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# Extraction and separation of uranium(VI) and Fe(III) from lanthanide chlorides with $N,N,N',N'$-tetrasubstituted alkyl diglycolamide extractants

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**Abstract** It is of great significance to separate impure elements from rare earth in high purity rare earth production. The extraction of uranium(VI) with three structurally related $N,N,N',N'$-tetrasubstituted alkyl diglycolamide extractants in kerosene was studied. The relationship between the chemical structure of diglycolamide and their uranium(VI) extraction behavior was discussed. The extraction of Fe(III) and Nd(III) from chloride media was compared with that of uranium(VI) under the same experimental conditions. The results showed that uranium(VI) and Fe(III) can be effectively removed from NdCl$_3$ solutions with $N,N,N',N'$-tetraoctyl diglycolamide using kerosene as diluent.

**Keywords** Extraction · Uranium(VI) · Fe(III) · Lanthanids chloride · $N,N,N',N'$-tetrasubstituted alkyl diglycolamide

## Introduction

Rare earths are important mineral resources in China. The rare earth ore in China can be roughly divided into three categories: bastnaesite, monazite, and ion-adsorption clays [1].Uranium and thorium are usually present in rare earth ores, resulting in radiation issues in rare earth production [2]. Xenotime usually contains up to 5% uranium. While uranium is rarely found in monazite, it can occasionally be found in very high amounts, up to 16% [3]. Bastnasite usually contains a little amount of uranium. There is another kind of rare earth resource, ion-adsorption clays, which are mainly found in China. These resources contain very small amounts of uranium and thorium, estimated to be about 20–30 ppm ThO$_2$ and U$_3$O$_8$ based on total REO (rare earth oxide) [4].

At present, rare earth chloride products are the main varieties of rare earth salts, and occupy an important position among rare earth products. Some Bayan Obo concentrates are processed using the alkaline method [5, 6]. In that process, rare earths and thorium are converted into their hydroxide by NaOH during caustic digestion. Following this, the hydroxide precipitation is leached with HCl. Then, the resultant leach solution is neutralized to pH 4–5 to remove thorium and iron by precipitation. The rare earth minerals in Sichuan Province are bastnasites. After beneficiation, the concentrates for rare earth production usually contain 60–70% REO, 0.2–0.3% ThO$_2$ and 0.002% U$_3$O$_8$ [7]. In hydrochloric acid leach liquor of these minerals, U(VI) exists in varying amounts. The extraction was conducted without attention to uranyl due to its low concentration and less environmental hazards. At the same time, there is a small amount of iron in acid leach liquor in the process. The precipitation method can't remove Fe(III) to the desirable trace concentration. Then developing a highly efficient extraction technology to remove uranium and iron from rare earth chloride solution is very important in the high purity rare earth preparation.

TBP was used to extract uranium(VI) and thorium from HCl solution by forming UO$_2$Cl$_2$·2TBP and ThCl$_4$·3TBP, respectively [8, 9]. However, their extractions require very high hydrochloric acid concentration, e.g. >5 mol dm$^{-3}$ HCl for essential uranium extraction and >8 mol dm$^{-3}$ HCl for thorium extraction. Zou Dong reported one

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recovery process for U, Th and RE from monazite U, Th residue HCl leach liquor. U(VI) and Fe(III) can be extracted effectively so as to separate from RE using 20% di(1-methyl-heptyl)methyl phosphonate-5% TBP in kerosene from 1.5 to 2.0 mol dm$^{-3}$ HCl medium [10].

The study on the extraction and separation of U(VI), Th(IV) and RE with Cyanex 923 (a mixture of trialkylphosphine oxides) showed that uranium could be separated well from rare earths in HCl solution [11]. Anitha studied the extraction of rare earths from chloride medium using dinonyl phenyl phosphoric acid [12]. D2EHPA-TBP as synergistic extractant was used for U(VI) recovery from the solutions obtained after leaching Polish uranium ores. The addition of TBP was favorable in preventing the formation of a third phase during the alkali treatment of a solvent containing D2EHPA [13]. The above mentioned phosphonic acid extractants, the most commonly used industrial extractants in individual REE separation, must be saponified before extraction, which usually discharges a large quantity of saponification waste water into the environment [14].

