Extraction/removal of uranium, U(VI) from chloride solutions by an environment-friendly extractant

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Abstract. The extraction/removal of uranium U(VI) from chloride solutions have been investigated in the pH region by using N,N-di(2-ethylhexyl)-diglycolamic acid (HDEHDGA, HA) as an environment-friendly extractant. The influence of acid concentration in the aqueous phase, the ligand concentration in the organic phase, and the temperature on the extraction of U(VI) have been studied. The results from slope analysis methods reveal that the extraction of uranium is strongly pH-dependent and directed by cation-exchange mechanism. The proposed composition of the extracted complex species is UO₂A₂●HA with a core UO₂A₂ and one protonated ligand molecule binding to the second coordination sphere of the metal ion via hydrogen bonding. The extraction thermodynamic data demonstrate an exothermic reaction. The considerably high extraction affinity for uranium makes the HDEHDGA/kerosene system a promising candidate for the purification of water solutions from radioactive pollutants.

1. Introduction

Uranium is categorized as a severe long-term prospective environmental hazard (U²³⁸ t₁⁄₂ = 4.51 x 10⁹ years) with a lot of dangerous effects on humans. This is because of its radiological and biological poisonousness caused by the current mining and human activities. Besides the harmful effects of uranium on the human beings, at present time, the nuclear power generation mainly depends on uranium as a fuel cycle due to its fission property. It is well known that world's uranium reserves gradually decrease as a result of the increasing demand for nuclear industries and power production [1-4]. Therefore, the recovery of uranium from its secondary sources is required. Consequently, the removal/recovery of uranium from contaminated wastewaters and other industrial leach solutions is of great interest both for environmental concerns and its potential utilization in the nuclear industries.

Solvent extraction (Liquid-liquid extraction) and back-extraction techniques are basic and powerful methods for separation/purification the interested metal ions. Several extractants have been employed for the extraction of lanthanides and actinides in the industry [5-7]. The extraction of radioactive elements from different solutions using various extracting systems such as acidic, neutral, and organophosphorus extractants have been extensively investigated [8-10]. However, there are some limitations for the currently deployed extractants used in the separation industry; for example,
organophosphorus extractants generate huge amounts of phosphorus wastes as byproducts [11, 12]. Furthermore, TBP is mainly used in the PUREX process. However, it undergoes degradation due to the exposure to high radiation field, as a result, it produces harmful radioactive wastes [13, 14]. In order to overcome the aforementioned drawbacks, a new group of organic extractants, namely, diglycolamides (DGAs) have been developed for the extraction of lanthanides and actinides [15-17]. The DGAs extractants are structurally different from the bidentate organophosphorus acids and the neutral organophosphorus extractants. Recently, Zhang et al. reported the extraction behavior of lanthanides and actinides from nitric acid media using \(N, N\)-di(2-ethylhexyl)-diglycolamic acid (HDEHDGA, HA as shown in Figure 1) [18].

There are no systematic studies have been reported so far for uranium extraction from chloride media using HDEHDGA. Therefore, this work aims to investigate the extraction/separation of uranium, U(VI) from chloride solutions. Also, the complexation reaction mechanism between HDEHDGA and uranium is reported.

2. Experimental

2.1. Reagents
The extractant, \(N, N\)-di(2-ethylhexyl)-diglycolamic acid with purity of > 97% was prepared in the laboratories of CIAE (China Institute of Atomic Energy) according to the procedure in the previously published work [19]. Uranium nitrate with purity > 99% was supplied by Aladdin Industrial Corporation, China. Kerosene (diluent), AR grade (from Tianjin hengxing chemical preparation Co., Ltd) was used without further purification. All other chemicals were analytical reagent grade or higher. Deionized water was utilized for the preparation of the stock and working solutions.

2.2. Stock solutions and methods.
A stock solution of uranium chloride was prepared by dissolving a proper amount of \(\text{UO}_2(\text{NO}_3)_2\cdot 5\text{H}_2\text{O}\) in 10 mL of deionized water. Then the solution was slowly evaporated to near dryness using a hot plate, then the residue was dissolved in 10 mL of 1 M HCl. The evaporation and the dissolving processes were repeated thrice to ensure the full conversion of uranium nitrate to the corresponding metal ion chloride. Finally, the solution was diluted with deionized water up to 100 mL. A similar procedure was performed elsewhere [20]. The stock solution of organic phase (0.5 M) was prepared by dissolving a desired amount of purified HDEHDGA in kerosene. The concentration of U(VI) in the stock/working solutions was determined using ICP-MS (Thermo Scientific-iCAP RQ, USA).

