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Effect of DGA substituent structure on rare earth extraction in nitric acid media

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Abstract. N substituent group structure has great influence on the extraction and separation ability of amide extractant. In this paper, four different extractants with different structures, namely TODGA (N,N,N',N'-tetraoctyl-3-oxa-diglycolamide), T2EHDGA (N,N,N',N'-tetraisoctyl-3-oxa-diglycolamide), DPDODGA (N,N'-dipropyl-N,N'-dioctyl-3-oxa-diglycolamide) and DIPDODGA (N,N'-diisopropyl-N,N'-dioctyl-3-oxa-diglycolamide) were investigated. The extraction ability of rare earth elements in nitric acid system was investigated to understand the relationship between chemical structure of the extractant and the extraction and separation properties of rare earth ions. The effects of nitric acid acidity, rare earth metal ion concentration and extractant concentration on the extraction were also investigated.

1. Introduction

Rare earth metals play an important role in new functional materials due to their unique electronic configuration and radius changes of atoms and ions, and are widely used in various industries[1]. Considering the economic, environmental and resource protection aspects, multi-channel recovery and separation of rare earth metals are of great significance[2].

At present, the extraction and separation processes of rare earth are mostly by solvent extraction, and the key of solvent extraction lies in the selection of extraction agents. Organic phosphoric extractant has better extraction and separation performance for rare earth. At present, P507 is widely used in industry to extract heavy rare earth, and there are some problems such as slow extraction kinetics, high acidity of reverse extraction and incomplete reverse extraction.

Amide extractant is a type of neutral extractant, which needs no saponification and is easy to reverse extraction. Jin Hong Yang et al.[3] studied the extraction of Sm and Nd with TBDGA (N,N',N',N'-tetrabutyl-3-oxa-diglycolamide) in hydrochloric acid system. Gergoric M et al.[4] studied the selective extraction of rare earths from other elements by using TODGA (N,N,N',N'-tetraoctyl-3-oxa-diglycolamide) as the extractant and using nitric acid to dissolve NdFeB magnetic waste to achieve the best recovery. Mowafy E A et al.[5] studied the extraction of Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), Er(III) in HNO₃ system with DHD2DGA (N,N-dihexyl-N',N' -didecyldiglycolamide). The results showed that Ln(III) could be effectively separated from Fe(III), Ni(II), Co(II), and Cs(I).

Compared with the organic phosphoric extractants, amides extraction agents are more environmentally friendly, and 3-oxa-diglycolamide extractants (DGAs) are an ideal choice for separation of adjacent lanthanide compounds. As for DGAs, most studies focus on the effect of N alkyl chain on the extraction of rare earth metal or the separation of rare earth from other metal ions[6]. The influence of different alkyl substituent structure on extraction capacity is an important component



to screen this kind of extractant. We designed and synthesized four extraction agents, and their structures are given in figure 1. With heavy rare earth Ho, Er, Tm, Yb, Lu and light rare earth Nd as research targets, the effects of asymmetric alkyl substituents and branch chain positions on extraction performance from nitric acid solution were investigated.

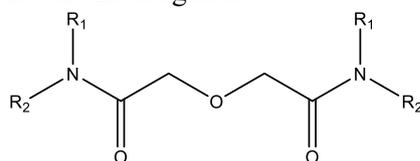


Figure 1. Extractant structure diagram (TODGA: R₁, R₂= n-octyl; T2EHDGA: R₁, R₂=isooctyl; DIPDODGA: R₁= n-octyl, R₂= isopropyl; DPDODGA: R₁= n-octyl, R₂= n-propyl).

2. Experimental Section

2.1. Materials

TODGA, T2EHDGA, DIPDODGA and DPDODGA were synthesized by referring to the three-step method we previously reported[7], and characterized by ¹H NMR, HPLC, IR with a purity of at least 93%. Other chemical reagents are AR grade and no further purification is required. The solution was prepared with n-octane: n-octanol =9:1 (V/V) dilution extract. Rare earth solution was developed by dissolving rare earth metal oxide (purity >99.9%) with high concentration hydrochloric acid. Different concentrations of nitric acid were established by diluting concentrated nitric acid with distilled water.

