Extraction of uranium (VI) from nitric acid with N-decanoylpyrrolidine (DPOD) in toluene

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Abstract The extraction behaviors of uranium (VI) from nitric acid by N-decanoylpyrrolidine (DPOD) in toluene has been studied at varying concentrations of nitric acid, extractant, salting-out agent $LiNO_3$ and at different temperatures. The mechanism of extraction is discussed in the light of the results obtained.

Keywords Extraction, Uranium(VI), N-decanoylpyrrolidine, Toluene

1 Introduction

The N,N-dialkylamide of carboxylic acids is good extractants of metallic ions[1] and they are considered as an alternative to TBP for the irradiated nuclear fuels reprocessing.[2] N,N-dialkylamide are resistant to hydrolysis and radiolysis and , unlike TBP , their degradation products do not interfere severely in the separation process.

Some N,N-disubstituted and N,N'- tetrasubstituted amides have been synthesized in our laboratory ,and the extraction behaviors of uranium (VI) and thorium (IV) with them has been described in our previous papers.[3,4] A new type of this extractants, N - acylpyrrolidines, has been synthesized now. The extraction of uranium (VI) from nitric acid by N -decanoylpyrrolidine in toluene is reported in this paper.

2 Experimental

DPOD was synthesized according to the papers described[5,6] and purified by distillation under reduced pressure. The purity of the product was checked by elemental analysis, IR and NMR spectroscopy, which is higher than 98%. Extraction were carried out by shaking equal volumes of DPOD diluted with toluene and uranyl nitrate solution containing nitric acid in a stopped tube at the required temperature for 2 h. Phase disengagement was rapidly obtained by centrifugation.

Uranium (VI) ion in aqueous solution was analyzed by the arsenazo-III spectrophotometry and then the distribution ratio of uranium (VI) ion was calculated.

3 Results and discussion

3.1 Dependence on acid concentration

Fig.1 shows that the distribution ratio for extraction of uranium (VI) into organic phase containing DPOD from nitric acid solutions increases greatly with increasing acidity below 2.5 mol·L^{-1}. Above this acidity the curve shows a gradual slope and there is a maximum at the

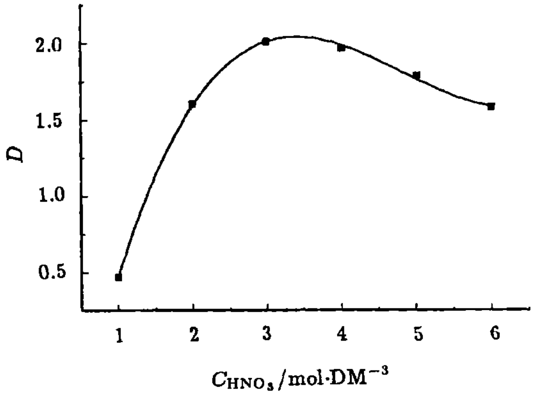


Fig.1 Variation of distribution ratio with initial aqueous nitric acid concentration for the extraction of U(VI) by solutions of DPOD in toluene
$[UO_2^{2+}]=5\cdot10^{-3}$mol·dm^{-3}, [DPOD]=0.30 mol·dm^{-3}, T=298K

Manuscript received date: 98-12-03

concentration of HNO_3 about 3.0 mol·L^{-1}, then the distribution ratios decrease at higher acidities. It is because that DPOD can also extract HNO_3 from aqueous solution, then at higher acidities the concentration of free extractant decreases which leads to the decrease of the partition, which is similar to the extraction of uranium(VI) by other N,N-disubstituted amides.[3]

3.2 Dependence on extractant concentration

The dependence of distributions ratios on DPOD concentration, examined at 5×10^{-3} mol/L U(VI) in 3.0 mol/L HNO_3, is shown in Fig.2. The plot of lg$D$ vs lg $[DPOD]_{(o)}$ gives a slope of 2.1 which indicates that two DPOD molecules coordinate to one, UO_2^{2+} and $UO_2(NO_3)_2(DPOD)_2$ can be determined by the stoichiometry of extracted complex. The coordination mechanism of uranyl (VI) ion extraction by DPOD may be represented by:

$$UO_2^{2+} + 2NO_3^- + DPOD_{(0)} = UO_2(NO_3)_2(DPOD)_{2(o)} \tag{1}$$

Where subscript "o" refers to the species presented in organic phase, For above reaction the equilibrium constant, K_{ex}, is

$$K_{ex} = \frac{[UO_2(NO_3)_2(DPOD)_2]_{(0)}}{[UO_2^{2+}][NO_3^-]^2[DPOD]^2_{(0)}} \tag{2}$$

Eq.(2) can be rearranged as:

$$\lg D = \lg K_{ex} + 2\lg[NO_3^-] + 2\lg[DPOD]_{(0)} \tag{3}$$

From Fig.2, the value of Kex for U(VI) with DPOD in toluene is calculated to be 3.84 mol^{-4}·dm^{12}, Which is smaller than that of extraction of uranium (VI) by N,N-dibutyldecanamide[7] (DBDEA) because the structure of the secondary amine affects the extraction ability.