All extraction experiments were carried out in duplicate and the average relative standard deviation was found < 5%. The extraction process was performed by equilibrating equal volumes (5 mL) from the aqueous phase and organic phase for 15 min at 25 °C unless otherwise mentioned. Preliminary experiments indicated that the extraction equilibrium could be reached in 5 min. After the extraction, the phase separation was facilitated by centrifugation. The U(VI) ion loaded in the organic phase was stripped using 1 M HCl, then the concentration of U(VI) ion in both the aqueous phase and the stripping solution was directly measured by ICP-MS after an appropriate dilution. The effect of temperature on the extraction behavior was tested in the range of 25 - 60 °C. All the experiments were
conducted at a fixed ionic strength of 1 M NaCl. In the stripping experiments, the organic phase loaded by U(VI) was contacted with different concentrations of HCl, HNO₃, and H₂SO₄, at 25 °C for 20 min. The distribution ratio \( D \) is defined as:

\[
D = \frac{[M]_{\text{org.}}}{[M]_{\text{aq.}}}
\]  

(1)

where \([M]_{\text{org.}}\) and \([M]_{\text{aq.}}\) stand for metal ion concentration in the organic and aqueous phases, respectively. Both extraction and stripping percentages are calculated as:

\[
\text{Ext.} \% = \left( \frac{D}{D_1} \right) \times 100
\]

(2)

\[
\text{St.} \% = \frac{[M]_{\text{aq.}}}{[M]_{\text{org.}}} \times 100
\]

(3)

\( V_{\text{aq}} \) and \( V_{\text{org}} \) denote the volumes of aqueous and organic solutions, respectively.

3. Results and discussion

3.1. Effect of acid concentration on U(VI) extraction

The dependency of U(VI) extraction on the acid concentration in the aqueous phase has been studied. In this experiment, the organic phase containing fixed ligand concentration (0.01 M) was mixed with a series of aqueous phase samples of fixed U(VI) concentration at 25 °C. As shown in Figure 2, the distribution ratio of U(VI) ion increases with the increasing pH of the equilibrated aqueous phase. These data indicate that the extraction of uranium is strongly pH-dependent, and the reaction under conditions of low HCl concentration is being controlled by the cation-exchange mechanism. The slope analysis method was utilized to determine the number of protons released in the aqueous phase during the extraction process. The linear plot of \( \log D \) versus pH suggests that there is only one major complex formed in the organic phase, and the slope of the straight line is 2. As expected, during the interaction between the organic and aqueous phases, one U(VI) ion is extracted into the organic phase and two H⁺ are released into the corresponding aqueous phase to balance the charge spontaneously. Typical observation was reported in the literature [2, 21].

3.2. Effect of HDEHDGA concentration on U(VI) extraction

The effect of ligand concentration on the extraction of uranium was examined at 25 °C with metal ion concentration (0.013 mM) and fixed acid concentration in the aqueous phase. The extraction was performed with initial ligand concentration ranging from 0.003 to 0.03 M. In general, with the ion-exchange mechanism, the extraction reaction for mono-basic carboxylic acids can be expressed as the following equation:

\[
UO_2^{2+} + nHA_{\text{org.}} \leftrightarrow UO_2H_{n-2}^+ A_n_{\text{org.}} + 2H^+_{\text{aq.}}
\]

(4)

Where \( n \) denotes the number of ligand molecules binding to U(VI) ion, \( n \geq 2 \). Therefore, based on equation (4), the extraction constant \( (K_{ex}) \) is defined as:

\[
K_{ex} = \frac{[UO_2H_{n-2}^+ A_n_{\text{org.}}][H^+]^{2}_{\text{aq.}}}{[UO_2^{2+}]_{\text{aq.}}[HA]^{n}_{\text{org.}}}
\]

(5)

Since \( D = \frac{[UO_2H_{n-2}^+ A_n]_{\text{org.}}}{[UO_2^{2+}]_{\text{aq.}}} \), the logarithmic relation of equation (5) can be written as:

\[
\log D = \log K_{ex} + n\log [HA]_{\text{org.}} + 2pH
\]

(6)

\[
\log D - 2pH = \log K_{ex} + n\log [HA]_{\text{org.}}
\]

(7)
As shown in Figure 3, the plot (logD – 2 pH against log[HA]) is in good linear relationship. The slope analysis method was used to determine the number of ligand molecules (n) attached to U(VI) ion. The value of n equals 2.54 which is close to 3, suggesting formation of neutral complex with ligand/U(VI) ratio equals 3. However, this result is not consistent with data obtained from the linear relationship (logD-pH), which declared that the ratio of the exchanged protons to metal ion is 2:1. This phenomenon can be explained by the speculation that two deprotonated ligand molecules (2 A⁻) have been involved in the first coordination sphere of the metal ion with the core UO₂A₂ and one additional neutral HA molecule exists in the second coordination sphere through hydrogen bonding. However, it is difficult to predict the exact mode of one protonated ligand molecule (HA) attaching to the core UO₂A₂ without further structural information. Therefore, the extraction mechanism in Eq. (4) can be proposed as follows:

\[ UO_2^{2+}aq + 3HA_{org} \leftrightarrow UO_2A_2.HA_{org} + 2H^+aq. \] (8)