As a new type of extractant, diglycolamideis considered to be a more environmentally friendly extraction agent because of consistency with the "CHON principle" resulting in the possibility of complete incineration [15]. Its homologue had been investigated extensively in the high-level radioactive waste processing, especially in the extraction of Am and Cm actinide elements from nitric acid system [16–19]. We had reported the extraction of uranium with $N,N,N',N'$-tetraoctyl diglycolamide and asymmetrical $N,N'$-dimethyl- $N,N'$-didodecyl diglycolamide from nitric acid solutions [20, 21].

To develop effective and environmentally friendly extraction techniques for the REE separation, this work was conducted to investigate the relationship between the chemical structure of diglycolamides and their U(VI) extraction behavior from hydrochloric acid, and to try to understand the dependence of the metal extraction mechanism on the structural characteristics of the as-synthesized extractants. The extraction of Nd(III) and Fe(III) in chloride medium was compared with that of U(VI) under the same conditions. Our aim is to evaluate the feasibility of using $N,N,N',N'$-tetrasubstituted alkyl diglycolamide extractants to separate U(VI) and Fe(III) from lanthanide chloride solutions.

## Experimental

### Chemicals and reagents

The extractants, $N,N'$-dimethyl-$N,N'$,-didodecyl diglycolamide (DMDDDGA), $N,N,N',N'$-tetra(2-ethylhexyl) diglycolamide (T2EHDGA) and $N,N,N',N'$-tetraoctyl diglycolamide (TODGA), were synthesized in our laboratory by a method similar to that described in our previous paper [22]. The corresponding molecular structures are given in Fig. 1. The purity, checked by IR, $^1$HNMR and HPLC, was found to be more than 98%. The extractants were dissolved in kerosene to prepare the organic solvent. The stock solutions of rare-earth ions were prepared by first digesting the corresponding rare earth oxide in minimum concentrated hydrochloric acid, then evaporating it to near dryness, and finally dissolving it with distilled water. Uranyl chloride was prepared from $U_3O_8$. $FeCl_3$ with analytical reagent grade was used without further purification. Feed solutions were made by diluting the stock solution. All other chemicals used were of analytical reagent grade.

DMDDDGA IR: 2924 cm$^{-1}$ ($\nu_{CH2}$), 2857 cm$^{-1}$ ($\nu_{CH3}$), 1665 cm$^{-1}$ ($\nu_{C=O}$), 1458 cm$^{-1}$ ($\delta_{CH3}$, $\delta_{CH2}$),1123 cm$^{-1}$ ($\nu_{C-O-C}$), 723 cm$^{-1}$ ($\nu_{(CH2)_n}$); $^1$HNMR (400 MHz, CDCl$_3$, ppm): 4.71–4.43 (4H, s, –CH$_2$COCH$_2$–), 3.46–3.30 (4H, s, –N–CH$_2$–), 3.28–3.12 (4H, s, –NCH$_2$CH$_2^*$–), 3.06–2.90 (6H, s, –N–CH$_3$), 1.38–1.16 (36H, m, –(CH$_2$)$_9$–), 0.94–0.82 (6H, m, –CH$_3$).

