Effect of Diglycolamide Ligands Structure on Extraction Performance of Heavy Rare Earth Ions

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The properties of four different extractants, TODGA (N,N,N',N'-tetraoctyl-diglycolamide), T2EHDGA (N,N,N',N'-tetraisoctyl-diglycolamide), DPDODGA (N,N'-dipropyl-N,N'-dioctyl-diglycolamide) and DIPDODGA (N,N'-diisopropyl-N,N'-dioctyl-diglycolamide), to extract heavy rare earth metal ions in hydrochloric acid were studied to understand the relationship between the chemical structure of the extractant and the extraction properties of rare earth metal ions. The extraction order of heavy rare earths in n-octane: n-octanol = 9:1 diluent was as follows: DIPDODGA > DPDODGA > TODGA > T2EHDGA. Alkyl chain shows great influence on extraction ability and the extractants with short chain can effectively extract heavy rare earth ions even at a concentration of less than 1.0 mol/L. The extraction mechanism was proposed with the results of slope methods, IR (Infrared) spectrometer and DFT (Density Functional Theory) theoretical study. T2EHDGA forms binuclear and the other three extractants form mononuclear extracted species with heavy rare earth ions.

1. Introduction

Rare earth metals have very similar chemical properties and are closely related. The 16 rare earth elements can be divided into three groups according to the solubility degree of rare earth sulfate: light rare earth or cerium group rare earth (lanthanum, cerium, praseodymium, neodymium, promethium and samarium), medium heavy rare earth or terbium group rare earth (europium, gadolinium, terbium and dysprosium), and heavy rare earth or yttrium group (holmium, erbium, thulium, ytterbium, lutetium and yttrium) [1].

Rare earth metals are widely used in steel, glass, ceramics, electronics, petroleum and other industries. The yttrium aluminum garnet (Ho:YAG) laser doped with holmium can be used to improve the efficiency and accuracy of surgery. Erbium-doped laser crystals can be used in the military to make a portable laser rangefinder for eye safety [2,3]. Thulium can be used in clinical diagnosis and treatment of tumors, because heavy rare earths are more closely related than light rare earths, and thulium has the greatest affinity. The addition of erbium, thulium, ytterbium, lutetium and other oxides greatly improve the charging efficiency of nickel electrode at high temperature. Due to these important roles, the demand for heavy rare earth keeps increasing, but the existing resource storage is sharply decreasing [4,5]. Therefore, the research on the extraction, purification, and separation of heavy rare earth metals has becomes particularly important.

In recent years, due to environmental protection and economic benefits, solvent extraction is often used for the extraction of rare earth [6,7]. Currently, di(2-ethylhexyl) phosphate (P204) ester and 2-ethylhexyl
dihydrogen phosphate (P507) are commonly used as extraction agents in industry. Saponification is needed for extraction with this kind of extraction agent and a large amount of ammonia nitrogen wastewater is produced. DGA type of extractant [8] is a neutral complexation extractant, which does not require acid-base neutralization process during extraction and basically produces no waste water. Therefore, it is of great environmental significance for rare earth extraction.

Jinhong Yang et al. studied the extraction of Sm and Nd in the hydrochloric acid system with TBDGA (N,N,N',N'-tetraoctyldiglycolamide) [9]. Fukai Li et al. [10] used TODGA as an extractant to provide a feasible method for simultaneous determination of trace rare earth elements in water samples. Marino Gergoric et al. [11] studied the selectivity of rare earth in its leaching solution by using nitric acid to dissolve NdFeB magnetic waste. Arijit Sengupta et al. used the combination of density functional theory and experiment to study the extraction efficiency of Pu$^{4+}$, UO$_2^{2+}$, Am$^{3+}$, and Eu$^{3+}$ by different DGA ligands.

It can be seen that the length of alkyl chain on $N$ increases from $n$-pentyl to $n$-dodecyl, and the extraction efficiency decreases monotonically [12]. Brigham et al. took into account the results of liquid-liquid extraction, X-ray absorption spectra (XAS) and simulation to provide a new structural perspective for the outer ion clusters of lanthanide (III) ions and DGA ligands, and described the formation of trilobate outer lanthanide chloride ions or nitrate ions clusters through spatial force and electrostatic force in the liquid-liquid extraction process [13].

