Coextraction of uranium(VI) from nitric acid solutions by N,N-diethyldecanamide and TBP*

Sun Guo-Xin, Wang You-Shao, Yang Yan-Zhao, Bao Bo-Rong,
(*Shanghai Institute of Nuclear Research, the Chinese Academy of Sciences, Shanghai 201800*)
Sun Si-Xiu
(*Department of Chemistry, Shandong University, Jinan 250100)*

Abstract The partition of uranium(VI) between nitric acid and N,N-diethyldecanamide, $C_9H_{19}CON(C_2H_5)_2$, (DEDEA) in kerosene has been investigated at various concentrations of nitric acid, extractant and salting-out agent $LiNO_3$. The mechanism of extraction is discussed in the light of the results obtained. The effect of TBP on the extraction of uranium(VI) with DEDEA has also been considered. There is apparent synergism between these two extractants at low concentration of TBP; however, at higher concentration, distribution ratio decreases.

Keywords N,N-diethyldecanamide, U(VI), TBP, Solvent extraction

1 Introduction

N, N-dialkylamides are good extractants for many metallic ions.[1] The actinides ions which prefer to bind with oxygen donor are well extracted from aqueous acidic nitrate solutions[2], so several scholars[3] proposed N, N-dialkylamides instead of TBP in the reprocessing of spent nuclear fuels. TBP has been suggested to be used in the extraction of uranium with amide to improve the phase separation, but its effect on the extraction was usually ignored.

The extraction of uranium(VI) from nitric acid solutions by DBODA in toluene has been described in our previous paper[4], which shows higher separation factor between U(VI) and Th(IV), but the present study concerns the mechanism of extraction with DEDEA (N, N-diethyldecanamide) in kerosene which is a preferential diluent due to its low volatility, high flash point, and so on[5], and also the extraction with combination of DEDEA and TBP.

2 Experimental

DEDEA was synthesized and purified as described previously.[6] Extraction was carried out by shaking equal volumes of extractant diluted in kerosene and uranyl nitrate solution containing nitric acid in a stoppered tube at the required temperature. After centrifugation and phases separation each phase was sampled and uranyl(VI) ion concentration in aqueous solution was analyzed by the Arsenazo-III spectrophotometry, then the amount of U(VI) in organic phase could be calculated.

3 Results and discussion

3.1 Extraction of uranium with DEDEA

3.1.1 Dependence on acid concentration

Fig.1 shows that the distribution ratio D_U of uranium(VI) into DEDEA from nitric acid solutions increases in line with increasing acidity up to 5.5 mol/L; this is similar to that obtained with DBODA in toluene.[4] We and others[7] have suggested that the amide extractant can also extract HNO_3 from aqueous solution, then at higher acidities the concentration of free extractant decreases which leads to the decrease in the distribution ratio.

3.1.2 Dependence on extractant concentration

It can be seen from Fig.2 that the slope of the line is 2.01, indicating that two molecules of DEDEA combine with one uranium(VI) ion. Therefore, the extraction reaction can be described as the following

$$UO^{2+}_{2(a)} + 2NO^{-}_{3(a)} + 2DEDEA_{(o)} = UO_2(NO_3)_2(DEDEA)_{2(o)} \qquad (1)$$

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The extraction equilibrium constant K_{ex} can be calculated from Eq.(2):

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

The value of K_{ex} obtained from Eq.(2) is 1.309 mol^4/L^4.

3.1.3 Dependence on $LiNO_3$ concentration in aqueous solutions

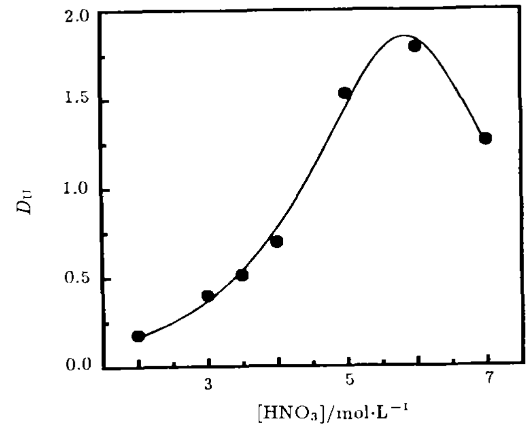

Fig.1 Dependence of D_U on aqueous nitric acid concentration by DEDEA in kerosene
$[UO_2^{2+}]= 5.0\times10^{-3}$ mol/L, $[HNO_3]=3.0$ mol/L, [DEDEA]=0.2 mol/L, $T=298$ K

