Effect of diluents on the extraction of uranium (VI) with N-octanoyl-2-methylpiperidine

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Abstract The extraction of uranium (VI) from nitric acid solution with N-octanoyl-2-methylpiperidine (OMPPD) in eight diluents and the dependence of distribution ratio on temperature and concentrations of both aqueous nitric acid and OMPPD were investigated. The interaction among OMPPD, the extracted species and diluent has been discussed. The experiments show that the extraction ability of OMPPD decreases gradually for eight diluents in the following order: benzene, toluene, n-octane, sulfonated kerosene, cyclohexane, carbon tetrachloride, 1,2-dichloroethene and chloroform. It cannot be interpreted only on the basis of polarity of diluents.

Keywords N-octanoyl-2-methylpiperidine, Diluents, Solvent extraction, Uranium (VI)

CLC numbers O615, O615.11

1 Introduction

Amide type extractants are regarded as one of prominent extractants for uranium(VI) from nitric acid media,[1-4] and N-octanoyl-2-methylpiperidine is a new member of these extractants, which is obtained by using 2-methylpiperidine as cyclic secondary amine, and its extraction performance for uranium(VI) in toluene has been reported.[5]

Many authors have shown that the diluent plays an important role in the liquid-liquid extraction.[6,7] Therefore, the present study was undertaken to extend our previous results and to have better understanding of the interaction of diluent with this extractant. A series of polar and non polar diluents were used.

2 Experimental

All diluents used here were purified by factional distillation. AR nitric acid and uranyl nitrate were used.

OMPPD was synthesized in our laboratory[8] and purified by distillation under reduced pressure. The purity of the product was checked by the elemental analysis, IR and NMR spectroscopy, which was higher than 98%.

The extraction of U(VI) was carried out by vibrating equal volumes of organic phase and aqueous solution in a stoppered tube of 10 mL volume. The equilibration took 30 min at (298±1) K after phase disengagement by centrifugation. U(VI) in aqueous solution was analyzed by Arsenazo-III spectrophotometric method[9] and U(VI) concentration in the organic solution was calculated from the difference between total quantity and that in the aqueous solution. The distribution ratio of U(VI), D_U, was thus calculated.

IR spectra of the extractant and extracted species in different diluents were collected using a Bio-Red FTS-IR spectrophotometer in a range of 400~4000 cm^{-1}.

3 Results and discussion

3.1 Effect of nitric acid concentration

In order to examine the variation of D_U as a function of aqueous nitric acid concentration, the extractibility of U(VI) from 1 to 6 $mol \cdot L^{-1}$ nitric acid into 0.30 $mol \cdot L^{-1}$ OMPPD in different diluents was systematically observed (Fig.1). The experimental results show that the trend of change in extraction distribution with increasing concentration of nitric acid is similar for all diluents, however, at the same concentration, the val-

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ues of the distribution ratios are different. Fig.1 also shows that at higher HNO_3 concentration (>4.0 mol·L^{-1}), the distribution ratios decrease, which is due to the decrease in the free extractant caused by the competing extraction of the nitric acid in all diluents used. It implies that the interaction between HNO_3 and OMPPD is stronger than that between OMPPD and diluent, even chloroform.

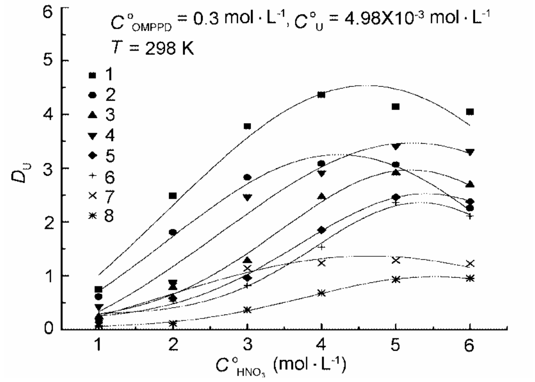

Fig.1 Influence of nitric acid concentration on D_U.

1. Benzene; 2. Toluene; 3. Sulfonated kerosene; 4. n-octane; 5. Cyclohexane; 6. Carbon tetrachloride; 7. 1,2-dichloroethene; 8. Chloroform

3.2 Effect of OMPPD concentration

Fig.2 shows the dependence of extraction distribution ratios of U(VI) on concentrations of OMPPD in different diluents at 1.5 mol·L^{-1} HNO_3. The plots of lgD_U vs lg[OMPPD]$_{(o)}$ gives a slope of about 2 in all diluents employed, which indicates that two OMPPD molecules coordinate to one UO_2^{2+}, and $UO_2(NO_3)_2(OMPPD)_2$ can also be determined by the stoichiometry of extracted complex. The coordination mechanism of uranyl (VI) ion extraction by OMPPD may be represented by:

$$UO_2^{2+}+2NO_3^-+2OMPPD_{(o)}=UO_2(NO_3)_2(OMPPD)_{2(o)} \quad (1)$$

where subscript (o) refers to the species presented in organic phase. For above reaction the equilibrium constant, K_{ex}, is:

$$K_{ex}=\frac{[UO_2(NO_3)_3(OMPPD)_2]_{(o)}}{[UO_2^{2+}][NO_3^-]^2[(OMPPD)]^2_{(o)}} \quad (2)$$

Introducing the distribution ratio:

$$D_U=\frac{[UO_2(NO_3)_2(OMPPD)_2]_{(o)}}{[UO_2^{2+}]} \quad (3)$$

one obtains

$$K_{ex}=\frac{D_U}{[NO_3^-]^2[(OMPPD)]^2_{(o)}} \quad (4)$$

K_{ex} values calculated from Eq. (4), with 0.30 mol·L^{-1} OMPPD in different diluents from 1.5 mol·L^{-1} HNO_3 medium, are given in Table 1.