TODGA IR: 2955 cm$^{-1}$ ($\nu_{CH2}$), 2928 cm$^{-1}$ ($\nu_{CH3}$), 1655 cm$^{-1}$ ($\nu_{C=O}$), 1457 cm$^{-1}$ ($\delta_{CH3}$, $\delta_{CH2}$),1122 cm$^{-1}$ ($\nu_{C-O-C}$), 723 cm$^{-1}$($\nu_{(CH2)_n}$); $^1$HNMR (400 MHz, CDCl$_3$, ppm): 4.30 (4H, s, –CH$_2$OCH$_2$–), 3.14–3.29 (8H, m, –N–CH$_2$–), 1.50 (8H, s, –NCH$_2$CH$_2^*$–), 1.25 (40H, s, –(CH$_2$)$_5$–), 0.84–0.87 (12H, m, –CH$_3$).

T2EHDGA IR: 2952 cm$^{-1}$ ($\nu_{CH2}$), 2930 cm$^{-1}$ ($\nu_{CH3}$), 1658 cm$^{-1}$ ($\nu_{C=O}$), 1461 cm$^{-1}$ ($\delta_{CH3}$, $\delta_{CH2}$), 1216 cm$^{-1}$ ($\nu_{C-N}$), 1116 cm$^{-1}$ ($\nu_{C-O-C}$); $^1$HNMR (400 MHz, CDCl$_3$, ppm): 4.35–4.37 (4H, s, –CH$_2$OCH$_2$–), 3.46–3.21 (4H, m, –N–CH), 1.53–1.50 (16H, s, –NCH (CH$_2^*$)$_2$–), 1.29–1.21 (24H, m, –(CH$_2$)$_3$–), 0.89–0.83 (24H, m, –CH$_3$).

### Extraction procedure

The extraction experiments were carried out in tube with stopper by equilibrating equal volumes (3 mL) of aqueous and organic phases for a given time to obtain the equilibration at 298 K. After equilibrium, the two phases were then centrifuged and separated. The concentration of $UO_2^{2+}$ in aqueous solution was determined by Arsenazo-III visible spectrophotometric method. The concentration in the organic phase was obtained by subtracting the aqueous concentrations from the total initial aqueous concentration of $UO_2^{2+}$.

The extractions of Nd(III) and Fe(III) were conducted in steps similar to those described above. The concentration of Fe(III) in the aqueous phase was determined by the 1,10-phenanthroline method after reduction to Fe(II) with hydroxylamine hydrochloride [23]. The concentration of
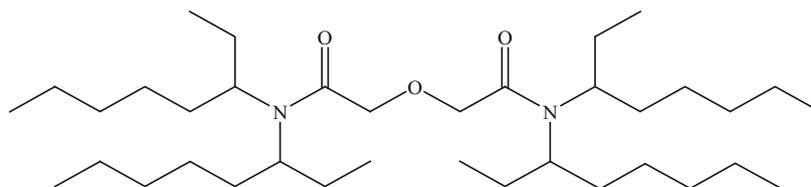
DMDDDGA
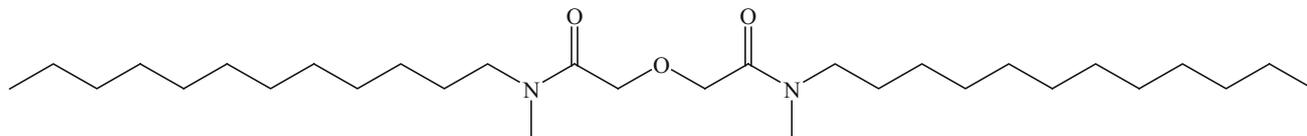


TODGA
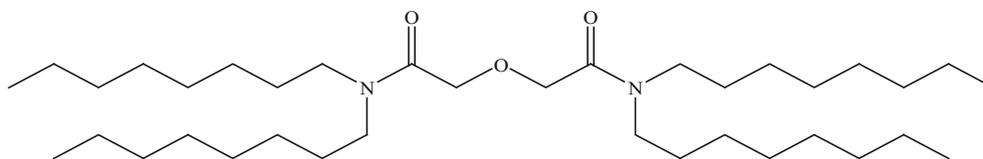


T2EHDGA



Fig. 1 The structures of as-prepared extractants

rare earth elements in aqueous solution was determined by Arsenazo-III visible spectrophotometric method [24].

