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# Extraction study of rare earth elements with *N*,*N*′-dibutyl–*N*,*N*′-di(1-methylheptyl)-diglycolamide from hydrochloric acid

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**Abstracts** A novel, unsymmetrical diglycolamide, *N*,*N*′-dibutyl–*N*,*N*′-di(1-methylheptyl)-diglycolamide (DBD1MHDGA), was synthesized. The extraction of rare earth elements (REEs) from a hydrochloric acid medium with DBD1MHDGA was investigated. The results of the extraction experiments indicated that the distribution ratios of RE(III) ions increase with an increase in HCl concentration, atomic number, and extractant concentration. The calculated thermodynamic data show that the extraction process is an exothermic reaction. The organic phase loaded rare earth ions were characterized by infrared spectroscopy. The composition of the extracted complex was determined.

**Keywords** Extraction · Rare earth · Hydrochloric acid · DBD1MHDGA

## 1 Introduction

Rare earth elements (REEs) have an irreplaceable position in industrial application due to their special and unique chemical properties [1–3] and are widely used in many sectors, including metallurgy, nuclear technology, catalysts [4, 5], and military hardware [6]. As a consequence, much attention has been paid to researching the separation of REEs. Solvent extraction has been considered to be the main technology in the separation of rare earth elements because of the advantages of the separation effects, continuous operation, and large production capacity [7]. Studies on solvent extraction of REEs have been conducted with various extractants. Organophosphorus extrantants are the industrial extraction agents used nowadays in the extraction and separation of REES, such as TBP, P204, and Cyanex272 [8–11]. However, their separation factors for the neighboring REEs is not good enough, resulting in nearly a thousand extraction processing stages to obtain a single rare earth element with a high purity.

Recently, many new structural amide extractants have been synthesized and studied. They show excellent extractability for lanthanides and actinides from nitric acid media and have good application prospects in nuclear fuel reprocessing [12, 13]. Among the amide extractants, diglycolamides are regarded as promising extractants due to their three coordination groups, which can effectively capture metal ions [14–19]. Chavan et al. [20] explored the assembled diglycolamide for f-element ions at a high acidity, and the result of the variation of $D_{\mathrm{Am}}$ as a function of the $HNO_3$ concentration shows that an acid medium plays an important role in the affinity of different diglycolamides toward f-element ions. The extraction behavior of lanthanides from a nitric acid medium was investigated using ten structurally related diglycolamides, and the distribution ratio of trivalent lanthanide ions studied as a function of $HNO_3$ concentration, diglycolamide concentration, and temperature increases with an increase in $HNO_3$ and diglycolamide concentrations and decreases with increasing temperature. Furthermore, the extraction of the studied Ln(III) was found to decrease slightly with an increase in alkyl chain length [21].

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Compared to the $HNO_3$ medium, the number of extraction studies of rare earth elements with an HCl medium is not enough yet. To explore the extraction and separation performance of this kind of extractant in the hydrometallurgy of rare earth elements in a hydrochloric acid medium is of practical significance [22–26]. Dutta et al. researched the separation of $^{90}$Y from $^{90}$Sr by solvent extraction using *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA) as the extractant from both HCl and $HNO_3$ acid mediums. The extraction efficiency in the $HNO_3$ medium increased with acid concentration, up to 3 M, and decreased thereafter. However, the extraction profiles in the HCl medium for both Y(III) and Sr(II) showed a continuous increase with increasing HCl concentration, and the separation factor values were also found to be much higher in the HCl medium compared to those obtained from an $HNO_3$ medium [27]. The extraction of rare earth elements with *N*,*N*,*N*′,*N*′-tetrabutyl-diglycolamide (TBDGA) and *N*,*N*′-dimethyl-*N*,*N*′-diphenyl-diglycolamide (DMDPhDGA) from the hydrochloric acid medium was studied in our laboratory, and the results indicated that the rare earth elements can be effectively extracted with diglycolamide, but benzene rings as substituent groups were unfavorable in the extraction of rare earth elements [28, 29]. In the recent years, it has been proved that extraction behavior was greatly influenced by the nature of the alkyl groups of amides [30]. The main aim of our project was to investigate new structural extractants and to clarify the relationship between the extracting agent structure and the extractability of rare earth elements.

In the present paper, the extraction of rare earth elements with *N*,*N*′-dibutyl–*N*,*N*′-di(1-methylheptyl)-diglycolamide (DBD1MHDGA) was investigated in a hydrochloric acid medium. The extraction mechanism for rare earth elements was discussed. The thermodynamic parameters and activity coefficients in the extracting process were also presented.