2.2. Experimental process

Taking such as volume of organic phase and water phase in the constant temperature water bath for liquid-liquid extraction, temperature of 25°C, the time for half an hour. Then the two phases were centrifuged and the concentration of rare earth ions in the aqueous phase was determined by Arsenazo III visible spectrophotometry and ICP-MS.

3. Results and Discussion

In this paper, nitric acid system and n-octane: n-octanol =9:1 were used as diluent to study the effect of substituent structure on rare earth extraction and separation.

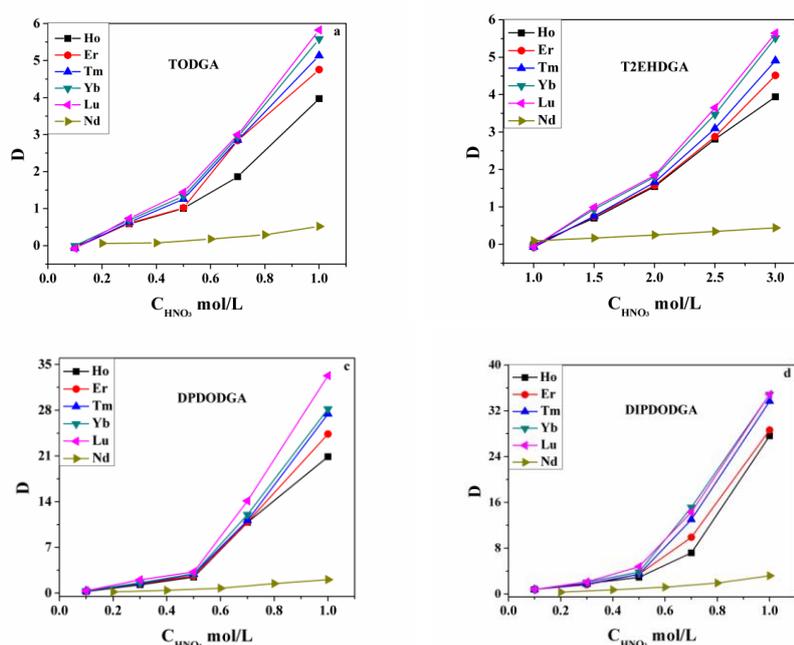


Figure 2. Effect of acidity on the distribution ratio of rare earth extracted by extractants.

Figure 2 shows the effects of extractants ($C_{ex}=0.02$ mol/L) and nitric acid concentration on the distribution ratio of single rare earth ions. Within the range of selected acidity, the corresponding distribution ratio increases with the increase of acidity, which is consistent with previous reports[4]. The extraction ability of the four extractants were in the following order: DIPDODGA > DPDODGA > TODGA > T2EHDGA. This shows that the change of the alkyl chain on the N atom has an important effect on the extraction capacity of rare earth. The branched alkyl chain of N increases the steric hindrance during coordination and decreases the extraction capacity, which is the reason why the extraction capacity of T2EHDGA is significantly lower than that of the other three extractants. Methyl groups in the 1-site DIPDODGA are supposed to have greater steric hindrance, meaning a lower extraction capability. However, experimental data demonstrate that it has a very good extraction capability, similar to that of DPDODGA with the same number of carbon atoms. Extraction capacity of TODGA with long alkyl structure was slightly lower than that of DPDODGA with a short propyl group. Regardless of the fact that substituents had a certain effect on the extraction performance of rare earth, they had little effect on the separation performance, and the separation coefficient (β) between heavy rare earth ions was low. When the acidity is 1 mol/L, the β values between Ho and Nd is as follows: $\beta_{DIPDODGA}=8.93$, $\beta_{DPDODGA}=10.07$, $\beta_{TODGA}=7.87$; When the acidity is 3 mol/L, the β of Ho and Nd is $\beta_{T2EHDGA}=7.57$, which is not much different from that of P507 extraction and separation of rare earth[8], and the separation of light and heavy rare earths can be achieved.

