Solvent extraction of uranium(VI) and europium(III) from nitrate media by picolinamide

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Abstract The solvent extraction of uranium(VI) and europium(III) from nitric acid solution was studied with picolinamide dissolved in ethylene dichloride. The distribution ratios of U(VI) and Eu(III) as a function of aqueous HNO_3 concentration , extractant concentration in organic phase and temperature as well as the salting-out agent concentration have been measured. The experiment results show that picolinamide has higher extractability for U(VI) than for Eu(III). The composition of extracted species, equilibrium constants and enthalpies of extraction reaction have also been presented.

Keywords Picolinamide, U(VI), Eu(III), Solvent extraction
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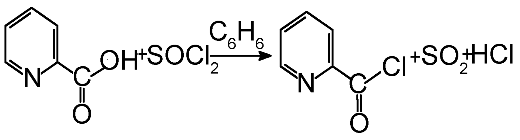
1 Introduction

The separation of actinide/lanthanide (An/Ln) from effluents generated during the nuclear fuel reprocessing cycle has been extensively studied in recent years for improving the management of radioactive wastes.[1-4] It was demonstrated that the ligand with soft donor atom (pyridinic nitrogen for example) had higher affinity for the An(III) than for the Ln(III).[2] Furthermore, owing to their complete flammability and non-harmful radiolytic and hydrolytic degradation products, picolinamide (NPPFA) was a promising extractant. In this paper, we synthesized picolinamide and studied systematically its extractions for U(VI) and Eu(III). The result shows that the distribution of U(VI) is higher than that of Eu(III). The extraction mechanisms of U(VI) and Eu(III) by picolinamide and thermodynamic parameters are also presented.

2 Experimental

2.1 Materials

Picolinamide was synthesized and purified for the first time in our laboratory. The synthetic route could be expressed as follows:



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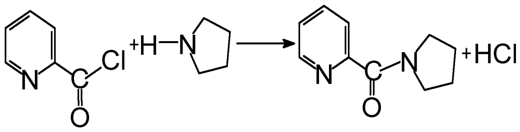

(2)

Its composition and structure were confirmed by IR, ^{1}HNMR and GS-MS. The result showed that purity of the product was high enough (over 98%) for use in extraction experiments.

2.2 Procedures

Distribution equilibrium was determined by contacting equal volumes of organic and aqueous phases in stopped tubes and shaking for about 30 min, which was found to be sufficient for reaching the equilibrium. Experiments were carried out at 25℃ except for temperature experiments. The uranium(VI) and europium(III) contents in aqueous phase were determined by Arsenazo-III spectrophotometric method[5] and those in organic phase were obtained by subtracting the aqueous concentration of U(VI) and Eu(III) from the

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initial aqueous concentration. The distribution ratio(D) defined as the metal concentration in organic phase to the metal concentration in aqueous phase was calculated.

3 Results and discussion

3.1 Effect of acidity of aqueous phase on distribution ratio

Under the conditions of 0.5 mol/L picolinamide in ethylene dichloride and 5.0×10^{-4} mol/L of U(VI) or 1.0×10^{-3} mol/L of Eu(III) in aqueous phase, picolinamide has almost no extractability for U(VI) and Eu(III) under high acidity and has extractability for them under low acidity, so we selected pH=2.04 in aqueous phase in our later experiment in order to prevent the hydrolysis of metal ions.

3.2 Effect of extractant concentration on distribution ratio

The influence of picolinamide concentration on the distribution ratios of U(VI) and Eu(III) was shown in Fig.1 and Fig.2. In the case of pH=2.04 and $C_{UO_2^{2+}}=5.0\times10^{-4}$ mol/L or $C_{Eu(III)}=1.0\times10^{-3}$ mol/L, the plots of lg$D$ vs lg$C_{NPPFA(o)}$ are straight lines with slopes of 0.85 and 0.88 for U(VI) and Eu(III) respectively. These values indicate that the compositions of extracted species are $UO_2(NO_3)_2$• (NPPFA) and $Eu(NO_3)_3$•(NPPFA).

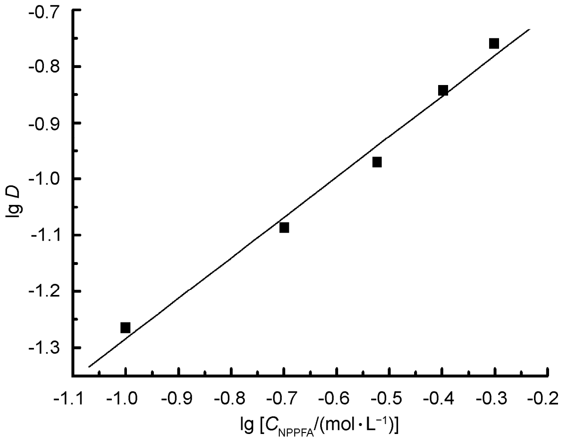


Fig.1 Effect of picolinamide concentration in ethylene dichloride on distribution ratio of U(VI).