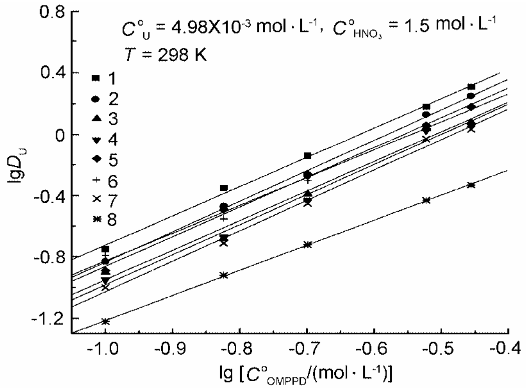

Fig.2 Effect of OMPPD concentration on distribution ratios.

1. Benzene; 2. Toluene; 3. Sulfonated kerosene; 4. n-octane; 5. Cyclohexane; 6. Carbon tetrachloride; 7. 1,2-dichloroethene; 8. Chloroform

Table 1 Extraction equilibrium constants of U(VI) with OMPPD in various diluents at 298 K*

Diluents	Benzene	Toluene	n-octane	Sulfonated kerosene	Cyclohexane	CCl_4	1,2-dichloro-ethene	Chloroform
D_U	1.51	1.35	1.15	1.12	1.10	1.09	0.93	0.37
K_{ex}	7.47	6.66	5.67	5.54	5.42	5.23	4.60	1.85

* $C°_{OMPPD}$ = 0.30 mol·L^{-1}, $C°_U$ = 4.98×10^{-3} mol·L^{-1}, $C°_{HNO_3}$ = 1.5 mol·L^{-1}

3.3 Effect of temperature

Fig.3 shows the plot of lgD_U vs. 1/T for 0.30 mol·L^{-1} OMPPD in different diluents. According to:

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

we get ΔH shown in Table 2.

Data in Table 2 show that all reactions of U (VI) extraction with OMPPD in different diluents are exothermic and low temperature is beneficial to extraction reaction.

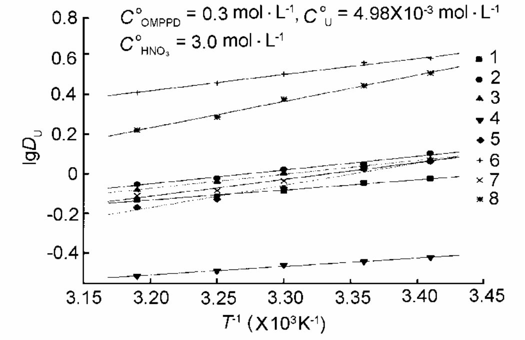

Fig.3 Effect of temperature on the extraction in various diluent system.

1. 1,2-dichloroethene; 2. Carbon tetrachloride; 3. n-octane; 4. Chloroform; 5. Sulfonated kerosene; 6. Benzene; 7. Cyclohexane; 8. Toluene

3.4 IR spectra analysis

The carbonyl (C=O) stretching vibration absorption peak of the extractant and extracted species in different diluents used here are listed in Table 3.

From the data in Table 3, it can be supposed that the interaction between OMPPD and diluent is different in various diluents. But the carbonyl (C=O) stretching vibration of the extracted species obtained in all diluents employed here are about the same. It implies that the property of diluent is one of the factors, which affect the extractability only, not the extracted species obtained.

4 Conclusions

Decreasing order of extraction ability of OMPPD is as follows: benzene, toluene, n-octane, sulfonated kerosene, cyclohexane, carbon tetrachloride, 1,2-dichloroethene, chloroform.

The extractability of U(VI) with OMPPD is different in various diluents, but the same extracted species is obtained.

The relationship between the extractibility of U(VI) with OMPPD and the properties of diluents is very complex. It cannot be interpreted only on the basis of polarity of diluents.

Table 2 Change in extraction enthalpy of U (VI) in 3.0 mol·L^{-1} HNO_3 with OMPPD in different diluent systems

Diluent	Benzene	Toluene	Sulfonated kerosene	n-octane	CCl_4	Cyclohexane	Chloroform
-△H (kJ · mol^{-1})	16.06	26.01	22.19	14.21	13.99	17.05	8.81

Table 3 Assignments for the infrared frequencies (cm^{-1}) of extractant and extracted species in different diluents

Diluent	Chloroform	1,2-dichloro- ethene	CCl_4	Benzene	Toluene	n-octane	Sulfonated kerosene	Cyclohexane
OMPPD (V_C=0)	1616.3	1629.1	1641.1	1642.0	1643.9	1655.2	1655.3	1654.1
U-OMPPD (V_C=0)	1562.8	1562.1	1563.5	1559.9	1559.2	1589.2	1590.5	1590.1
△V (cm^{-1})	53.5	67.0	77.6	82.1	84.7	66	64.8	64.0
O=U=O	929.0	-	938.2	943.9	943.5	937.6	936.7	939.2

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