The extraction behaviors of Nd(III), Sm(III), Gd(III), Dy(III), Er(III), Yb(III) with N,N'-dibutyl-N,N'-dioctyl-3-oxyglutaramide from hydrochloric acid solution

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Abstract. The extraction behavior of rare earth ion (RE (III)) using N, N'-dibutyl-N, N'-dioctyl-3-oxy-glutaramide from hydrochloric acid was investigated. The influences of hydrochloric acid concentrations, extract ant concentration, and temperature on the extraction distribution ratio were studied. The extraction mechanism was established and the stoichiometry of the main extracted species was confirmed by the slope analysis method.

1. Introduction
The novel properties of rare earth elements (REEs) have led to their application in more consumer products than nearly any other element group. REEs are also essential for the production of clean energy technologies, and they are mostly obtained by rear-earth minerals [1, 2]. Many methods have been developed for the preparation of the individual REE, and the most important of these is solvent extraction [3]. Since they are rare and valuable, REEs are considered critical raw materials, and there recycling is mandatory for economic, technical, environmental and resource conservation reasons. The traditional mining is laborious with slow efficiency and environmental problems, liquid-liquid extractions represent an attractive alternative for the separation of REEs from rear-earth minerals and high level waste nuclear fuel solutions.

In recent years, the amide-based extractants draw more and more attention of researchers. Compared with traditional phosphorus-containing extractants, the products of radiolytic and hydrolytic degradation of amides are less detrimental to the separation progress. In addition, they can be washed or burnt out, according to the CHON principle [4]. Solvent extraction and the technological process play an important role in nuclear fuel reprocessing and hydrometallurgy process. Many studies have reported that the application of amide-based extractants is efficient for separating REEs from aqueous solutions [5]. However, the reported medium most was nitrate acid, and there are only a few examples that studied the extraction of REEs from hydrochloric acid medium [6].

The diluent can affect the solubility of the extracted species and the extraction distribution ratio because of its polarity [7].
2. Experimental

2.1. Reagents.
N,N'-dibutyl-N,N'-dioctyl-3-oxy-glutaramide (DBDODGA) was synthesized according to the reported procedure [8], and the structure was shown in Fig. 1. DBDODGA was characterized by 1H NMR. The corresponding date are given as follows: $^1$H NMR (400 MHz, CDCl$_3$) δ ppm: 4.32 (s, 4H, -CH$_2$O-), 3.16~3.3 (m, 8H, -N-CH$_2$-), 1.48~1.53 (m, 8H, -N-CH2-CH$_3$), 1.27~1.35 (m, 24H, -CH$_2$-), 0.86~0.95(m, 12H, -CH$_3$). The RE (III) solutions were prepared by dissolving rare earth oxides (>99.9%) with concentrated HCl solution. Other chemical reagents in this work were all A.R. grades and used without further purification.

![Fig. 1 Structure of the extractant (DBDODGA)](image)

2.2. Extraction procedure.
Equal volumes of DBDODGA in diluent and RE (III) solution were shaken vigorous to obtain equilibrium (30 minutes) at a constant temperature. The experiment was conducted at 25°C except when the effects of temperature were investigated. The IR spectra were recorded with liquid cell on Nicolet 6700 Fourier Transform Infrared Spectrometer (Thermo Fisher Scientific) in the range of 400-4000 cm$^{-1}$.

3. Results and discussion

3.1. Effect of the concentration of HCl.
The extraction behaviors of Nd (III), Sm (III), Gd (III), Dy (III), Er (III), Yb (III) with 0.075 mol·dm$^{-3}$ DBDODGA in kerosene-(n-octanol) ($V_{\text{kerosene}:V_{\text{n-octanol}}}=7:3$) from hydrochloric acid solutions were investigated. Fig.1 shows the distribution ratio of RE (III) increases in the range of 1.00-5.00 mol·dm$^{-3}$ hydrochloric acid concentration, which is somewhat similar to the extraction behavior in the reported papers[9], where the distribution ratios of rare earth ions increased with hydrochloric acid concentration using N,N,N',N'-tetrabutyl-3-oxy-glutaramide. This phenomenon can be explained as co-ion effect. As the atomic number increasing, the extraction distribution ratio also rises in kerosene-(n-octanol) from hydrochloric acid, which shows that DBDODGA has better affinity for heavy lanthanides.
Fig. 2 Effects of the concentration of HCl on the extraction capability of RE (III) from kerosene-(n-octanol) (V kerosene:V n-octanol = 7:3)

\[ C_{\text{M}^{3+}} = 4.00 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}; C_{\text{DBDODGA}} = 0.075 \text{ mol}\cdot\text{dm}^{-3} \]

3.2. Effect of the concentration of DBDODGA.
To get an insight on the nature of the extracted species in the organic phase, the concentration of DBDODGA in kerosene-(n-octanol) (V kerosene:V n-octanol = 7:3) was investigated. The extraction progress can be described as:

\[
\text{M}^{3+} + 3\text{Cl}^- + n\text{DBDODGA}_{(o)} = \text{MCl}_3 \cdot n\text{DBDODGA}_{(o)}
\]  

Where M\(^{3+}\) is Nd (III), Sm (III), Gd (III), Dy (III), Er (III), and Yb (III), respectively, subscribe (o) refers organic phase. The value of n which shows the stoichiometry of the predominant extracted species can be determined by the slope analysis method. The logarithm distribution ratio was plotted as a function of logarithm concentration of DBDODGA in Fig.2 and the results were shown in Table.1

| RE(III) | slope | extracted species               |
|---------|-------|-------------------------------|
| Nd\(^{3+}\) | 1.79  | NdCl\(_3\) \cdot 2\text{DBDODGA} |
| Sm\(^{3+}\) | 2.26  | SmCl\(_3\) \cdot 2\text{DBDODGA} |
| Gd\(^{3+}\) | 2.41  | GdCl\(_3\) \cdot 2\text{DBDODGA} |
| Dy\(^{3+}\) | 2.58  | DyCl\(_3\) \cdot 3\text{DBDODGA} |
| Er\(^{3+}\) | 2.24  | ErCl\(_3\) \cdot 2\text{DBDODGA} |
| Yb\(^{3+}\) | 2.65  | YbCl\(_3\) \cdot 3\text{DBDODGA} |