The distribution ratio ($D$) was calculated as $(C_i–C_e)/C_e$, where $C_i$ is the metal ion concentration in the aqueous phase before extraction and $C_e$ is the metal ion concentration in the aqueous phase after extraction.

## Results and discussion

### Extraction of uranium(VI)

The extraction behavior of uranium(VI) with three prepared DGA extractants using kerosene as diluent from chloric acid media was investigated.

The effect of hydrochloric acid concentration on $D_U$ values of U(VI) with TODGA and T2EHDGA in kerosene under 298 K is shown in Fig. 2. It can be seen that the $D_U$ values increase slightly with the increase in hydrochloric acid concentration up to 3.0 mol dm$^{-3}$, and then increase markedly. The formation of emulsions was observed in the DMDDDGA system under the studied acid concentration range. The phase separation is slow and difficult. The other two systems using TODGA and T2EHDGA as extractants show good phase separation behavior. This established that
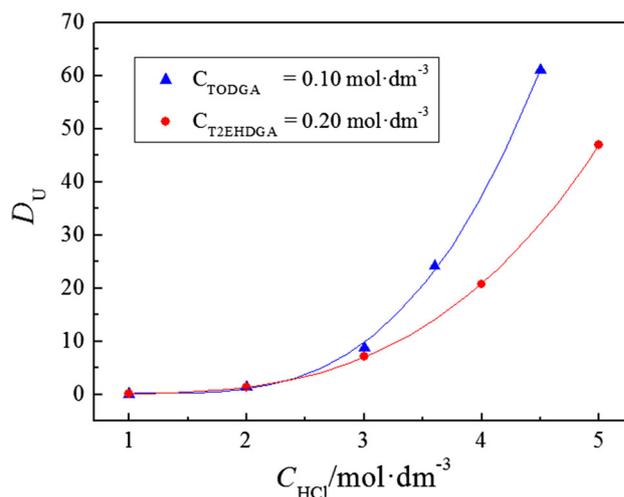


Fig. 2 Distribution ratio of uranium(VI) with TODGA and T2EHDGA as a function of hydrochloric acid concentration

the methyl of DMDDDGA with a small steric hindrance plays an important role for its interfacial activity. It appears more reasonable that DMDDDGA molecules interact with HCl at interface more strongly than those of TODGA and T2EHDGA [23].
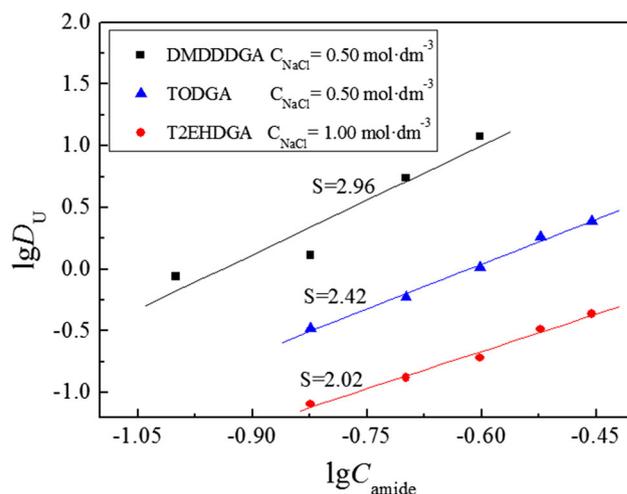
The distribution ratios as a function of NaCl concentration with three extractants were studied to check the effect of Cl$^-$ concentration. The result is shown in Fig. 3. The $D_U$ values increase with the chloride anion concentrations. Compared with the data of Fig. 2, we found that $D_U$ value is higher in the presence of NaCl than that of HCl at the same concentration. If the extractant concentration is kept constant and polymerization in the organic phase is assumed to be negligible, the plots of log $D_U$ versus log[Cl$^-$] at constant DGA concentration would give straight lines, whose slopes will determine the number of Cl$^-$ in the extracted species. However, we obtained three curves of log $D_U$ versus log[Cl$^-$] for three extractants respectively. Their tangent slopes increase gradually from about 2 to 4 in the concentration range studied with the increase in NaCl concentration. This result can perhaps be attributed not only to the chloride ions promoting the extraction, but also to the salting out effect of NaCl [21].