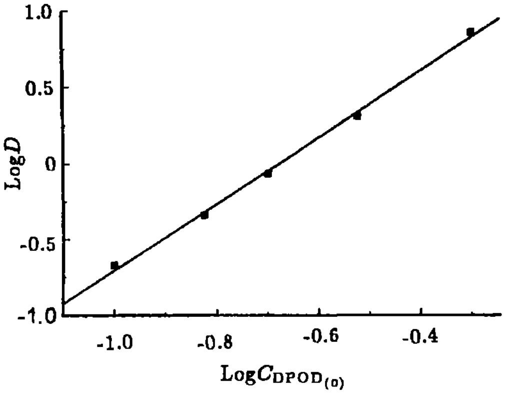


Fig.2 Dependence of the distribution ratio of U(VI) on DPOD concentration in toluene $[UO_2^{2+}]=5\cdot10^{-3}$ mol·dm^{-3}, $[HNO_3]=3.0$ mol·dm^{-3}, $T=298$K

3.3 Dependence on $LiNO_3$ concentration in aqueous solutions

Fig.3 shows the influence of the concentration of lithium nitrate on the distribution ratio of U (VI). The extraction of uranium (VI) increases rapidly with increasing $LiNO_3$ concentration. $LiNO_3$ here plays an important role of not only salting-out agent which increases the uranyl (VI) ion activity but also homo-ion shifting the extraction equilibrium to the right.

3.4 Effect of temperature on extraction of U (VI)

Fig. 4. Illustrates the effect of temperature on the distribution ratio of uranium (VI) ion. The lg$D$ values increase linearly with increase of $1/T$.This result indicates that the extraction reaction is an exothermal one which is similar to the extraction behaviors of other N,N-dialkylamides on the extraction of uranium (VI). The change in enthalpy, ΔH, associated with reaction (1) can be evaluated by means of Van't Hoff equation. The heat of reaction for the extraction of uranium (VI) by N-decanoylpyrrolidine (DPOD) in toluene was estimated to be -26.75 kJ/mol.

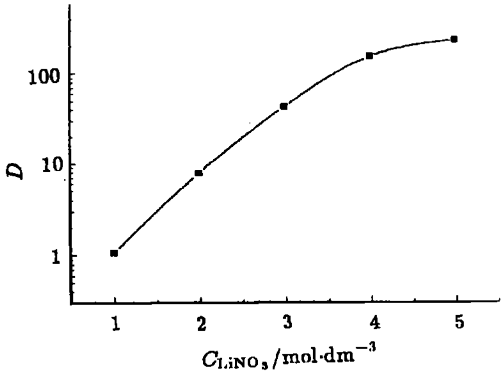


Fig.3 Variation of distribution ratio with concentration of $LiNO_3$ in aqueous solution for the extraction of uranium (VI)
$[UO_2^{2+}]=5\times10^{-3}$mol·dm^{-3},
$[HNO_3]=0.01$ mol·dm^{-3},
$[DPOD]=0.30$ mol·dm^{-3}, $T=298$K

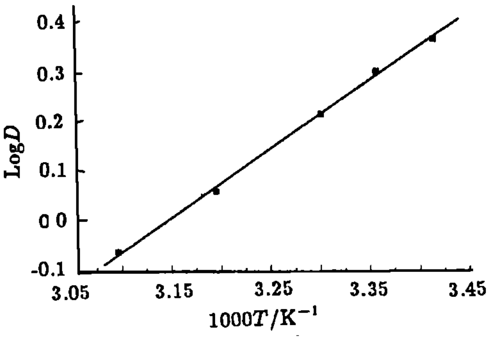
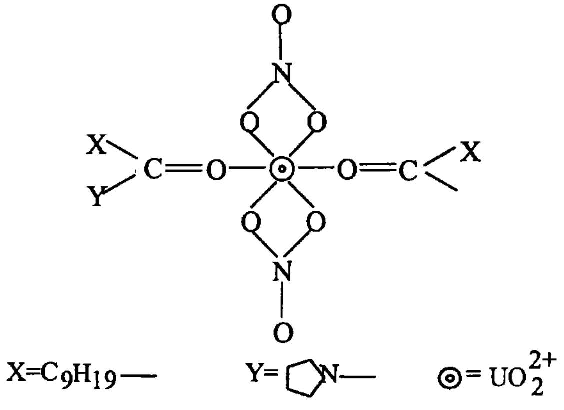


Fig.4 Effect of temperature on the distribution ratio
$[UO_2^{2+}]=5\cdot10^{-3}$mol·dm^{-3},
$[HNO_3]=3.0$ mol·dm^{-3}, $[DPOD]=0.30$ mol·dm^{-3}

4 Conclusions

N-decanoylpyrrolidine (DPOD) in toluene can extract U(VI) from nitric acid media efficiently and the extracted species can be expressed as $UO_2(NO_3)_2(DPOD)_2$. The IR spectrums shows that the characteristic absorption peak value of C=O group is 1646.1 cm^{-1} and it decreased to 1573.6 cm^{-1} after extraction of uranyl(II), which indicats that the DPOD is coordinated with the metal ion through its C=O groups. The suggested structure of the extraction complex can be expressed as follows:



The value of ΔH is negative which means that the decrease in the temperature will rise the distribution ratio of U (VI). There is no third phase formation under the conditions studied.

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