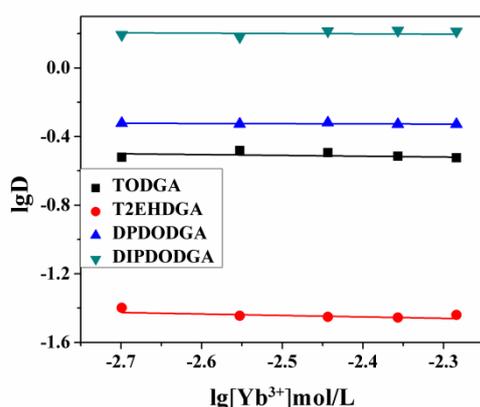


Figure 3. Effect of Yb^{3+} concentration on distribution Ratio.

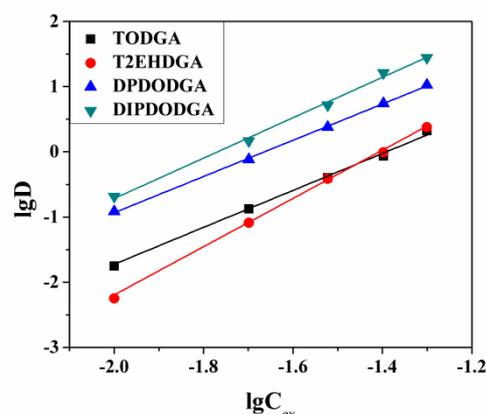
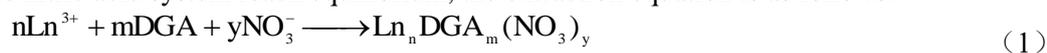


Figure 4. Effect of extractant concentration on Distribution ratio.

In order to further understand the coordination relationship between the extractant and rare earth ions after extraction, acidity and concentration of the extractant were taken as the premise to discuss the influence of the concentration and distribution ratio of rare earth metal ions (Yb^{3+} was taken as an example due to the similar chemical properties of rare earth ions). When the rare earth ions extracted by DGAs in the nitric acid system reach equilibrium, the extraction equation is as follows:



$$K_{ex} = \frac{[Ln_n DGA_m (NO_3)_y]}{[Ln^{3+}]^n [DGA]^m [NO_3^-]^y} \quad (2)$$

$$K_{ex} = \frac{D}{[Ln^{3+}]^{n-1} [DGA]^m [NO_3^-]^y} \quad (3)$$

$$LgD = LgK_{ex} + (n-1)lg[Ln^{3+}] + mLg[DGA] + yLg[NO_3^-] \quad (4)$$

The Plot of lgD against $lg[Ln^{3+}]$ was shown in figure 3. The stoichiometric number $n=1$ of TODGA (Slope=-0.18, $C_{HNO_3}=0.2$ mol/L), T2EHDGA (Slope=-0.048, $C_{HNO_3}=1.5$ mol/L), DPDODGA (Slope=-0.086, $C_{HNO_3}=0.1$ mol/L) and DIPDODGA (Slope=-0.011, $C_{HNO_3}=0.1$ mol/L). The results

show that four kinds of extractants may form mononuclear extractions in coordination with rare earth ions. The plots of $\lg D$ with $\lg C_{\text{ex}}$ (figure 4) show that the stoichiometric number m is 3 for TODGA (Slope=2.83, C_{HNO_3} =0.2 mol/L), DPDODGA (Slope=2.78, C_{HNO_3} =0.1 mol/L), DIPDODGA (Slope=3.11, C_{HNO_3} =0.1 mol/L) and the stoichiometric number $m=4$ in the corresponding extracts of T2EHDGA (Slope=3.71, C_{HNO_3} =1.5 mol/L). In addition to T2EHDGA, the extractant molecules formed by the other three extractants all contain three extractant molecules. Three oxygen coordination atoms were given for each extractant molecule, and the coordination number of rare earth ions in the center was 9, forming a three-strand helix structure with nine coordination, D3 symmetry[9]. In order to preserve charge balance, three nitrate ions are located in the second coordination layer[10]. The extraction compound formed by T2EHDGA contains four extractant molecules, which may form singular rare earth raffinate with 12 coordination[11].