## 2 Experimental

### 2.1 Synthesis and characterization of DBD1MHDGA

*N*,*N*′-dibutyl–*N*,*N*′-di(1-methylheptyl)-diglycolamide (DBD1MHDGA) was synthesized by a three-step process below (Fig. 1).

Firstly, $PBr_3$ (1 equiv) was added dropwise into 2-octanol (1 equiv) at 0 °C. Then, the mixture was heated up to 50 °C and stirred for 2 h. 2-bromo octane was purified by distillation (124 ∼ 127 °C/0.09 MPa), and the yield was 55 %. $^1$HNMR (400 MHz, $CDCl_3$): $\delta$ 4.109–4.159(*m*, 1H, –CH–Br), 1.697–1.868(*m*, 5H, $–CH_2–CH–$, $–CH–CH_3$), 1.349–1.511(*m*, 8H, $–CH_2–$), 0.854–0.945(*m*, 3H, $–CH_3$).

Secondly, 2-bromo octane (1 equiv), n-butylamine (10 equiv) was stirred at 110 °C for 48 h in 200 mL of autoclave. The unreacted n-butylamine was removed by distillation. The residue was washed with 0.05 M NaOH solution and extracted with ethyl acetate. The organic phase was washed with 0.1 M HCl solution, water, and brine and then dried over sodium sulfate. After removing the solvent, the product was obtained as light yellow oil. The yield was 80 %. $^1$HNMR (400 MHz, $CDCl_3$): $\delta$ 2.525–2.639(*m*, 3H, $–NH–CH_2–$, –NH–CH–), 1.278–1.482(*m*, 14H, $–CH_2–CH_2–N$), 1.035–1.020(*d*, 3H, $–CH–CH_3$), 0.866–0.936(*m*, 6H, $–CH_3$).

The final step deals with the reaction of diglycolyl chloride (1 equiv) with dialkyl amine (2.5 equiv) in the presence of triethylamine (2.5 equiv) dissolved in methylene chloride. The reaction was stirred at room temperature for 6 h. Then the mixture was washed sequentially with 3 mol $dm^{-3}$ HCl solution, 1 mol $dm^{-3}$ NaOH solution, water, and brine and then dried over sodium sulfate. The crude product was achieved by removing the solvent. Purification of the crude product was carried out through column chromatography. The yield was 90 %. $^1$HNMR (400 MHz, $CDCl_3$), $\delta$ 4.148–4.410(*s*, 4H, $–C–CH_2–O–$), 2.997–3.712(*m*, 6H, –N–CH–), 1.255–2.046(*m*, 28H, $–CH_2–CH_2–$), 1.128–1.172(*t*, 6H, $–CH–CH_3$), 0.794–0.974(*m*, 12H, $–CH_3$). Infrared spectrum (IR) ($cm^{-1}$/film): $\nu_{-CH_3}$, 2958; $\nu_{-CH_2-}$, 2927; $\nu_{-CO-}$, 1651 and $\nu_{-C-O-C-}$, 1117.

### 2.2 Extraction procedures

The extraction procedures were carried out as follows: equal volumes of rare earth elements solution (weighing the theoretical calculation of rare earth oxides, dissolved in hydrochloric acid, then evaporated to dryness, the residue was dissolved in ultrapure water, transferring this solution to volumetric flask), and DBD1MHDGA in the diluents ($v_{kerosene}$:$v_{n\text{-}octanol} = 7:3$) was shaken in a constant temperature bath oscillator for 30 min, which was determined to be sufficient to obtain equilibrium. All the experiments were conducted at 25 ± 0.2 °C, except when temperature effects were investigated. The two phases were then separated by centrifugation. The concentrations of REEs in the aqueous phase were determined by the arsenazo III (0.2 % in water) visible spectrophotometric method (722 s visible–infrared spectrophotometer, $\lambda = 655$ nm) [31]. The concentrations in the organic phase were calculated by subtracting the aqueous concentrations from the total initial aqueous concentration of rare earth. Distribution ratios (*D*) were calculated as the ratios of the concentrations of REEs in the organic phase to those in the aqueous phase.

