If the synergistic extraction reaction is presented as

$$UO_2^{2+} + 2NO_3^- + mTBP_{(o)} + nPSO_{(o)} \overset{K_{TP}}{\rightleftharpoons} UO_2(NO_3)_2 \cdot mTBP \cdot nPSO_{(o)} \tag{8}$$

The synergistic equilibrium constant is

$$K_{TP} = [UO_2(NO_3)_2 \cdot mTBP \cdot nPSO]_{(o)}/\{[UO_2^{+2}][NO_3^-]^2[TBP]^m_{(o)}[PSO]^n_{(o)}\} \quad (9)$$

The synergistic extraction distribution ratio is

$$D_{TP} = K_{TP}[NO_3^-]^2[TBP]^m_{(o)}[PSO]^n_{(o)} \quad (10)$$

D_{TP} can be expressed as

$$D_{TP} = D - D_T - D_P \quad (11)$$

Where D is the distribution ratio with the mixture of extractants. D_T and D_P are the distribution ratios with TBP and PSO, respectively.

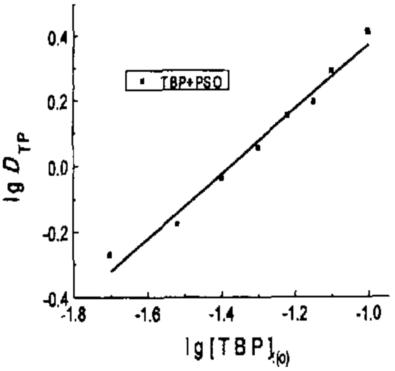

Fig.2a The effect of TBP equilibrium concentration on synergistic extraction distribution ratio,
C^0_{PSO}=0.10mol/L, $C^0_{UO_2^{2+}} = 1 \times 10^{-3}$mol/L

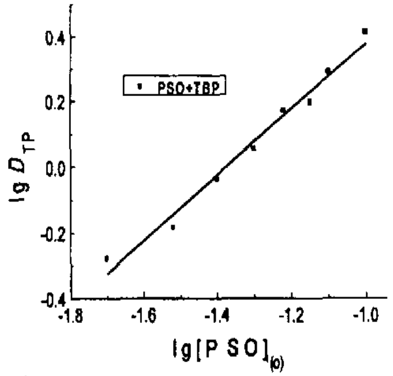

Fig.2b The effect of PSO equilibrium concentration on synergistic extraction distribution ratio,
$C^0_{UO_2^{2+}}=1\times10^{-3}$mol/L, C^0_{TBP}=0.10 mol/L

It can be seen from Fig.2a and Fig.2b that the slope of the line is 0.99 and 0.98, respectively. Therefore, the synergistic extraction reaction can be described as:

$$UO_2^{2+} + 2NO_3^- + TBP_{(o)} + PSO_{(o)} \overset{K_{TP}}{=} UO_2(NO_3) \cdot TBP \cdot PSO_{(o)} \quad (12)$$

$$D_{TP} = K_{TP}[NO_3^-]^2[TBP]_{(o)}[PSO]_{(o)} \quad (13)$$

The experimental data show that the average value of the equilibrium constant K_{TP} is 57.44. Possible homogeneous reactions are as follows:

$$UO_2(NO_3)_2 \cdot 2TBP_{(o)} + UO_2(NO_3)_2 \cdot 2PSO_{(o)} \overset{\beta_1}{=} 2UO_2(NO_3)_2 \cdot TBP \cdot PSO_{(o)} \quad (14)$$

$$\beta_1 = K_{\mathrm{TP}}^2 / K_{\mathrm{T}} K_{\mathrm{P}} \tag{15}$$

$$\mathrm{UO_2(NO_3)_2 \cdot 2TBP_{(o)} + PSO_{(o)}} \overset{\beta_2}{=} \mathrm{UO_2(NO_3)_2 \cdot TBP \cdot PSO_{(o)} + TBP_{(o)}} \tag{16}$$

$$\beta_2 = K_{\mathrm{TP}} / K_{\mathrm{T}} \tag{17}$$

$$\mathrm{UO_2(NO_3)_2 \cdot 2PSO_{(o)} + TBP_{(o)}} \overset{\beta_3}{=} \mathrm{UO_2(NO_3)_2 \cdot TBP \cdot PSO_{(o)} + PSO_{(o)}} \tag{18}$$

$$\beta_3 = K_{\mathrm{TP}} / K_P \tag{19}$$

K_{T}(19.03), K_{P} (74.41) and K_{TP} (57.44) refer to Eqs.(6),(7) and (13). From K_{TP}, K_{T} and K_{P} the values obtained for β_1 , β_2 and β_3 are 2.33, 3.02 and 0.77, respectively. Therefore, we think the synergistic extraction effect is duo to the compound $\mathrm{UO_2(NO_3)_2 \cdot TBP \cdot PSO_{(o)}}$ produced in the organic phase. The suggested structure can be seen in Fig.3.