3.3. Effect of temperature on the extraction of U(VI)

The temperature effect is considered an important factor affecting the equilibrium in solvent extraction processes. The effect of temperature on the extraction of U(VI) was investigated by equilibrating the two phases for 15 min at varying temperatures. The data demonstrate that D values decrease with the increasing temperature. The Gibbs free energy (ΔG), the enthalpy (ΔH), and the entropy (ΔS) of the system can be determined using the following thermodynamic relations:

\[ \Delta G^0 = -RT\ln K_{ex} \] (9)

\[ \Delta G^0 = \Delta H - T\Delta S \] (10)

\[ \frac{\Delta\log D}{\Delta T} = \frac{-\Delta H}{2.303R} \] (11)
Figure 4. Extraction behavior of U(VI) with 0.01 M HDEHDGA in kerosene, [HCl] = 0.0025 M in 1 M NaCl at varying temperatures. By plotting $\log D$ versus ($1000/T$), a linear relationship was obtained as seen in Figure 4. The calculated $\Delta H$, $\Delta G$, and $\Delta S$ values of the extraction are listed in Table 1. The negative values of $\Delta G$, and $\Delta H$ indicating that the extraction process is exothermic and spontaneous. While the negative value of entropy $\Delta S$ implies decreasing in the randomness of the studied system [22].

| Thermodynamic parameters |
|--------------------------|
| $\Delta G$ (kJ mol$^{-1}$) | -8.5 |
| $\Delta H$ (kJ mol$^{-1}$) | -14.56 |
| $\Delta S$ (J mol$^{-1}$ K$^{-1}$) | -20.3 |

4. Stripping U(VI) from HDEHDGA
The recovery of uranium from HDEHDGA was performed using HCl, HNO$_3$, and H$_2$SO$_4$ as stripping solutions. Series of aqueous phases at the same conditions (pH 3.3, [U(VI)] = 1 mM, and 1 M NaCl) were mixed with HDEHDGA (0.05 M) for 15 min at 25 °C. Under those conditions, most of the uranium was extracted in the organic phase (Ext. % = 98.9 %). The loaded organic phases after the extraction were contacted with various concentrations from stripping reagents (HCl, HNO$_3$, and H$_2$SO$_4$) over the range 0.01 - 1 M. It was found that the stripping efficiency increases with the increase in acids’ concentration. As shown in Table 2, when HCl and HNO$_3$ were used as stripping solutions, the quantitative recovery of uranium occurred at 0.5 M and 0.7 M of HCl and HNO$_3$, respectively. While diluted H$_2$SO$_4$ (0.05 M) presents the maximum stripping efficiency, then the stripping efficiency tends to decrease when the concentration of H$_2$SO$_4$ > 0.05 M, which hints a strong extraction at higher H$_2$SO$_4$ concentrations.

5. Effect of uranium concentration on the extraction process
Effect of initial uranium ion concentration in the aqueous phase on the distribution ratio and extraction percent was examined. Series of aqueous samples containing various U(VI) concentrations ranging from $0.7 \times 10^{-3}$ to 0.049 M were shaken with the organic phase, (0.1 M HDEHDGA). As illustrated in Figures 5 and 6, HDEHDGA offers a high extraction affinity under the investigated conditions. The extraction percentage decreases as the metal ion increases due to the decrease in free ligand concentration at higher metal concentrations in addition to the increase of H$^+$ protons in the aqueous phase leading to decrease the pH value in the aqueous phase resulting in decrease the extraction efficiency.
Table 2. Stripping uranium from HDEHDGA as a function of acid concentration.

| Acid concentration, M | HCl  | HNO₃ | H₂SO₄ |
|-----------------------|------|------|-------|
| 0.01                  | 21.3 | 12.7 | 78.5  |
| 0.05                  | 78.9 | 79.2 | 96.3  |
| 0.1                   | 93.3 | 92.8 | 89.8  |
| 0.5                   | > 99 | > 99 | 90.5  |
| 0.7                   | > 99 | > 99 | 87.3  |
| 1                     | > 99 | > 99 | 85.9  |

Figure 5. Aqueous and organic phases before and after the extraction of uranium.

Figure 6. Effect of U(VI) concentration on the distribution ratio and extraction percentage. Organic phase; 0.1 M HDEHDGA, aqueous phase; 0.005 M HCl and 1 M NaCl.

6. Conclusions
The extraction behavior and the recovery of U(VI) from chloride solution using N,N-di(2-ethylhexyle)-diglycolamic acid has been investigated. The data reveal that in low pH region, the extraction is mainly governed by the cation-exchange mechanism and exothermic reaction. The extraction stoichiometry suggests that the major extracted species might be 1:2 (metal/ligand) complex, UO₂A₂ (A = deprotonated HDEHDGA), while in the second coordination sphere, one HA molecule might connect with the core through hydrogen bonding. HDEHDGA presents considerable high extraction efficiency toward uranium, where the removal efficiency reached about 99%. The high extractability of HDEHDGA and easily recovery of the metal ion present great promise for developing new processes of extraction/removal of the radioactive pollutants from waste solutions.

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