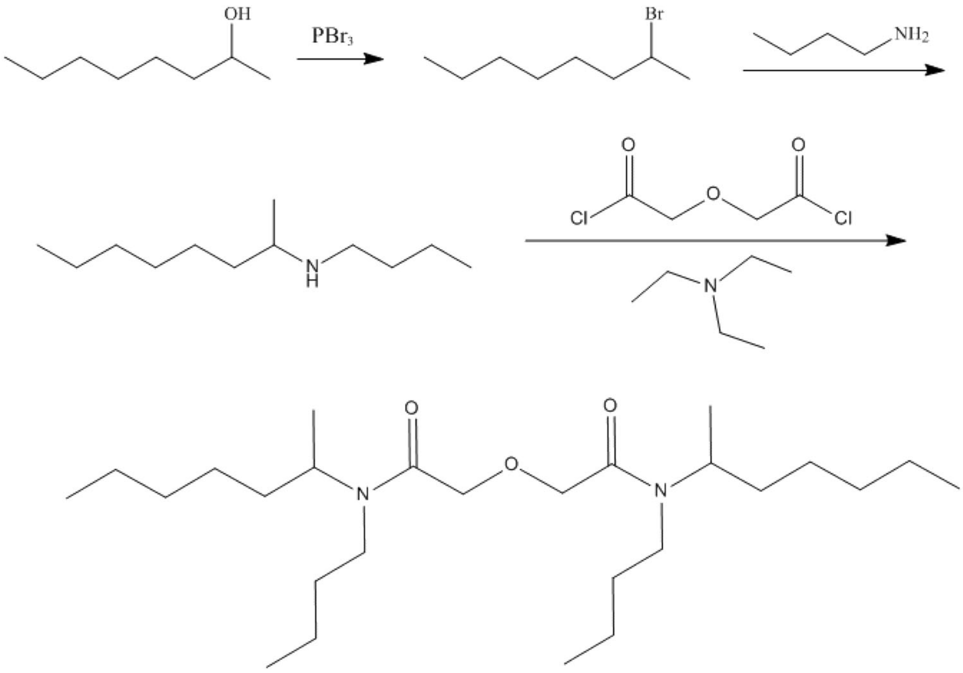

**Fig. 1** Synthesis scheme of DBD1MHDGA

## 3 Results and discussion

### 3.1 Effect of HCl concentration

The extraction of Nd(III), Sm(III), Gd(III), Dy(III), Er(III), and Yb(III) with different HCl concentrations in kerosene/n-octanol ($v_{\text{kerosene}}$:$v_{\text{n-octanol}} = 7:3$) is shown in Fig. 2. The tendency shows that the distribution ratios of rare earth ions increase with an increase in hydrochloric acid concentration from 1 to 5 mol dm$^{-3}$, which reveals that DBD1MHDGA has good affinity for the rare earth elements studied. In addition, there is a steep rise in the distribution ratio over 3 mol dm$^{-3}$ HCl for all the studied rare earth elements, except Nd(III). The results are in agreement with our previous findings [28].

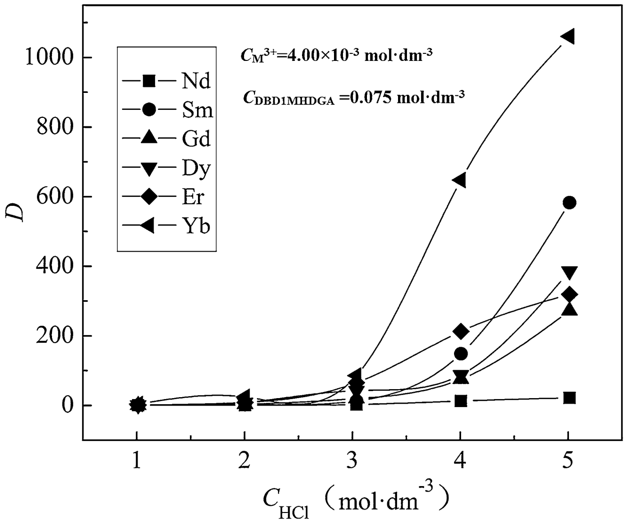

**Fig. 2** Influence of HCl concentration on the extraction of different metals

### 3.2 Effect of the concentration of DBD1MHDGA

The influence of extractant concentration on the extraction capability of different metals in kerosene/n-octanol ($v_{\text{kerosene}}$:$v_{\text{n-octanol}} = 7:3$) was conducted. The concentrations of HCl and rare earth elements remained unchanged. The logarithm distribution ratio was plotted as a function of the logarithm concentration of DBD1MHDGA in Fig. 3. From Fig. 3, the extraction distribution ratio apparently rises with an increase in atomic number, which established that this extractant has better affinity for heavier lanthanides.

