LETTER TO THE EDITOR

The effect of diluents on extraction of uranium(VI) with petroleum-sulfoxides (PSO)

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The effect of diluents on the extraction of uranium(VI) with petroleum sulfoxides (PSO) was studied. The decreasing order of extraction ability of PSO is as follows: benzene, toluene, cyclohexane, heptane, kerosene, carbon tetrachloride and chloroform. The effect of temperature on the extraction equilibrium was also investigated and enthalpy of the extraction was obtained. The relationship between the extraction equilibrium constants K_{ex} and the physical parameters of diluents can be derived.

Introduction

Tri-n-butyl phosphate(TBP) has been used for several decades as the most successsful extractant for recovery of uranium from spent nuclear fuel (c.f. Purex Process). However, there exist two major disadvantages: (1) The selectiviity 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 develop some new extractants instead of TBP. Sulfoxides contain the S=O group, and have stronger coordination ability to metal ions. So sulfoxides have been considered as potential extractants for use in nuclear applications for many years.[2–7]

Petroleum sulfoxides (PSO) obtained as by products from petroleum refining are being employed most commonly for good solubility, abundant and economical supply, nontoxicity, noncorrosivity and radiation stability. So scientists are very interested in PSO.[8,9] Extraction of uranium with PSO has a lot of influence factors. The diluent is one of the most important factors. In order to make clear the effect of diluents on extraction ability, this paper studied the distribution equilibrium of extraction of uranium(VI) with PSO in different diluents.

Experimental

Instruments and reagents

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

Benzene (AR, made by Shanghai First Reagent Factory). Toluene (AR, made by Qilu Petrochemistry Company Research Institute Reagent Factory).

Cyclohexane (AR, made by Jining Chemical Industry Research Institute). Heptane (AR, made by Shanghai Chemical Reagent Purchasing Supply Station). Kerosene (sulfonating kerosene). Tetrachloride (AR, AR, made by Jinan Chemical Industry Factory). Chloroform (AR, made by Shandong Yucheng Industry and Commerce General Company Chemical Reagent Factory). Uranyl nitrate (AR, made in China), Nitric acid (industry superpurity, Shanghai First Reagent Factory). Petroleum sulfoxides (the sulfurous content 8.88%).

Methods

The experimental temperature was controlled in 298± 1 K. The experimental acidity is controlled in 2.0 mol/l. The extraction coefficients were determined through shaking two phases with same volume up to equilibrium. In all cases, to ensure the equilibrium two phases were shaken mechanically for 15 minutes. Uranium(VI) concentration in aqueous solution was determined with photo spectrometer,[10] and uranium(VI) concentration in organic solution was calculated from the difference between total quantity and that in aqueous solution.

Results and discussion

Influence of nitric acid concentration

In order to examine the variation of Du as a function of aqueous nitric acid concentration, the extractibility of U(VI) from 1 to 7 mol/l nitric acid into 0.25 mol/l petroleum sulfoxides(VI) in different diluents was systematically examined (Fig. 1). With increasing aqueous nitric acid concentration, the extraction of U(VI) first increased, passed through a maximun and then decreased. The initial increase of Du may be caused by the salting-out effect of nitric acid. With further increasing of nitric acid concentration, the concentration of free extratant decreased as a result of coextraction

nitric acid. The decrease of Du at higher acid concentration 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 mol/l nitric acid aqueous medium.

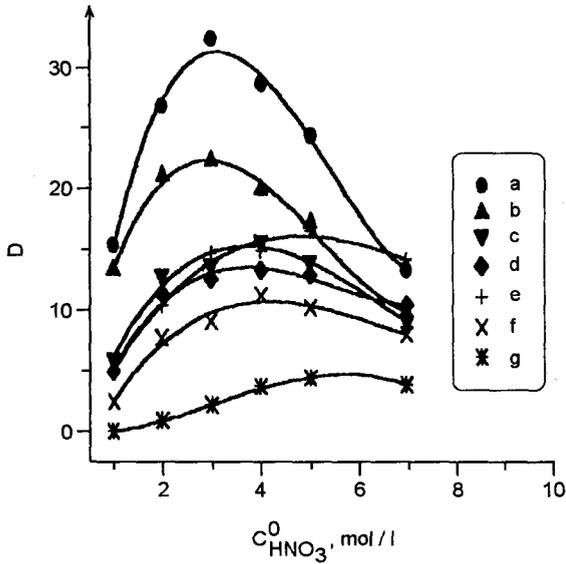Fig. 1. The effect of nitric acid concentration on distribution ratio $(C^0_{PSO} = 0.25$ mol/l $T = 298 \pm 1$ K, $C^0_{[UO_2]^{2+}} = 4.00 \cdot 10^{-3}$ mol/l; a. Benzene; b. Toluene; c. Cyclohexane; d. Heptane; e. Kerosine; f. Carbon tetrachliride; g. Chloroform