The structure of the extractant is closely related to the extraction performance. The study on the relationship between the structure and performance of DGA extractant and the search for the optimization rules of the extractant are conducive to the development of the extraction process of DGA. There are relatively few studies on the structure and performance of DGA extractant in hydrochloric acid media [14,15]. In order to investigate the influence of the structure of $N$-substituted alkyl chain, we designed and synthesized four extraction agents, whose structures were shown in Figure 1. Heavy rare earths, which are commonly found in ionic ores in southern China, were taken as research targets. The effect of the structure on the extraction properties of heavy rare earth from hydrochloric acid solution was studied.

![Figure 1. Extractant structure diagram.](image)

(TODGA: R1,R2= n-octyl; T2EHDGA: R1, R2= iso-octyl; DIPDODGA: R1= n-octyl, R2= isopropyl; DPDODGA: R1= n-octyl, R2= n-propyl)

2. Experimental

2.1 Materials

TODGA, T2EHDGA, DIPDODGA and DPDODGA were synthesized by referring to the three-step method we previously reported [16,17], and characterized by $^1$H NMR (Bruker DPX-400 Nuclear Magnetic Resonance Spectrometer, Bruker), HPLC (Easy Sep 1010 High Performance Liquid Chromatograph, Unimicro (Shanghai) Technologies), IR (SPECTRUM ONE Fourier Transform Infrared Spectrometer, PerkinElmer) with a purity of at least 93%. Other chemical reagents were AR grade, without further
purification. The solution was prepared with \( n \)-octane: \( n \)-octanol= 9:1 to dilute extractant (Initial concentration of extractant \( C_{\text{ex}} \)=0.2 mol/L). \( \text{Ho}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Tm}_2\text{O}_3, \text{Yb}_2\text{O}_3, \text{Lu}_2\text{O}_3 (>99.9\%) \) was dissolved with concentrated hydrochloric acid to prepare \( \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu} \) solution (Initial concentration of rare earth metal ions \( C_{\text{Ln}}=0.1 \) mol/L). The working solution was obtained by dilution.

2.2 Experimental process

The volume of organic phase and water phase was kept at 1:1 and the liquid was mixed on the oscillator at 25 °C for 1 hour. Then two phases were centrifugally separated and the samples were analyzed with Arsenazo III visible spectrophotometry for the concentration of heavy rare earth ions in water phase [9,18]. The metal ion concentration in organic phase was calculated by mass balance, and the distribution ratio \( D \) was calculated as follows:

\[
D = \frac{C_i - C}{C}
\]

(1)

\( C_i \): The initial concentration of heavy rare earth ions; \( C \): The concentration of heavy rare earth ions in aqueous phase after extraction equilibrium.

The concentration of HCl in organic phase was determined by acid-base titration (phenolphthalalin as indicator). All calculations were performed using DFT method with the Gaussian 09, Revision D.01 using the DFT/B3LYP/6-31+G(d) basis set. The extracted organic phase solution was dripped onto KBr slice to obtain IR spectra.

3. Results and Discussion

Extraction experiments were conducted under conditions related to rare earth refining process. Chloride solution was usually employed in the industrial extraction of lanthanide. DGA ligand extractant is an ideal choice for separation of lanthanide compounds [19]. In this paper, the hydrochloric acid system was adopted and the structure of the branched chain on extraction agent \( N \) on the extraction of heavy rare earths was investigated.

Figure 2 shows the effect of concentration of hydrochloric acid on the distribution ratio of heavy rare earth ions with TODGA, T2EHDGA, DIPDODGA and DPDODGA as extractants (concentration \( C_{\text{ex}}=0.10 \) mol/L). It can be seen from the Figure 2a that both of the corresponding distribution ratio of TODGA increase with the increase of acidity within the range of selected acidity. The influence trend of various factors on extraction performance for the other three extractant systems was similar, that is, with the increase of acidity, the extraction distribution ratio increases. This is consistent with previous reports on the extraction of rare earth ions by DGA extractant [20-23]. In Figure 2b, \( \text{Ho} \), a rare earth ion, is taken as an example. Under the same conditions, it was found that the ability of these four extractants to extract heavy rare earth was in the following order: DIPDODGA \( > \) DPDODGA \( > \) TODGA \( > \) T2EHDGA. This shows that the change of alkyl chain on \( N \) atom has an important effect on the extraction ability of rare earth.
Figure 2. Effect of acidity on the distribution ratio of rare earth extracted by extractants.