Figure 3 also shows the linear relationship of REE extraction with DBD1MHDGA concentration and the values of the slope for Nd(III), Sm(III), Gd(III), Dy(III), Er(III), and Yb(III), which are 2.10, 2.70, 2.93, 3.00, 2.88, and 2.86, respectively. It revealed that Nd$^{3+}$ can combine with two molecules of DBD1MHDGA and the others with three [32]. Hence, the composition of the extracted complex of RE(III) can be expressed as $NdCl_3 \cdot 2DBD1MHDGA$, $MCl_3 \cdot 3DBD1MHDGA$ in kerosene/n-octanol ($v_{\text{kerosene}}$: $v_{\text{n-octanol}} = 7:3$). Therefore, the chemical reactions involved during the extraction of metal ions from a hydrochloric acid medium by DBD1MHDGA in different diluents can be described as:

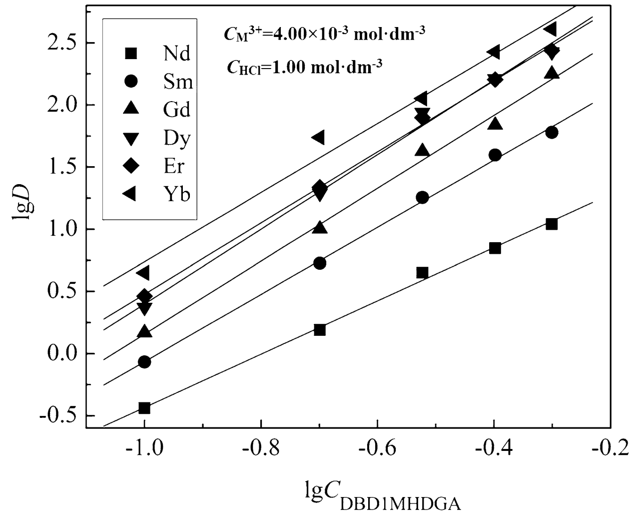

**Fig. 3** Influence of extractant concentration on the extraction of different metals

$$\begin{aligned} &Nd^{3+} + 3Cl^- + 2DBD1MHDGA_{(O)} \\ &\quad = NdCl_3 \cdot 2DBD1MHDGA_{(o)} \end{aligned} \tag{1}$$

$$\begin{aligned} &M^{3+} + 3Cl^- + 3DBD1MHDGA_{(O)} \\ &\quad = MCl_3 \cdot 3DBD1MHDGA_{(o)} \end{aligned} \tag{2}$$

M = Sm, Gd, Er, Dy, Yb.

According to the Pitzer equation [33, 34]:

$$\ln\gamma_\pm = |Z_M Z_X| f + m\frac{2v_M v_X}{v}B + \frac{3}{2}m^2\left[\frac{2(v_M v_X)^{\frac{3}{2}}}{v}\right]C^{\Theta}, \tag{3}$$

$$v = v_M + v_X. \tag{4}$$

From Eqs. (3) and (4), we can obtain the mean activity coefficient:

$$\begin{aligned} \ln\gamma_\pm = {} & |Z_{H^+} Z_{Cl^-}| f + m\frac{2v_{H^+} v_{Cl^-}}{v}B \\ & + \frac{3}{2}m^2\left[\frac{2(v_{H^+} v_{Cl^-})^{\frac{3}{2}}}{v}\right]C^{\Theta}, \end{aligned} \tag{5}$$

$$\ln\gamma_\pm = f + mB + \frac{3}{2}m^2 c^{\Theta}, \tag{6}$$

$$f = -A\left[\frac{I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} + \frac{2}{b}\ln\left(1 + bI^{\frac{1}{2}}\right)\right], \tag{7}$$

$$B = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I}\left[1 - \left(1 + \alpha I^{\frac{1}{2}} - \frac{1}{2}\alpha I^2\right)\exp\left(-\alpha I^{\frac{1}{2}}\right)\right], \tag{8}$$

$$I = \frac{1}{2}\sum m_i z_i. \tag{9}$$

When $C_{HCl} = 1.0$ mol kg$^{-1}$, the value of $I$ is 1.0 mol kg$^{-1}$. (Here, $A$, $B$ are the Debye–Hückel coefficients, $m$ is the molar concentration, $v$ is the valence state, $I$ is the ionic strength, and $Z$ is equal to the charge of the ion.)