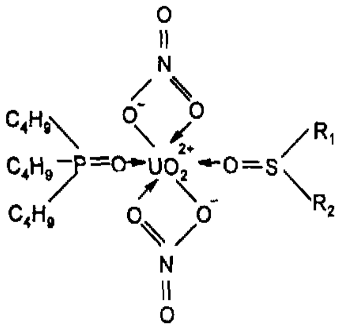

Fig.3 The structure of $\mathrm{UO_2(NO_3)_2 \cdot TBP \cdot PSO}$

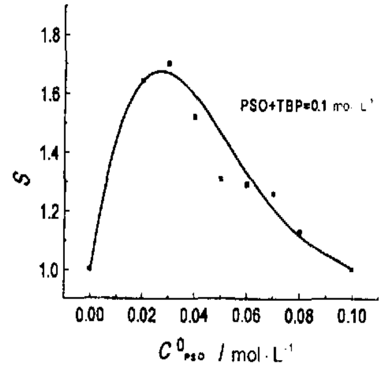

Fig.4 Synergistic extraction coefficient vs. C^0_{PSO}
$C^0_{\mathrm{UO_2^{2+}}} = 1.0 \times 10^{-3}$ mol/L

3.3 Influence of extractant concentration on synergistic extraction coefficient

Synergistic extraction coefficient

$$S = D/(D_{\mathrm{T}} + D_{\mathrm{P}}) = (D_{\mathrm{T}} + D_{\mathrm{P}} + D_{\mathrm{TP}})/(D_{\mathrm{T}} + D_{\mathrm{P}}) \tag{20}$$

The S values from 2.0 mol/L HNO_3 are shown in Fig.4. The synergistic enhancement of the extraction of uranium (VI) is clearly seen in Fig.4, obtained by keeping the total concentration of TBP and PSO constant and varying the fraction of each extractant. It has been found that the maximum synergistic extraction effect occurs where the molar ratio of petroleum sulfoxides (PSO) to tri-n-butyl phosphate (TBP) is one to two.

According to Eqs.(6), (7), (13) and (20), the synergistic extraction coefficient S is presented as follows:

$$S = \{K_{\mathrm{T}}[\mathrm{NO_3^-}]^2[\mathrm{TBP}]^2_{(\mathrm{o})} + K_{\mathrm{P}}[\mathrm{NO_3^-}]^2[\mathrm{PSO}]^2_{(\mathrm{o})} + K_{\mathrm{TP}}[\mathrm{NO_3^-}]^2[\mathrm{TBP}]_{(\mathrm{o})}[\mathrm{PSO}]_{(\mathrm{o})}\}/$$

$$\{K_{\mathrm{T}}[\mathrm{NO_3^-}]^2[\mathrm{TBP}]^2_{(\mathrm{o})} + K_{\mathrm{P}}[\mathrm{NO_3^-}]^2[\mathrm{PSO}]^2_{(\mathrm{o})}\}$$

$$= \{K_{\mathrm{T}} + K_{\mathrm{P}}[\mathrm{PSO}]^2_{(\mathrm{o})}/[\mathrm{TBP}]^2_{(\mathrm{o})} + K_{\mathrm{TP}}[\mathrm{PSO}]_{(\mathrm{o})}/[\mathrm{TBP}]_{(\mathrm{o})}\}/\{K_{\mathrm{T}} + K_{\mathrm{P}}[\mathrm{PSO}]^2_{(\mathrm{o})}/[\mathrm{TBP}]^2_{(\mathrm{o})}\} \tag{21}$$

$$\text{If} \quad x = [\mathrm{PSO}]_{(\mathrm{o})}/[\mathrm{TBP}]_{(\mathrm{o})} \tag{22}$$

$$\mathrm{S} = [K_{\mathrm{T}} + K_{\mathrm{P}}x^2 + K_{\mathrm{TP}}x]/[K_{\mathrm{T}} + K_{\mathrm{P}}x^2] = 1 + K_{\mathrm{TP}}x/[K_{\mathrm{T}} + K_{\mathrm{P}}x^2] \tag{23}$$

Because S is the maximum value where $dS/dx=0$

$$x = (K_{\mathrm{T}}/K_{\mathrm{P}})^{1/2} = (19.03/74.41)^{1/2} = 0.5057 \tag{24}$$

$$[\mathrm{PSO}]_{(\mathrm{o})}/[\mathrm{TBP}]_{(\mathrm{o})} = \mathrm{x} = 0.5057$$

Owing to

$$[\mathrm{PSO}]_{(\mathrm{o})} + [\mathrm{TBP}]_{(\mathrm{o})} = 0.10\,\mathrm{mol/L}$$

$$[\mathrm{PSO}]_{(\mathrm{o})} = 0.0336\,\mathrm{mol/L} \tag{25}$$

So the calculated value of the maximum synergistic extraction coefficient S is near the experimental value.

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