The investigation shows that the stoichiometry of the extracted species is different. The phenomenon may be caused by the change of DBDODGA’s structure in the extraction progress. The ether oxygen bond (C-O-C) in DBDODGA is a flexible bond, so the extractant can adjust its structure as increasing the number of atom to coordinate to the rare earth ions, which results the different n value [9].

3.3. Effect of temperature on distribution ratio.
Temperature plays an important role in an extraction technique. The effect of temperature on the distribution of RE (III) was investigated in the range of 15-55°C. Fig.3 reveals that the distribution
decreases with increasing of temperature, which demonstrates the reaction was exothermic. Therefore, high-temperature was disadvantageous for the extraction of RE (III) with DMDODGA.

![Graph showing the effect of extractant concentration on the extraction capability of different metal ions from kerosene-(n-octanol) (V_kerosene:V_n-octanol = 7:3) C_{M3+}=4.00\times10^{-3}\text{ mol}\cdot\text{dm}^{-3}; \ C_{HCl}=4.00\ \text{mol}\cdot\text{dm}^{-3}]

From the slope of the straight lines, ΔH has been evaluated using the van’t Hoff equation, and the value was shown in Table 2. The negative ΔH value further suggests that the extraction reaction is driven by enthalpy.

**Table 2.** The thermodynamic data of the extraction of RE (III) with DBDODGA

| RE (III) | Nd^{3+} | Sm^{3+} | Gd^{3+} | Dy^{3+} | Er^{3+} | Yb^{3+} |
|----------|---------|---------|---------|---------|---------|---------|
| ΔH_{m}^{θ}(kJ\cdot\text{mol}^{-1}) | -39.08  | -57.18  | -68.25  | -75.87  | -67.20  | -75.17  |

\[
\left. \frac{\partial \log D}{\partial (1/T)} \right|_p = -\frac{\Delta H_{m}^{θ}}{2.303R}
\]

(2)

Where \( R \) is the gas constant (8.314 J\cdot\text{mol}^{-1}\text{K}^{-1}).

![IR spectra of DBDMDGA and loading RE (III). (a) DBDODGA; (b) DBDODGA-Gd; (c) DBDODGA-Sm; (d) DBDODGA-Nd; (e) DBDODGA-Er; (f) DBDODGA-Yb; (g) DBDODGA-Dy]
3.4. **Spectroscopic studies of the extracted species.**

The experimental spectra of the organic phase loading extracted species was studied, the results were shown in Fig.4. Compared with the free extractant, the wave number of the strong absorption bands of C=O was shifted to low numbers. The shift was 21, 24, 35, 45, 38 and 32 cm$^{-1}$ in the carbonyl group for DBDODGA-Gd, DBDODGA-Sm, DBDODGA-Nd, DBDODGA-Er, DBDODGA-Yb, and DBDODGA-Dy, respectively. The IR stretching frequency of the ether group had a weak shift. The above results indicate that the oxygen atom of the carbonyl function group and ether oxygen are all coordinated with RE (III) [10].

4. **Conclusion**

The effects of different extraction conditions, such as hydrochloric acid concentration, extractant concentration and temperature, were investigated. In dilute of kerosene-(n-octanol) ($V_{\text{kerosene}}: V_{\text{n-octanol}} = 7:3$), the extraction results indicated that there is an increase in the extraction of all the RE(III) investigated as a function of the hydrochloric acid concentration, which was attributed to the co-ion effect. The number of DBDODGA molecules coordinated to RE (III) was estimated by slope analysis, and the IR spectrum of the extracted species indicated that DBDODGA was a tridentate extractant and the three oxygen atoms of DMDODGA were all coordinated with RE (III). In addition, the effect of temperature revealed the extract reaction was exothermic, and low-temperature is beneficial to the extract reaction.

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**References**

[1] Noack C W, Dzombak D A, Karamalides A K (2015) Environ. Sci. Technol. 49:9423-9430.
[2] APS Energy Critical Elements: Securing Materials for Emerging Technologies; American Physical Society (2011).
[3] Xu L, Xiao Y H, Li D Q (1992) J. Chem. Inf. Comput. Sci. 32:437-442
[4] Gasparini G M, Grossi G (1986) Solv. Extr. Ion Exch. 4 (6):1233-1271
[5] Cui Y, Hu Y F, Zhang Y J, Yin S H, Sun G X (2010) J. Inorg. Chem. 55 (3):468-471
[6] Sun G X, Liu M, Cui Y, Yuan M L, Yin S H (2010) Solv. Extr. Ion Exch. 28 (4):482-494.
[7] Ye G A, Luo F X, Jiang Y Q, Ding S D, Chen W J (2000) Atomic Energy Sci. Technol. 34 (6):528-533.
[8] Sasaki Y, Zhu Z X, Sugo Y, Kimura T (2007) J. Nucl. Sci. Technol. 44 (3):405-409.
[9] Wu G P, Yang J H, Xia G M, Cui Y, Sun G X (2011) Chinese Journal of Inorganic Chemistry. 27 (2):315-320.
[10] Shimojo K, Kurahashi K, Naganawa H (2008) Dalton Trans 37:5083-5088.