$C_{UO_2^{2+}}=5\times10^{-4}$mol/L, pH=2.04, T=(298±1)K, $V_{(O)}$:$V_{(W)}$=1:1, t=30min.

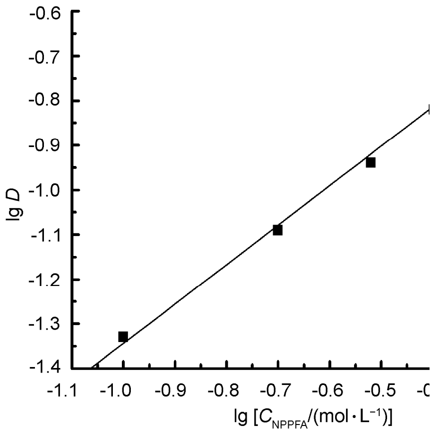


Fig.2 Effect of picolinamide concentration in ethylene dichloride on distribution ratio of Eu(III).

$C_{Eu(III)}=1\times10^{-3}$mol/L, pH=2.04, T=(298±1)K, $V_{(O)}$:$V_{(W)}$=1:1, t=30min, C_{LiNO_3}=4mol/L.

Extraction reaction might be presented as follows:

$$UO_2^{2+}{}_{(a)}+2NO_3^-{}_{(a)}+NPPFA_{(o)}=UO_2(NO_3)_2\bullet(NPPFA)_{(o)}$$

$$Eu^{3+}{}_{(a)}+3NO_3^-{}_{(a)}+NPPFA_{(o)}=Eu(NO_3)_3\bullet(NPPFA)_{(o)}$$

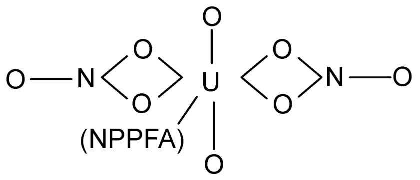
where the subscripts “o” and “a” represent organic phase and aqueous phase, respectively and the equilibrium constants, K_{ex}, are

$$K_{ex1}=\frac{[UO_2(NO_3)_2\cdot(NPPFA)_{(o)}]}{[UO_2{}^{2+}{}_{(a)}][NO_3^-{}_{(a)}]^2[NPPFA_{(o)}]}$$

$$K_{ex2}=\frac{[Eu(NO_3)_3\cdot(NPPFA)_{(o)}]}{[Eu^{3+}{}_{(a)}][NO_3^-{}_{(a)}]^3[NPPFA_{(o)}]}$$

From the equations, we can get the value of $K_{ex1}=1.56$ mol^{-3}•L^3 for U(VI) and $K_{ex2}=1.24$ mol^{-4}•L^4 for Eu(III) in ethylene dichloride.

The IR spectra show a shift of the pyridinic ring stretching vibration from 996.31 cm^{-1} to 1011.66 cm^{-1} and a shift of the carbonyl stretching vibration from 1628.56 cm^{-1} to 1594.78 cm^{-1}. These features imply the formation of a bidentate complex. The metal-picolinamide was bonded through the oxygen of the carbonyl group and the nitrogen of the pyridinic ring. The appearance of bands at 1033.96 cm^{-1}, 1276.85 cm^{-1} and 1479.07 cm^{-1} in the spectra is attributed to the N-O stretching vibration and to the asymmetric stretching vibration of trans-coordinated nitrate groups, respectively[6]. An additional band described as stretching vibration of the uranyl ion is noted at 928.37 $\mathrm{cm^{-1}}$.[7,8] Thus, the structure of picolinamide/metal nitrate complex is depicted in the following scheme:



3.3 Effect of temperature on extraction distribution ratio

The effect of temperature on the extraction distribution ratio is shown in Fig.3 and Fig.4, which indicate that $D_{\mathrm{(metal)}}$ decrease with the increase of temperature for the extraction reactions of U(VI) and Eu(III). This means that the extraction reactions of U(VI) and Eu(III) are exothermic.

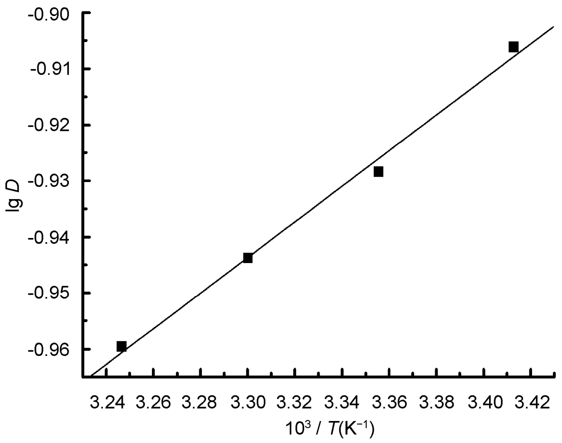


Fig.3 Dependence of distribution ratio of U(VI) on temperature.

