DBC solvent extraction of U(VI) from thiocyanate medium

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Abstract The extraction behavior of uranium(VI) from thiocyanate medium with dibenzo-18-crown-6 (DBC) in nitrobenzene and the effects of alkali cations on the extraction were investigated. The results showed that the uranium (VI) can be effectively extracted in the presence of potassium cation, uranium (VI) is extracted as complex anionic species $UO_2(SCN)_3^-$, and the stoichiometry of the extracted complex is $KUO_2(SCN)_32DBC_{(O)}$.

Keywords Crown ethers, Extraction, Uranium(VI), Thiocyanate, Nitrobenzene

CLC numbers O615.11, O652.62, TL283

1 INTRODUCTION

For many years much effort has been invested in studying the solvent extraction of actinides, such as thorium, neptunium, americium, and uranium with crown ethers.[1,2] Among those papers on extraction of uranium with crown ethers, most experiments were performed in HCl or HNO_3 media.[1~9] It was considered that the uranium(VI) was extracted as a form of complex anion $UO_2Cl_4^{-2}$ in HCl and chlorides media.[4,9] Even thiocyanate is somewhat similar to halogen in chemical properties, only Godhole *et al*[10] investigated the extraction of uranium(VI) with 15-crown-5 from NH_4SCN solution, without studying the effect of alkali cations on extraction of uranium(VI). Here we report the extraction of uranium(VI) from thiocyanate medium with dibenzo-18-crown-6 in nitrobenzene and the effects of K^+, NH_4^+ and Na^+ on extraction of uranium(VI). Also, the extractive mechanism of uranium(VI) with DBC from aqueous phase containing potassium cation is discussed.

2 EXPERIMENTAL

2.1 Reagents

U_3O_8 was brought from Chemapol Co (Czechoslovakia) and used to prepare stock solution of $UO_2(NO_3)_2$ in 0.1 mol/L HNO_3. The concentration of uranium(VI) in the stock solution was determined by the volumetric method. Debenzo-18-crown-6 (DBC) (A.R.) was obtained from Chengdu Chemical Reagent Factory (Chengdu) and dissolved in nitrobenzene. All other chemicals were of A.R. grade and used without further purification.

Supported by Nuclear Industrial Science Foundation of China (J 95 GY 403)
Manuscript received date:2000-01-05

2.2 Experiments

Equal volume of the organic solution of DBC-nitrobezene and the aqueous solution containing uranium(VI) and thiocyanate were shaken for 30 min at room temperature. The phases were separated by centrifugation and the concentration of uranium(VI) in the aqueous phase was determined as described earlier.[9] The concentration of uranium(VI) in the organic phase was calculated from the concentration in the aqueous phase.

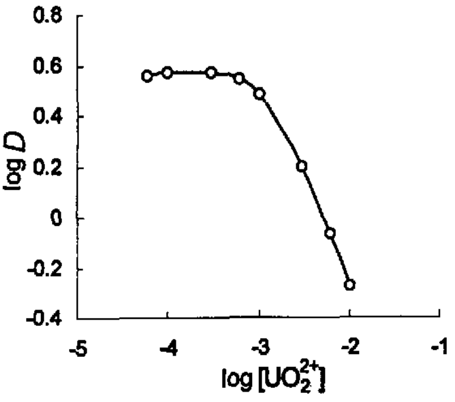

Fig.1 Variation of log$D$ as a function of log[UO$_2^{2+}$]
Organic phase: 3×10^{-2} mol/L DBC
Aqueous phase: 3×10^{-2} mol/L KSCN

3 RESULTS AND DISCUSSION

3.1 Effect of concentration of uranium(VI) on the extraction

The effect of the concentration of UO$_2^{2+}$ on the distribution ratio of uranium (VI) is described in Fig.1. The log$D$ is near constant in the region of uranium (VI) concentration of (6×10^{-5} ~ 1×10^{-3})mol/L, implying that the extracted species are mononuclear complexes.

3.2 Influence of alkali cations on the extraction

Fig.2 shows that DBC-nitrobenzene extracts uranium (VI) from potassium thiocyanate solution much better than from sodium or ammonium thiocyanate solutions. But there was no obvious difference between ammonium and sodium thiocyanate solution. The effects of alkali metals on the extraction of uranium (VI) are in accord with the sequence: $K^+ \gg NH_4^+ \sim Na^+$. Similar effects were observed in our earlier work in HCl and chloride media, in which the sequence of alkali cations is $K^+ > Na^+ > Li^+ \sim H^+$.[9,11] The effects of alkali cations on the extraction of uranium (VI) are related to the complexing power of the alkali cations with the DBC. Because of the better complexing power of K$^+$ with DBC than that of other alkali cations, extraction of uranium (VI) from K$^+$ solutions is much better than from NH$_4^+$ and Na$^+$ solutions.

The relationship between K$^+$ and D was given in Fig.3. The plot of log$D$- log[K$^+$] is a straight line with a slope of 0.93 (close to 1) (Fig.3). This suggests that the ratio of U(VI) to K$^+$ is 1:1 in extracted specie. Analysis of the organic phase after extraction confirmed the presence of potassium cation, in which the variation of $[K^+]_{(o)}$ is corresponding to$[U]_{(o)}$.

