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磺化煤油为稀释剂 *N*,*N*,*N*′,*N*′-四(2-乙基己基)-3-氧戊二酰胺从硝酸中萃取 U(Ⅵ)

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摘要：本文研究了以磺化煤油为稀释剂,*N*,*N*,*N*′,*N*′-四(2-乙基己基)-3-氧戊二酰胺(T2EHDGA)从硝酸中对 U(Ⅵ)的萃取性能。考察了 HNO_3 浓度、T2EHDGA 浓度、盐析剂浓度及温度对萃取性能的影响。该萃取过程为一放热过程,在所研究的条件下没有三相的形成。给出了萃取机理,确定由 2 个萃取剂分子参与 U(Ⅵ)配位,其萃合物组成为 $UO_2(NO_3)_2$·2T2EHDGA。通过红外光谱确定了由羰基及醚氧键参与配位。

关键词：萃取；铀(Ⅵ)；*N*,*N*,*N*′,*N*′-四(2-乙基己基)-3-氧戊二酰胺；磺化煤油
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Extraction of U(Ⅵ) from Nitric Acid Medium by *N*,*N*,*N*′,*N*′-Tetra-2-ethylhexyldiglycolamide in Sulfonated Kerosene

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Abstract: The extractive properties of *N*,*N*,*N*′,*N*′-tetra-2-ethylhexyldiglycolamide (T2EHDGA) were examined for the extraction of uranium(Ⅵ) from nitric acid medium, in which sulfonated kerosene was used as diluent. There′s no third phase formation under the studied conditions. The number of ligand molecules present in the stoichiometry of the extracted species of U(Ⅵ) was found to be two. Thermodynamics studies suggested that the extraction is exothermic. The extraction influence of nitric acid concentration and T2EHDGA concentration as well as salting-out agent and temperature on the extraction distribution ratio was investigated. The extraction mechanism was established and the stoichiometry of the main extracted species was confirmed to be $UO_2(NO_3)_2$·2T2EHDGA. The IR spectra of the loaded organic phase were also recorded.

Keywords: extraction; U(Ⅵ); *N*,*N*,*N*′,*N*′-tetra-2-ethylhexyldiglycolamide; sulfonated kerosene

Uranium (Ⅵ) is both the major constituent of nuclear fuel and one of the key nuclides in spent fuel reprocessing[1]. Separating uranium(Ⅵ) from High Level Waste (HLW) solution generated during the reprocessing of the spent nuclear fuel is useful both for the storage of nuclear waste and for recycling of nuclear fuel[2-3]. Solvent extraction, in combination with chelation chemistry, has been one of important method in separation and recovery of uranium(Ⅵ)[4-5]. Designing appropriate chelation agents is a crucial task in the application of innovative solvent extraction techniques to the efficient separation and recovery of uranium(Ⅵ) from HLW solution or raw materials[6-7]. Recently, new class of diamide extractants, diglycolamides have been

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the focus of many extraction groups working on actinide partitioning in view of offering several advantages like high radiolytic stability, innocuous nature of degradation products and complete incinerability as well as the easy of synthesis[8-14]. This class of extractants exhibit higher extraction of actinide ions from acidic solutions as compared to malonamides due to containing ether linkage between two amide groups[9,15-16].

The stereochemical hindrance around the potential binding sites of diglycolamides is likely to play important roles on the metal ion extraction and separation performances, study on the relationships between ligand structures and metal extraction are still important. Amongst various derivatives of diglycolamides, *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA) has attracted considerable attention and has been investigated intensively[17-20]. However, studies on its homologue, viz. T2EHDGA having ethyl branched chain are scarce[21-24]. Sharma et al. investigated the extraction behavior of uranium, thorium and nitric acid for TEHDGA/isodecyl alcohol/n-dodecane solvent system, they found the extracted species of uranium and thorium in the organic phase were $UO_2(NO_3)_2 \cdot 2TEHDGA$ and $Th(NO_3)_4 \cdot 2TEHDGA$. A workable separation factor (D_{Th}/D_U) of the order of 300 was observed between thorium and uranium, which indicated that TEHDGA solvent system could be a potential candidate for separation of thorium from uranium[23].

As we all know, diluents play an important role in the solvent extraction techniques[11,25]. In this paper, sulfonated kerosene, a diluent widely used in industrial scale extraction process, was selected as solvent considering its high flash point and low cost compared with isodecyl alcohol/n-dodecane. The extraction properties of uranium(Ⅵ) by T2EHDGA in sulfonated kerosene from nitric acid media was investigated in detail and the results has great reference value for practical application.