The study on the extraction properties of extractants for hydrochloric acid is of great significance to further explore the extraction mechanism. Figure 3 shows the extraction of hydrochloric acid by different DGA extractants at different acidity. The figure clearly shows that the concentration of hydrochloric acid in organic phase also increases with the increase of water phase concentration, which is consistent with the previous report for extraction of HCl by \( N,N'-\text{dimethyl-}N,N'-\text{didodecyl} \)-diglycolamide (DMDDdDGA), \( N,N'-\text{di-ethyl-}N,N'-\text{didodecyl} \)-diglycolamide (DEDDdDGA), \( N,N'-\text{dipropyl-}N,N'-\text{didodecyl} \)-diglycolamide (DPDDdDGA) and \( N,N'-\text{dibutyl-}N,N'-\text{didodecyl} \)-diglycolamide (DBDDdDGA) in sulfonated kerosene [24]. The ability of different extractants to extract hydrochloric acid was also different. The ability of the four extractants was in the following order: DPDDDGA > T2EHDGA > DIPDODGA > T2EHDGA. The change of alkyl chain structure on N atom has a significant effect on the extraction ability.

Figure 3. Effect of DGA extractant on hydrochloric acid concentration in organic phase under different acidity of water phase.

Arijit Sengupta et al. [12] found that extraction efficiency with DGA extractants could be reduced with the increase of the length of alkyl chain on N atom, and the branching of alkyl chain further reduced the extraction efficiency. Complexation between metal and extractant ligands is most likely to occur...
at the interface between water phase and organic phase. With the increase in alkyl chain length, its lipophilicity obviously increases, which may be one of the reasons for the poor extraction ability. In addition, bigger substituents on the N atom affect the steric hindrance around the linkage site, increasing the resistance of metal ions to the coordination of access, which is another factor leading to the decrease of extraction ability. The three-dimensional structure and the charge distribution of O atoms were shown in Figure 4. The carbon chain around the O atoms in T2EHDGA is significantly denser, followed by the density of TODGA.

The difference of the charge distribution of the O atoms is not very significant. Therefore, we think that the long straight chain and the branching of the long chain have a major effect on coordination ability. The steric hindrance of T2EHDGA is significantly higher than that of the other three extractants, which is the reason why the extraction ability of T2EHDGA is lower than that of other extractants. TODGA has lower extraction performance due to a longer alkyl chain than that of DIPDODGA and DPDODGA, which increases its lipophilicity and spatial steric resistance.

![Figure 4. Three-dimensional structure and charge distribution of DGA extractant.](image)

In order to further understand the coordination relationship between the extractant and the rare earth ions, the effect of the concentration of rare earth metals as well as acidity and the concentration of the extractant was discussed. (Yb$^{3+}$ was taken as an example due to the similar chemical properties of heavy rare earth ions). The extraction equation of rare earth ions extracted by DGA extractant in the hydrochloric acid system is shown as follows [24]:

\[ n\text{Ln}^{3+} + m\text{DGA} + y\text{Cl}^- \rightarrow \text{Ln}_n\text{DGA}_m\text{Cl}_y \] (2)
\[ K_{n\alpha} = \frac{[{\text{Ln}}_{n}\text{DGA}_{\alpha}\text{Cl}_{\gamma}]}{[{\text{Ln}}^{3+}]^n[{\text{DGA}}^\alpha][{\text{Cl}}^-]^\gamma} \] (3)

\[ K_{n\alpha} = \frac{D}{[{\text{Ln}}^{3+}]^n[{\text{DGA}}^\alpha][{\text{Cl}}^-]^\gamma} \] (4)

\[
\lg D = \lg K_{n\alpha} + (n-1)\lg[Ln^{3+}] + m \lg[DGA] + y \lg[Cl^-]
\] (5)