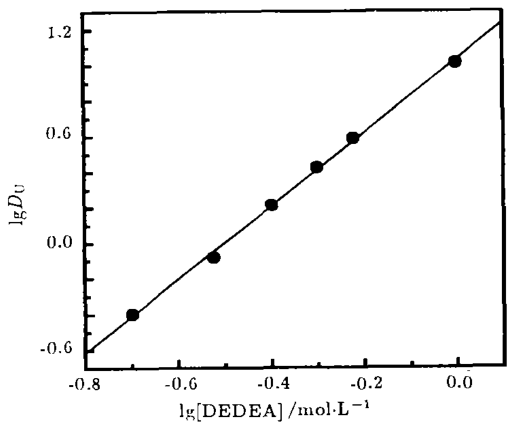

Fig.2 Dependence of D_U on the concentration of DEDEA
$[UO_2^{2+}]=5.0\times10^{-3}$ mol/L, $[HNO_3]=3.0$ mol/L, $T=298$ K

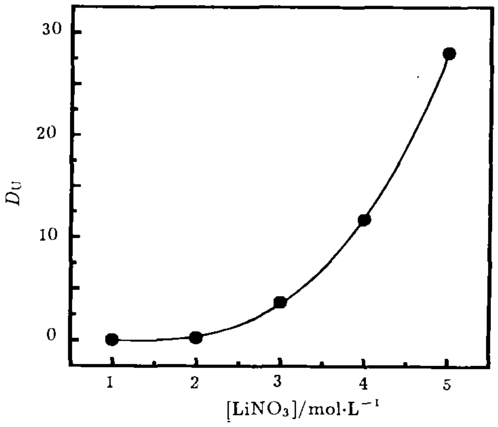

Fig.3 Dependence of D_U on the concentration of $LiNO_3$
$[UO_2^{2+}]= 5.0\times10^{-3}$ mol/L, $[HNO_3]=0.02$ mol/L, [DEDEA]=0.2 mol/L, $T=298$ K

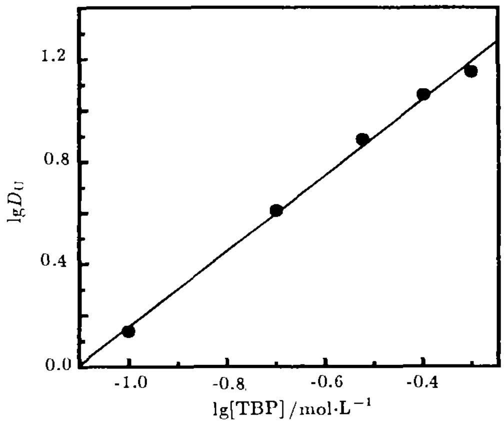

Fig.4 Dependence of D_U on the concentration of TBP
$[UO_2^{2+}]=5.0\times10^{-3}$ mol/L, $[HNO_3]=3.0$ mol/L, $T=298$ K

Fig.3 shows that distribution ratio D_U increases rapidly with increasing $LiNO_3$ concentration. $LiNO_3$ here not only plays as salting out agent that increases the uranyl ion activity, but also homo-ion shifting the extraction equilibrium(1) to the right.

3.2 Extraction of uranium(VI) with TBP

The dependence of distribution ratio D_U on TBP concentration was examined in Fig.4. It can be seen that the extractability of TBP is slightly higher than that of DEDEA in kerosene.

3.3 Extraction of uranium(VI) by mixture of DEDEA and TBP

For a binary mixture of extractants, such as DEDEA and TBP, the synergistic distribution ratio D_{DT} can be expressed as

$$D_{DT} = D - D_D - D_T \qquad (3)$$

where D is the observed distribution ratio with the mixture of extractants, D_D and D_T are the distribution ratios with DEDEA and TBP, respectively. The values of distribution ratio of uranium with DEDEA and TBP in kerosene are summarized in Table 1, where $[UO_2^{2+}]$ is 5.0×10^{-3} mol/L, $[HNO_3]$ is 3.0 mol/L.

Table 1 shows that the effect of TBP on the extraction of uranium with DEDEA is very complex. The reason is the presence of a great amount of TBP changing the polarity of the organic phase which influences the extraction with DEDEA. The other reason may be that the free amide molecules bind with the complex of TBP and HNO_3 in organic phase due to the higher extractability of TBP for HNO_3, which can also decrease the distribution ratio of U(VI).

Table 1 Extraction of uranium from nitric acid solution by DEDEA and TBP mixtures in kerosene

C_D /mol·L^{-1}	C_T /mol·L^{-1}	D_D	D_T	D	D_{DT}
0.1	0.2	0.101	4.003	4.030	-0.074
0.2	0.2	0.400	4.003	4.322	-0.081
0.3	0.2	0.831	4.003	5.711	0.877
0.4	0.2	1.633	4.003	5.940	0.304
0.5	0.2	2.660	4.003	7.620	0.957
0.2	0.05	0.400	0.342	1.123	0.381
0.2	0.1	0.400	1.367	2.053	0.286
0.2	0.3	0.400	7.444	7.202	-0.642
0.2	0.4	0.400	10.870	9.707	-1.563

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