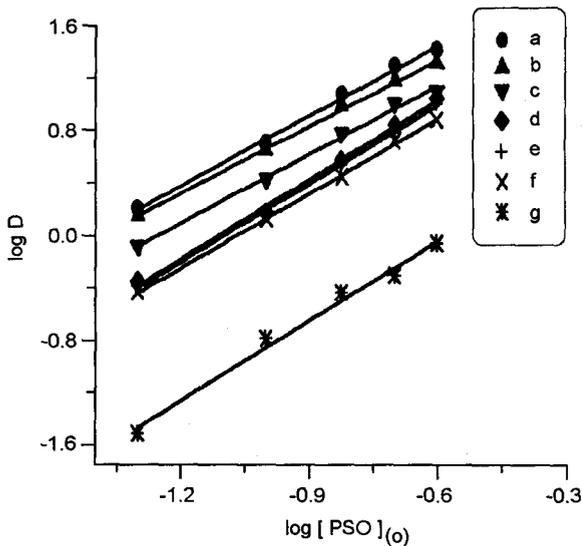Fig. 2. The effect of PSO concentration on distribution ratio $(C^0_{HNO3} = 2.00$ mol/l, $T = 298 \pm 1$ K, $C^0_{[UO_2]^{2+}} = 4.00 \cdot 10^{-3}$ mol/l); a~g are the same as in Fig. 1

Influence of extractant concentration

The extractabilities of uranium(VI) from 2.00 mol/l nitric acid aqueous medium by PSO (0.05 to 0.25 mol/l) in different diluents increase with increasing extractant concentration (Fig.2).

The extraction reactions are presented as follows:

$$UO_2^{2+} + 2NO_3^- + nPSO \xrightleftharpoons{K_{ex}} UO_2(NO_3)_2 \cdot nPSO_{(o)} \quad (1)$$

Equilibrium constant

$$K_{ex} = \frac{[UO_2(NO_3)_2 \cdot nPSO]_{(o)}}{[UO_2^{2+}][NO_3^-]^2[PSO]^n_{(o)}} \quad (2)$$

Distribution ratio

$$D = K_{ex}[NO_3^-]^2[PSO]_{(o)}^n \quad (3)$$

The effect of PSO comcentration on Du is shown in Fig. 2. The plots of log D vs. $\log[PSO]_{(o)}$ give slopes in different diluents which are close to 2 (Table 1), so the extracted compound in different diluents should be $UO_2(NO_3)_2 \cdot 2PSO$.

Influence of the temperature

Figure 3 shows the plot of log K_{ex} vs. $1/T$ for 0.25 mol/l PSO in different diluents.
According to

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

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

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

we get ΔH^0, ΔG^0 and ΔS^0 (Table 2).

Data in Table 2 show that all reactions of uranium(VI) extraction with PSO in different diluents are exothermic reactions, low temperature is benefit to extraction reaction, thus uranium can be obtained by distillatory method.

Influence of diluent characters on extraction equilibrium

The extraction ability of U(VI) with PSO in different diluents is as follows: benzene > toluene > cyclohexane > heptane > kerosene > carbon tetrachloride > chloroform. The values of physical parameters of various diluents and extraction equilibrium constants are listed in Table 3.

Table 3 shows that the equilibrium constants of extraction reaction in different diluents are not alike. The difference has relation to weak interaction between diluent, extract and extractant molecule. Any single empirical solvent parameter must have a fixed relative sensitivity to each of the various interaction mechanisms implied. Thus, it is difficult to describe the weak interaction using single physical parameter of diluents.