Figure 3 also shows the different extraction ability of DMDDDGA, TODGA and T2EHDGA for U(VI) from chloride media. The order of the extractability is DMDDDGA > TODGA > T2EHDGA. From Fig. 1, we can easily find that this order is consistent with the space steric hindrance of the alkyl substituents. Namely, smaller alkyl steric hindrance yields higher extraction ability.

Based on the principle of electroneutrality in extraction theory, it is reasonable to suggest that the stoichiometry of the extracted species in the organic phase maybe UO$_2$Cl$_2$·nDGA. In order to understand the nature of species formed by DGAs with U(VI), the effect of extractant concentrations on the distribution ratios was considered to further explore the values of n in different extractant systems. Figure 4 illustrates the distribution ratios as a function of the concentration of DMDDDGA, TODGA and T2EHDGA in kerosene, respectively.
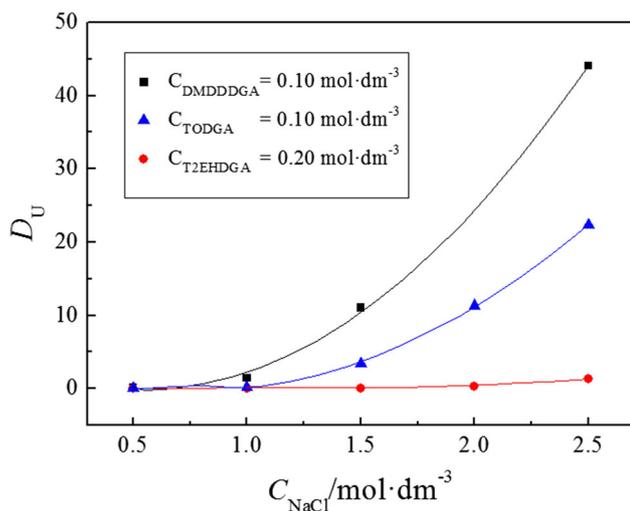


**Fig. 3** Effect of NaCl concentration on the extraction of U(VI)



**Fig. 4** Distribution ratios as a function of the concentration of extractants

The slopes of the log–log plot of $D_U$ versus [DGAs] were calculated by a slope analysis method [25] as shown in Fig. 4 giving 2.96, 2.42, and 2.02 for DMDDDGA, TODGA and T2EHDGA, respectively. For DMDDDGA, a mechanism involving uranium(VI) extraction through the coordination of UO$_2^{2+}$ with three extractant molecules seems to occur. For T2EHDGA, the solvation of UO$_2^{2+}$ with two extractant molecules appears to be the predominant U(VI) extraction pathway. But for TODGA, the process is somewhat complex. The slope of the line is 2.42, which shows that two kinds of extracted species, UO$_2$·2TODGA and UO$_2$·3TODGA, may be formed. Mowafy found that there are three or four amide molecules in the extracted species at different nitric acid concentrations in the extraction of trivalent lanthanides from nitric acid medium by selected structurally related diglycolamides [26]. Sasaki et al. suggested that three or four diglycolamid molecules were coordinated for trivalent ion by slope analysis [27]. That is to say, it is reasonable that two kinds of extracted species formed in the extraction process.