1 Experimental

1.1 Reagents

T2EHDGA, yellow oil, 98% purity, was synthesized by a three-step process as reported in Manoha′s paper[26]. However, thionyl chloride was used to convert diglycolic acid to diglycolyl chloride[9] rather than phosphorus pentachloride. T2EHDGA was characterized by IR, ^{1}H NMR and ^{13}C NMR. The corresponding data are given as follows: IR (KBr, cm^{-1}) ν_{max}: 2 959, 2 874(C-H), 1 658(C=O), 1 463, 1 456(-CH_3), 1 117(C-O), 728(-CH_2-); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 4.43 (d, *J*=7.8 Hz, , 4H, 2 -OCH_2-), 3.07~3.35 (m, 8H, 4 -N-CH_2-), 1.55~1.66 (s, 4H, 4 -CH-), 1.21~1.29 (s, 32H, 16 -CH_2-), 0.84~0.90 (d, *J*=7.0, 3.5 Hz, 24H, 4 -CH_3); ^{13}C NMR (400 MHz, $CDCl_3$, TMS) δ: 169.80, 69.35, 50.18, 48.04, 38.06, 36.82, 30.69, 30.63, 28.96, 28.85, 23.91, 23.23, 14.22, 14.17, 11.08, 10.76.

Other reagents employed in this work were all AR grades.

1.2 Extraction and analytical procedures

Equal volumes of T2EHDGA in sulfonated kerosene and $UO_2(NO_3)_2$ solution were shaken mechanically for 30 min (to obtain equilibrium) at (25±0.2) ℃. The two phases were then centrifuged and assayed by taking known aliquots (0.05 ~0.10 mL) from the aqueous phases. The analytical procedures were just like those described in our previous paper[27].

1.3 Preparation and characterization of the extracted species

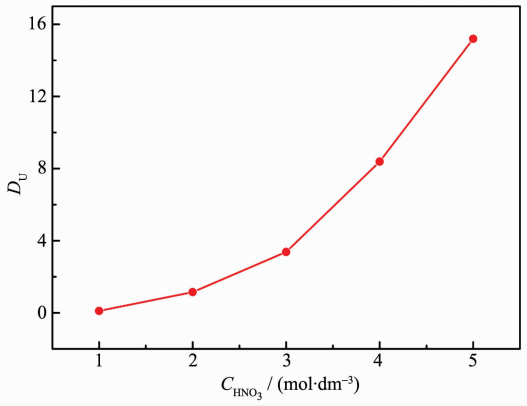
The extracted species were prepared. The extractant solutions were shaken with a concentrated solution of $UO_2(NO_3)_2$ and centrifuged. The organic phase separated was dropped on a potassium bromide plate and the diluent was removed by evaporation. FT-IR spectra of the residuals were recorded on Perkin Elmer-Spectrum One in the range of 400 ~ 4 000 cm^{-1}. The scan times and the resolution were 60 and 2 cm^{-1}, respectively.

2 Results and discussion

2.1 Effect of nitric acid concentration on the extraction of U(Ⅵ)

The extraction of uranium(Ⅵ) with 0.20 mol·dm^{-3} T2EHDGA in sulfonated kerosene from nitric acid solutions has been investigated. As shown in Fig.1, in the range of 1.00 ~5.00 mol ·dm^{-3} nitric acid

concentrations, the distribution ratio of UO_2^{2+} increases with increasing concentration of nitric acid, which can mainly be attributed to co-ion effect of NO_3^- and, possibly, also to classic salting out effect[28]. It also indicates that no obvious competing extraction of nitric acid appeared in all the range of concentrations tested in the proposed condition. This phenomenon is somewhat similar to that reported with *N*,*N*,*N*′,*N*′-tetrahexyl-4-oxa-heptanediamide in nitric acid medium systems[19]. There′s no third phase formation under the studied conditions.



$C_{UO_2^{2+}}$=1.00×10^{-3} mol·dm^{-3}, $C_{T2EHDGA(o)}$=0.20 mol·dm^{-3}

Fig.1　Effect of HNO_3 concentration on the extraction of UO_2^{2+}

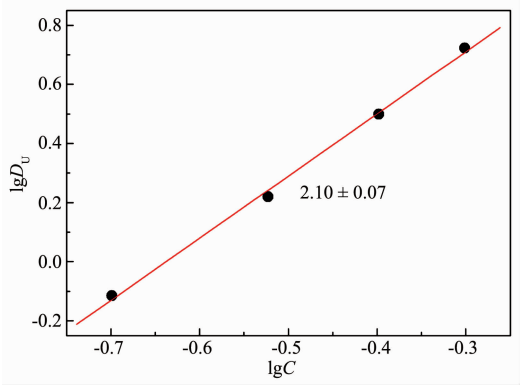
2.2　Effect of extractant concentration on the extraction of U(Ⅵ)