Table 1. The number of solvation of extraction of U(VI) with PSO in different diluents

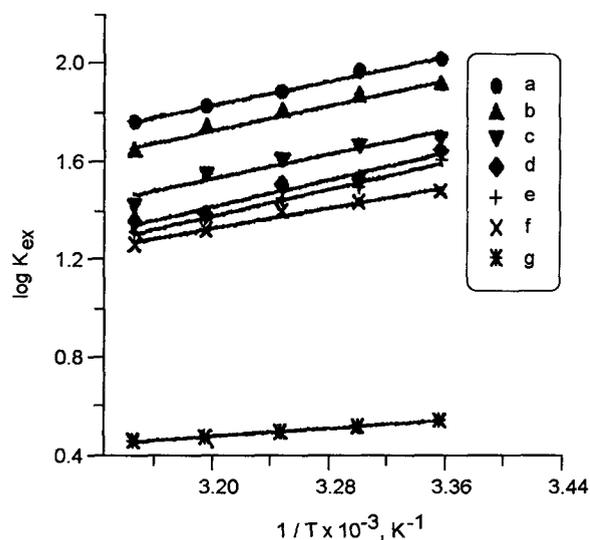| Diluents	Benzene	Toluene	Cyclohexane	Heptane	Kerosene	Carbon tertrachlorid	Chloroform
Number of solvation	2(1.89)	2(1.85)	2(1.86)	2(2.02)	2(1.99)	2(1.90)	2(2.04)

Fig. 3. The effect of temperature on extraction equilibrium. C^0_{PSO}, $C^0_{[UO_2]^{2+}}$ and a~g are the same as in Fig. 1

Table 2. The thermodynamics constant of extraction reaction

Diluent	ΔH^0, kJ·mol^{-1}	ΔG^0, kJ·mol^{-1}	ΔS^0, J·K^{-1}·mol^{-1}
Benzene	–24.8	–11.6	–44.3
Toluene	–25.5	–11.0	–48.7
Cyclohexane	–25.0	–9.77	–51.1
Heptane	–27.7	–9.46	–61.2
Kerosene	–27.3	–9.22	–60.7
Carbon tetrachlorid	–21.0	–8.49	–42.0
Chloroform	–8.66	–3.14	–18.5

$C^0_{PSO} = 0.25$ mol/l, $C^0_{[UO_2]^{2+}} = 4.00 \cdot 10^{-3}$ mol/l, $T = 298\pm1$ K.

A more rigorous approach has been suggested by KOPPEL and PALM, who argue that a complete description of all solute-solvent interactions must include both nonspecific and specific effects. They proposed the general four parameter equation which related the variation of a given property A to two nonspecific (Y and P) and two specific characteristics of the solvent (E and B):

$$A = A_0 + y \cdot Y + p \cdot P + e \cdot E + b \cdot B \qquad (7)$$

where A is the value of a solvent-dependent physico-chemical property (here log K_{ex}) in a given solvent, and A_0 is the statistical quantity corresponding to the value of this property in an inert solvent. The nonspecific parameters Y and P measure solvent polarization and polarizability, respectively, according to classical dielectric theory. Dielectric constants, ε, are the basis of Y, and were used in form of the KIRKWOOD function, $(\varepsilon-1)/(2\varepsilon+1)$, a function based on the expression for molar polarization. The functions $(n_D^2-1)/(n_D^2+1)$ of the refractive index for sodium light were used for the polarizability parameter, P. E and B are specific parameters measuring the LEWIS acidity (electrophilic solvating power) and LEWIS basicity (nucleophilic solvating power) of solvent, respectively, with α and β. And y, p, e and b are the corresponding regression cofficients indicating the sensitivity of A to the four different solvent parameters.

Therefore, the following equation are obtained:

$$\log K_{ex} = 2.01-14.4 \ (\varepsilon-1)/(2\varepsilon+1)+$$
$$+7.53(n_D^2-1)/(n_D^2+1)+2.37 \ \alpha+4.24 \ \beta$$

Correlation coefficient is $R = 0.999$.

This equation can satisfactorily describe the effect of diluents on physical chemical behavior in extraction system, such as chloroform with specific interaction diluents. The equilibrium constant of extraction of uranium with PSO in chloroform is rather low. It may be attributed to the formation of hydrogen bond between chloroform and PSO . Thus, the effective concentration of PSO was reduced, and influenced the combination between PSO and $UO_2(NO)_2$.

Table 3. The values of physical parameters of various diluents and extraction equilibrium constants

Diluents	ε (20 °C)[11]	n_D^{20} [11]	α^{12}	β^{12}	$\log K_{ex}$ (25 °C)
Benzene	2.27	1.5011	0.00	0.10	2.030
Toluene	2.38	1.4969	0.00	0.11	1.924
Cyclohexane	2.02	1.4262	0.00	0.00	1.712
Heptane	1.92	1.3876	0.00	0.00	1.658
Kerosene*	2.016	1.4216	0.00	0.00	1.617
Carbon tetrachlorid	2.23	1.4602	0.00	0.00	1.489
Chloroform	4.81	1.4459	0.44	0.00	0.550

* The physical parameters of dodecane.[13]

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