$C_{\mathrm{UO_2^{2+}}}$ =5×10^{-4} mol/L, pH=2.04, $V_{\mathrm{(O)}}$:$V_{\mathrm{(W)}}$=1:1, t=30min, C_{NPPFA}=0.4 mol/L.

From the slope of Fig.3 and Fig.4, enthalpies of the extraction reaction could be evaluated by the following equation:

$$\frac{\partial(\lg D)}{\partial(1/T)} = -\frac{\Delta H}{2.303R}$$

and $-\Delta H$ for U(VI) and Eu(III) were calculated to be 6.1 kJ/mol and 7.81 kJ/mol respectively.

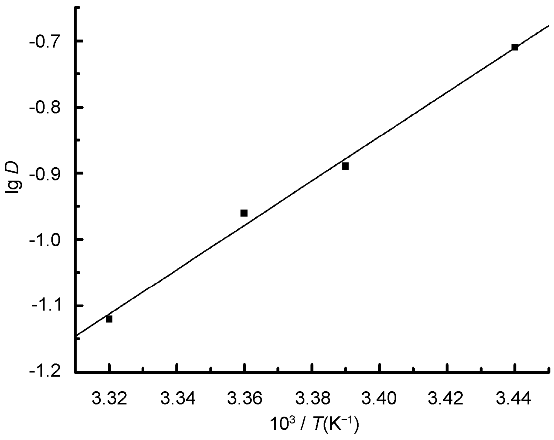


Fig.4 Dependence of distribution ratio of Eu(III) on temperature.

$C_{\mathrm{Eu(III)}}$=1×10^{-3}mol/L, pH=2.04, C_{NPPFA}=0.3 mol/L, $V_{\mathrm{(O)}}$:$V_{\mathrm{(W)}}$=1:1, t=30min, $C_{\mathrm{LiNO_3}}$ =4 mol/L.

3.4 Effect of salting-out agent concentration on distribution ratio of U(VI) and Eu(III)

In order to examine the variation of D_{U} and D_{Eu} as a function of salting-out agent concentration, the extractability of U(VI) and Eu(III) from 1 to 5 mol/L salting-out agent into 0.4 mol/L picolinamide in ethylene dichloride was observed (Fig.5). The experimental results show that the trend of increasing in extraction distribution for U(VI) is more obvious than that of increasing in extraction distribution for Eu(III) with the increase of salting-out agent concentration. In addition, Table 1 shows that a separation factor in dis-ratio $\beta_{\mathrm{U/Eu}}$ of 14.36 is obtained at 5mol/L of $\mathrm{LiNO_3}$ (see Table 1).

Table1 Variation of partion coefficient and separation factor $\beta_{\mathrm{U/Eu}}$ with $\mathrm{LiNO_3}$ concentration in aqueous solution for the extraction of U(VI) and Eu(III)

$C_{\mathrm{LiNO_3}}$ (mol/L)	D_{U}	D_{Eu}	$\beta_{\mathrm{U/Eu}}$
1	0.33	0.041	8.05
2	0.61	0.08	7.63
3	0.93	0.12	7.75
4	1.95	0.17	11.47
5	3.16	0.22	14.36

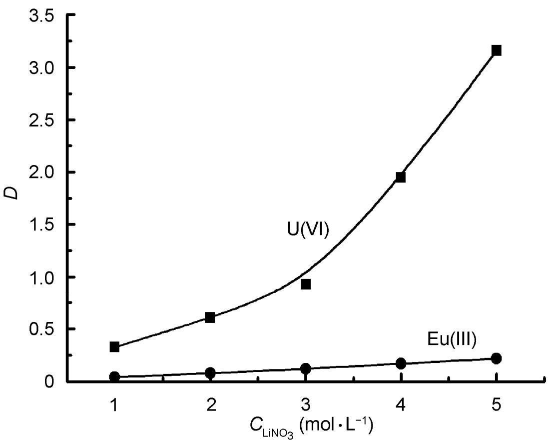


Fig.5 Extraction of U(VI) and Eu(III) nitrate by 0.5mol/L picolinamide in ethylene dichloride at room temperature. The aqueous phase contained HNO_3(0.01mol/L) and $LiNO_3$.

4 Conclusion

Picolinamide has a better ability to extract U(VI) than to extract Eu(III), the reason is that picolinamide with soft donor atom (pyridinic nitrogen) has higher affinity for An than for Ln. The addition of salutingout agent can improve the separation of An and Ln. The extraction reactions for U(VI) and Eu(III) are exotheromic, and compositions of extracted species are $UO_2^{2+}(NO_3)_2$•(NPPFA) and $Eu(NO_3)_3$•(NPPFA).

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