The logarithm distribution ratio is plotted as a function of the logarithm concentration of T2EHDGA in Fig.2. The distribution ratio increases linearly with an increase in the T2EHDGA concentration. The calculated slope of the line is about two. Hence, the reaction equilibrium of UO_2^{2+} from nitric acid solution by T2EHDGA can be described as follows:

$$UO_2^{2+}{}_{(a)}+2NO_3^-{}_{(a)}+2T2EHDGA_{(o)}=UO_2(NO_3)_2\cdot 2T2EHDGA_{(o)} \quad (1)$$

where subscripts (a) and (o) refer to aqueous and organic phase, respectively.

As we known, the coordination number of uranium in UO_2^{2+} manner is 6[29]. Thus, the present result suggests T2EHDGA functions as a tridentate ligand, which is in good agreement with Sharma et al. [23]. From Fig.2, there are two molecules of T2EHDGA in



$C_{UO_2^{2+}}$=1.00×10^{-3} mol·dm^{-3}, C_{HNO_3}=0.01 mol·dm^{-3}, C_{NaNO_3}=3.00 mol·dm^{-3}

Fig.2　Effect of T2EHDGA concentration on the extraction of UO_2^{2+}

one extracted species molecule. However, Panja et al.[30] reported a species of the type $UO_2(NO_3)_2\cdot T2EHDGA_{(o)}$ in *n*-dodecane with 30% *iso*-decanol as the phase modifier, which is in sharp contrast to the species reported by us. This is probably connected with the diluents that have a major impact on the extraction due to their polarity[31]. Moreover, Panja et al mentioned that at higher nitric acid concentration the ligand dependence is close to **1**, while at lower nitric acid concentration which is close to **2** with T2EHDGA[32]. In this experiment, nitric acid concentration is controlled at 0.01 mol·dm^{-3}, it is exactly at low nitric acid concentration range, and the result is consistent with that reported by Panja et al.[32].

The conditional equilibrium constant is

$$K_{ex}=\frac{C_{UO_2(NO_3)_2\cdot 2T2EHDGA(o)}}{C_{UO_2^{2+}(a)}C^2_{NO_3^-(a)}C^2_{T2EHDGA(o)}} \quad (2)$$

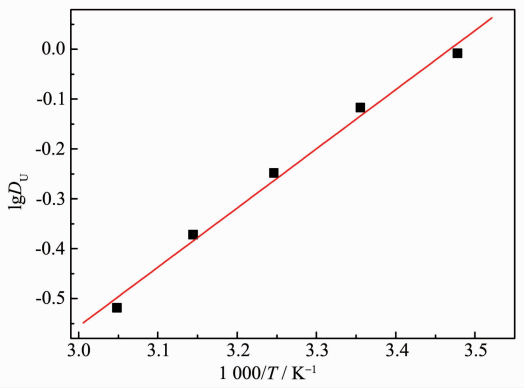
$$K_{ex}=\frac{D_U}{C^2_{NO_3^-(a)}C^n_{T2EHDGA(o)}} \quad (3)$$

The value of K_{ex} is calculated to be (2.18±0.13) mol^{-4}·dm^{12}. We had reported the extraction of UO_2^{2+} with *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide under the same conditions and found that the value of K_{ex} is (26.45±1.05) mol^{-4}·dm^{12} [33]. These results show the steric hindrance of ethyl branched chain.

2.3　Temperature effect on the extraction of U(Ⅵ)

The effect of the temperature on the extraction equilibrium of uranium (Ⅵ) was studied at different temperatures (15~55 ℃), and shown in Fig.3. It was

found the distribution ratio decreases with increasing temperature, which demonstrates that the extraction reaction is an exothermic process and it is disadvantageous for the extraction reaction at high temperature. The change in enthalpy, ΔH, associated with Eq.(**1**), evaluated by means of the Van′t Hoff equation[34], is $-(30.0\pm1.27)$ kJ·mol^{-1}.