The structure of the extractant had a great influence on the extraction performance [28]. The steric hindrance of the studied extractants is in the order: T2EHDGA > TODGA > DMDDDGA from the point of view of substituent alkyl sizes on N atom of DGAs. From Fig. 4, we can find that the ratio of the numbers of extractant molecules and that of UO$_2^{2+}$ in the extracted species declines with the increase in space steric hindrance of the extractant molecules.

## Extraction and separation of Fe(III), U(VI) and Nd(III)

Iron is the main impure element in the lanthanides chloride products. Study of the separation of iron from lanthanides is very important in the preparation of high purity

**Table 1** The extraction and separation of Fe(III), U(VI) and Nd(III) by TODGA

| Stages | First-stage extraction | | Second-stage extraction | | Third-stage extraction | |
|---|---|---|---|---|---|---|
| $C_{TODGA}$ (mol dm$^{-3}$) | 0.20 | 0.36 | 0.20 | 0.36 | 0.20 | 0.36 |
| $C_{Fe}$ (mol dm$^{-3}$, $\times 10^3$) | 12.8 | 2.66 | 3.57 | 1.94 | 2.33 | 1.08 |
| $C_U$ (mol dm$^{-3}$, $\times 10^7$) | 18,600 | 288 | 370 | 48.7 | 9.92 | 1.24 |
| $\beta$Nd/Fe | 38.48 | $1.84 \times 10^2$ | $1.38 \times 10^2$ | $2.53 \times 10^2$ | $2.10 \times 10^2$ | $4.54 \times 10^2$ |
| $\beta$Nd/U | 62.30 | $4.02 \times 10^3$ | $3.13 \times 10^3$ | $2.37 \times 10^4$ | $1.17 \times 10^5$ | $9.32 \times 10^5$ |

lanthanides products [29]. In this paper, neodymium was selected as the representative of light rare earths.

In order to evaluate the actual separation effect, we conducted a multi-stage extraction experiment. In the extraction experiment, the simulated feed solution was used [30] with the concentrations of U (VI) 1 g/L, Fe(III) 5 g/L, Nd$_2$O$_3$ 32 g/L and HCl 2 mol dm$^{-3}$, respectively. Two kinds of organic phase were used where TODGA concentrations in kerosene were of 0.20 and 0.36 mol dm$^{-3}$, respectively. In the first-stage extraction experiment, 5 mL organic phase and 10 mL water phase (V/V, 1:2) were taken and shocked for half an hour at room temperature to achieve equilibrium, then the metal ions concentrations were determined with ICP-MS (Thermo Elemental, X Series). In the Secondary stage extraction experiment, 4 mL organic phase and 8 mL water phase of the first-stage extraction were mixed and analyzed. Third stage extraction experiment was conducted with 3 mL organic phase and 6 mL water phase of the secondary stage extraction. The results were given in Table 1.

Under the studied conditions, Nd(III) can not be extracted substantially. Fe(III) can be extracted effectively. We had studied the extraction of Fe(III) from chloric acid media and found that the structure of the extracted species is $[H\cdot(2TBDGA)]^+[FeCl_4]^-$ [23].

The separation factor, $\beta$, is defined as the ratio of the concentrations of two kind of ions compared. From Table 1, the values of $\beta$ increase with the stages. And the concentration of Fe(III), especially U(VI) are very low. Our results show that the use of TODGA is very promising in the separation of Fe(III) and U(VI) from NdCl$_3$ solutions. This technique may be used in the hydrometallurgy of light rare earth ores, such as Bayan Obo minerals.

## Conclusions

The extraction of uranium(VI) with three structurally related diglycolamide extractants from chloride media was investigated. The extraction ability of the studied extractants decreases with the increase in the steric hindrance of the extractant molecule. TODGA as a novel extractant is suitable to extract uranium(VI) from chloride solution due to its good extraction ability and phase behavior. TODGA shows high extraction ability for Fe(III) and poor ability for light rare earth elements. TODGA has extensive application prospects in the separation techniques of uranium and iron from light rare earth chloride.

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