The Plot of \( \lg D \) against \( \lg[Ln^{3+}] \) was shown in Figure 5. It can be seen that the stoichiometric number \( n=1 \) of TODGA (slope=-0.057, \( C_{\text{HCl}}=0.8 \) mol/L, \( C_{\text{ex}}=0.1 \) mol/L), DPDODGA (slope=-0.089, \( C_{\text{HCl}}=0.4 \) mol/L, \( C_{\text{ex}}=0.1 \) mol/L) and DIPDODGA (slope=-0.068, \( C_{\text{HCl}}=0.1 \) mol/L, \( C_{\text{ex}}=0.1 \) mol/L). However, the stoichiometric number \( n=2 \) was obtained for T2EHDGA (slope=0.92, \( C_{\text{HCl}}=4.0 \) mol/L, \( C_{\text{ex}}=0.1 \) mol/L).

The extraction compounds formed with rare earth ions are different when coordination occurs with different DGA extractants. The plots of \( \lg D \) with \( \lg C_{\text{ex}} \) show that the stoichiometric number is 3 for TODGA (slope=2.89, \( C_{\text{HCl}}=0.8 \) mol/L, \( C_{\text{Yb}}=4.00 \times 10^{-3} \) mol/L), T2EHDGA (slope=2.82, \( C_{\text{HCl}}=4.0 \) mol/L, \( C_{\text{Yb}}=4.00 \times 10^{-3} \) mol/L), DPDODGA (slope=2.76, \( C_{\text{HCl}}=0.4 \) mol/L, \( C_{\text{Yb}}=4.00 \times 10^{-3} \) mol/L) and DIPDODGA (slope=3.03, \( C_{\text{HCl}}=0.1 \) mol/L, \( C_{\text{Yb}}=4.00 \times 10^{-3} \) mol/L) (see Figure 6). It can be concluded that the extractants of TODGA, DPDODGA, and DIPDODGA were coordinated with rare earth ions to form mononuclear extracted species, \( \text{Yb}(\text{DGA})_3\text{Cl}_3 \) [13]. With T2EHDGA as extractant, binuclear extracted species maybe formed \( \text{[Yb(DGA)]}_3(\text{YbCl}_6) \) [25-27] just like the structure reported by Kannan et al. [27]. The structure of T2EHDGA complex is different from that formed with other three extractants. Because of the large steric hindrance of T2EHDGA, the stable constant of the extracted species is not high, which results in lower extraction performance.
To further understand the structure of extracted species, we compared the IR spectra of organic phases before and after the extraction of rare earth metal ions. Figure 7(a-d) shows the IR spectra of organic phases before and after extraction of rare earth metal ions with TODGA, T2EHDGA, DIPDODA and DPDODGA, respectively. The stretching vibration bands of C=O of the four extractants also moved slightly. After extracting rare earth and HCl with extractant, the position of C=O stretching vibration band shifted, indicating simultaneous extraction of HCl and rare earth ions, which is consistent with previous reports [24]. The stretching vibration peak displacement of C=O before and after extraction of HCl and rare earth ions is shown in Table 1. The carbonyl absorption peaks of the extractant all shifted significantly, indicating that carbonyl groups coordinate directly with rare earth metal ions [28].
4. Conclusion

In this work, four structure related extractants, TODGA, T2EHHDGA, DPDODGA and DIPDODGA, were synthesized. The extraction ability of rare earth metals in the hydrochloric acid system was as follows: DIPDODGA > DPDODGA > TODGA > T2EHHDGA. The extraction ability of hydrochloric acid was as follows: DPDODGA > TODGA > DIPDODGA > T2EHHDGA. Small alkyl chain is beneficial to improve the extraction ability. The steric hindrance effect of ethyl branched chain is obvious, and the extraction ability of T2EHHDGA is low. The influence of methyl branched chain is not obvious. The extracted species with TODGA, DPDODGA and DIPDODGA were mononuclear, Ln(DGA)$_3$Cl$_3$, and that with T2EHHDGA was binuclear, [Ln(DGA)$_3$] (LnCl$_6$). DIPDODGA not only has high loading capacity, but also has a high extraction ability of heavy rare earth at a concentration of hydrochloric acid less than 1 mol/L, which has potential applications in the extraction of ionized rare earth minerals in southern China.

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