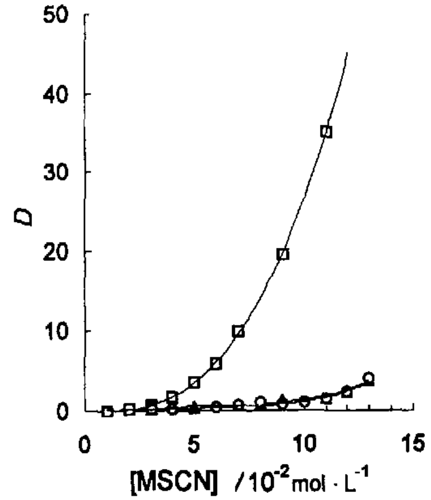

Fig.2 Effect of thiocyanate on the distribution ratio of uranium (VI)
□ KSCN, △ NH_4SCN, ○ NaSCN
Organic phase: 3×10^{-2}mol/L DBC,
Aqueous phase: 3×10^{-4}mol/L UO_2^{2+}

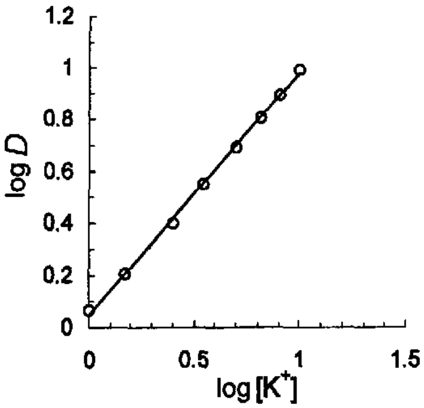

Fig.3 Variation of log$D$ as a function of log [K^+]
Organic phase: 3×10^{-2}mol/L DBC,
Aqueous phase: 3×10^{-4}mol/L UO_2^{2+},
3.5×10^{-2}mol/L NaSCN

3.3 Effect of DBC concentration on the extraction of U(VI)

Fig.4 shows that the effect of concentration of the DBC on the distribution ratio at constant [KSCN]. The plot of log$D$-log [DBC] is a straight line with slope of 1.60, instead of an expected integer value.

The methods of isomolar series were used for further identifing the composition of extracted complex. Fig.5 shows that the concentration of U in organic phase reaches the highest at DBC /U (VI) =2:1, implying that most of the extracted species are formed in 2:1 complex.

Table 1 Comparison between the measured and calculated values of extracted complexes

	U/%	K/%	C/%	H/%	N/%
Measured values	17.28	3.81	43.68	3.85	3.80
Calculated values	19.28	3.24	42.89	3.99	3.49

Usually, the extraction of metal cations with crown ethers is performed through ion pairs formation, but part of the ion pairs is dissociated in polar solvent. In this experiment, when concentration of uranium (VI) in organic phase is ($1\times10^{-4} \sim 3\times10^{3}$) mol/L, the molar conductance of organic phase is (34~45) $\Omega^{-1}cm^2mol^{-1}$. It is suggested that here exists the dissociation, too. Further the ion exchange experiment showed that more than 90% of uranium (VI) was adsorbed in anion exchange resins. This result indicates that the extracted complex should be $UO_2(SCN)_3^-$. According to the result described above and the electrical neutrality principle, the extracted complex was suggested as $KUO_2(SCN)_3\ 2DBC_{(o)}$.

In order to demonstrate the constituent of the complex, its elements were analyzed and the results are summarized in Table 1. The result shows that the complex is $KUO_2(SCN)_3\ 2DBC_{(o)}$. The apparent extraction reaction of uranium (VI) is given by

$$K^+ + UO_2^{2+} + 3SCN^{-1} + 2DBC_{(o)} = KUO_2(SCN)_3 2DBC_{(o)}$$

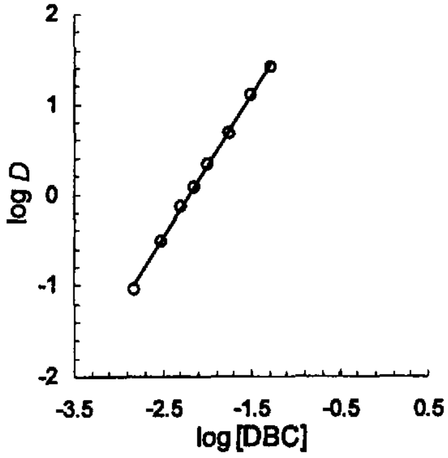

Fig.4 Variation of log$D$ as a function of log [DBC]
Aqueous phase: 5×10^{-4}mol/L UO_2^{2+}, 5×10^{-2}mol/L KSCN

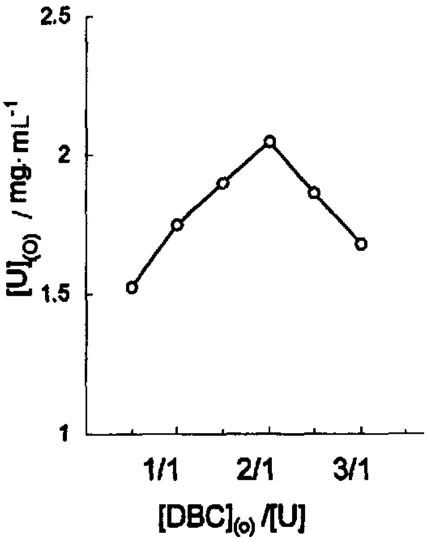

Fig.5 Variation of $[U]_{(o)}$ as a function of molar ratio of $[DBC]_{(o)}$ to [U]
Aqueous phase: 5×10^{-2}mol/L KSCN

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