It is worth pointing out that the π orbital of carbonyl and the p orbital of neighbouring N atom form a delocalized π bond through p - π conjugate in crystal structure of amide extractant. The carbonyl group and the adjacent carbon atoms of the N atom are basically in the same plane[9-10].

When carbonyl coordination happens, C on the carbonyl side has the greatest effects on the steric hindrance of substituents. It shows up the problems of weak extraction ability of T2EHDGA with 2-bit ethyl branched chain substituents. Both TODGA and DPDODGA are straight-chain alkyl groups with few of difference in steric hindrance. Compared to DPDODGA, DIPDODGA showed no significant steric hindrance effect, because the straight chain of the extractant was located in the inner coordination layer, but the methyl group on its branched chain was located in the C side away from the coordination site, so that its branching had no effect on the steric hindrance of the coordination site. The other cause of weak extraction ability of T2EHDGA is the form of $\text{Yb}(\text{DGA})_4(\text{NO}_3)_3$ -a compound include four T2EHDGA molecules[11].

Table 1. Stretching vibration band of C=O before and after the extraction.

Complex	Stretching vibration band of C=O before and after the extraction		
	before extraction	after HNO_3 extraction	after extraction of Yb^{3+}
TODGA	1648 cm^{-1}	1618 cm^{-1} red-shift 30 cm^{-1}	1559 cm^{-1} red-shift 89 cm^{-1}
T2EDGA	1637 cm^{-1}	1612 cm^{-1} red-shift 25 cm^{-1}	1612 cm^{-1} 、1564 cm^{-1} red-shift 73 cm^{-1}
DPDODGA	1649 cm^{-1}	1618 cm^{-1} red-shift 31 cm^{-1}	1556 cm^{-1} red-shift 93 cm^{-1}
DIODODGA	1645 cm^{-1}	1614 cm^{-1} red-shift 31 cm^{-1}	1614 cm^{-1} 、1552 cm^{-1} red-shift 93 cm^{-1}

In order to understand the coordination of DGAs and rare earth ions, we compared the FT-IR spectra of organic phases before and after the extraction. Due to the superposition of multiple peaks, a wide peak appeared in the range of 1650-1500 cm^{-1} . Peaks separated by splitting, the stretching vibration peak displacement of C=O before and after extraction of nitric acid and rare earth ions is shown in Table 1. The stretching vibration peaks of C-O of the four extractants also moved slightly. Two new peaks were generated after extraction of rare earth ions by T2EHDGA and DIPDODGA, indicating simultaneous extraction of HNO_3 and rare earth ions were consistent with previous experimental reports[12]. From the FT-IR spectra, it can be seen more clearly to observe the carbonyl peak moves relatively small between before and after T2EHDGA extraction, TODGA is a little bit stronger than T2EHDGA. It is consistent with the previous extraction capacity research results.

4. Conclusion

In this paper, four extractants, TODGA, T2EHDGA, DPDODGA and DIPDODGA, were synthesized to investigate the effect of the substituent structure on the extraction and separation of rare earth. The extraction ability of the rare earth metal in the nitric acid system is this: DIPDODGA > DPDODGA > TODGA > T2EHDGA. With the increase and branching of the alkyl chain on N, the extraction ability decreases. The abnormality of DIPDODGA is due to the fact that when participating in the coordination, the methyl group on the branch is located away from the side of the coordination point,

making it branched. Although the substituents have definite influence on the performance of the rare earth extraction, they have little effect on the separation performance. T2EHDGA and Yb form a mononuclear tetradentate extract, $\text{Yb}(\text{DGA})_4(\text{NO}_3)_3$, while the other three extractants and Yb form a mononuclear tridentate extract, $\text{Yb}(\text{DGA})_3(\text{NO}_3)_3$.

Acknowledgments

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