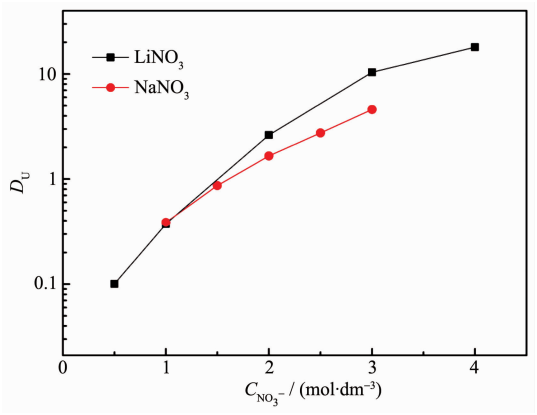


$C_{UO_2^{2+}}$=1.00×10^{-3} mol·dm^{-3}, $C_{T2EHDGA(o)}$=0.20 mol·dm^{-3}, C_{NaNO_3}=3.00 mol·dm^{-3}

Fig.3 Effect of temperature on the extraction of UO_2^{2+}

2.4 Effect of salting-out agent concentration

Fig.4 shows the influence of the salting-out agent ($LiNO_3$ and $NaNO_3$) concentration on the distribution ratio of uranium(Ⅵ). The distribution ratio of uranium(Ⅵ) increases sharply with increasing $LiNO_3$ concentration. Here nitrate plays an important role not only as a salting-out agent which increases the $LiNO_3$ activity owing to hydration of cation but also as a homo-ion solution, shifting the extraction reaction equilibrium to the right[35]. However, the distribution ratio changes little with $NaNO_3$ concentration. That is say, the extractant in $LiNO_3$ system shows a stronger extraction propensity to uranium(Ⅵ) than that in $NaNO_3$ solution. This behavior of lithium has sometimes been explained by invoking the small size and hydration properties of Li^+[36].



$C_{UO_2^{2+}}$=1.00×10^{-3} mol·dm^{-3}, $C_{T2EHDGA(o)}$=0.20 mol·dm^{-3}

Fig.4 Effect of salting-out agent concentration on the extraction of UO_2^{2+}

2.5 IR spectra of extracted species

The IR spectra of the organic phase loading extracted species (Fig.5) have been studied to give insight into the structure of the extracted species. The wave number of the stretching frequency of C=O band was shifted to lower numbers: 1 658 to 1 608 cm^{-1}. Sasaki reported that the C=O band of TODGA was shifted to 1 614 cm^{-1} after complexation with Eu(Ⅲ)[37]. The IR stretching frequency of the ether group was shifted from 1 117 to 1 130 cm^{-1}. The above result indicates that the three oxygen atoms of T2EHDGA molecule are all coordinated with UO_2^{2+} ion in the extracted species, in other words, T2EHDGA is tridentate ligand. The experimental bands assigned to N-O asymmetric and symmetric stretching modes of the coordinated nitrate anion are observed at 1 275 and 1 024 cm^{-1}. The band at 932 cm^{-1} is correspond to asymmetric O-U-O uranyl stretching vibration, which is similar to the IR data of U(Ⅵ) nitrate monoamides complexes[38]. It is worthy to note that there′s a strong band at 1 352 cm^{-1}. The non-metal bonded nitrate ions is of D_{3h} symmetry and are easily recognized by the very strong band usually found at 1 380~1 350 cm^{-1}[39-40]. Then the band at 1 352 cm^{-1} is assigned to ν_3 of not coordinated NO_3^-.

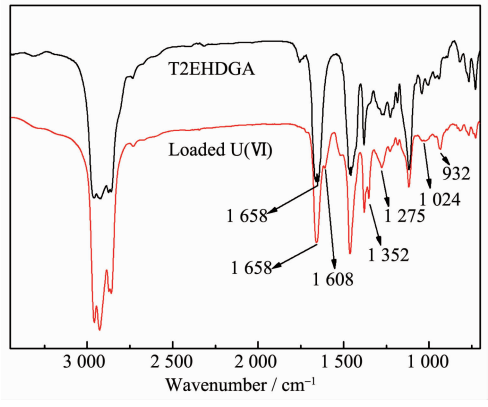


Fig.5 IR spectra of T2EHDGA and loading U(Ⅵ)

3 Conclusions

Uranium (Ⅵ) can be extracted effectively from nitric acid medium by T2EHDGA in sulfonated kerosene. The values of distribution ratio UO_2^{2+} increases with increasing concentration of nitric acid, extractant and salting-out agent. The stoichiometry of the extracted species is confirmed to be $UO_2(NO_3)_2 \cdot 2T2EHDGA$ and the value of K_{ex} is calculated to be (2.18±0.13) $mol^{-4} \cdot dm^{12}$. In addition, the extraction reaction is exothermic and it is disadvantageous for the extraction reaction at high temperature. The extractant in $LiNO_3$ system shows a stronger extraction propensity to uranium (Ⅵ) than that in $NaNO_3$ solution.

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