Then Eq. (7) can be represented as follows:

$$f = -A\left[\frac{1}{1 + b} + \frac{2}{b}\ln(1 + b)\right]. \tag{10}$$

The equation below can be obtained with the same method:

$$B = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2}\left[1 - \left(1 + \alpha - \frac{1}{2}\alpha\right)\exp(-\alpha)\right]. \tag{11}$$

When $C_{HCl} < 6$ mol kg$^{-1}$, $b$ is known as 1.2, and $A = 0.391$, $\alpha = 2.0$, $\beta^{(0)}(HCl) = 0.1775$, $\beta^{(1)}(HCl) = 0.2945$, and $C^{\Theta} = 0.00080$.

Taking these constants into Eqs. (10), (11), and (6), the following values are obtained: $B = 0.4820$, $f = -0.6915$, and $\gamma_\pm = 0.812$. Then, we deduced the related activity coefficients as $\gamma_{Cl^-} = 0.9001$ and $\gamma_{M^{3+}} = 0.9659$. For chemical reactions (1) and (2), the conditional constants of extraction equilibrium can be described as:

$$\begin{aligned} K &= \frac{[NdCl_3 \cdot 2DBD1MHDGA]_{(o)}}{[Nd^{3+}][Cl^-]^3[DBD1MHDGA]^2_{(o)}} \\ &= \frac{D}{[Cl^-]^3[DBD1MHDGA]^2_{(o)}} \end{aligned} \tag{12}$$

$$\begin{aligned} K &= \frac{[MCl_3 \cdot 3DBD1MHDGA]_{(o)}}{[M^{3+}][Cl^-]^3[DBD1MHDGA]^3_{(o)}} \\ &= \frac{D}{[Cl^-]^3[DBD1MHDGA]^3_{(o)}} \end{aligned} \tag{13}$$

M = Sm, Gd, Er, Dy, Yb.

The equilibrium constants are:

$$K_{ex} = \frac{D}{[DBD1MHDGA]^2_{(o)}[Cl^-]^3\gamma_{Nd^{3+}}\gamma^3_{Cl^-}}, \tag{14}$$

$$K_{ex} = \frac{D}{[DBD1MHDGA]^3_{(o)}[Cl^-]^3\gamma_{M^{3+}}\gamma^3_{Cl^-}}. \tag{15}$$

Let

$$Y_M = \frac{D}{[Cl^-]^3\gamma_{M^{3+}}\gamma^3_{Cl^-}}. \tag{16}$$

Taking Eq. (15) into account for Eqs. (13) and (14), the following equations are obtained:

$$\lg D = \lg K_{ex} + 2\lg[DBD1MHDGA]_{(o)} - \lg Y_{Nd} \tag{17}$$

$$\lg D = \lg K_{ex} + 3\lg[DBD1MHDGA]_{(o)} - \lg Y_{M} \tag{18}$$

The values of log$K$ and log$K_{ex}$ can be calculated and given in Table 1.

## 3.3 Effect of temperature

The effect of temperature on extraction was determined by varying the temperature from 288 to 338 K. Figure 4 clarifies the influence of temperature on the values of D in kerosene/n-octanol ($v_{\text{kerosene}}$: $v_{\text{n-octanol}} = 7{:}3$).

It is evident that the extraction of RE(III) decreased with an increase in temperature. The negative values of the enthalpy change for the extraction calculated from the slopes of the lines indicates the exothermic nature of the extraction process. The thermodynamic parameters for the reaction can be calculated using these equations below:

$$\left[\frac{\partial \lg D}{\partial\left(\frac{1}{T}\right)}\right]_P = \frac{-\Delta_r H_m^0}{2.303R}, \tag{19}$$

$$\Delta_r G_m^0 = -RT \ln K^0, \tag{20}$$

$$\Delta r S_m^0 = \left(\Delta_r H_m^0 - \Delta_r G_m^0\right)\!/_T. \tag{21}$$

The thermodynamic constants are given in Table 2.

## 3.4 Spectroscopic studies of the extracted species

An analysis of the IR spectra of the loaded organic phase was also performed (Fig. 5). The spectra of DBD1MHDGA were studied before and after rare earth elements extraction from HCl. Compared to the free extractant, the carbonyl group (CO) stretching vibration of the extracted species was shifted from about 1651 $\text{cm}^{-1}$ to about 1605 $\text{cm}^{-1}$. These data indicate that metal ions are mainly coordinated to the oxygen of the carbonyl group of DBD1MHDGA.

## 3.5 Effect of diluents

The diluents play an important role in the solvent extraction process, which should have low volatility, low surface tension, and should be stable [35]. In this context, by adjusting the volume ratio of kerosene/n-octanol, the extraction of Dy(III) with DBD1MHDGA was investigated.

**Table 1** Values of log*K* and log$K_{\text{ex}}$ of the extraction of rare earth elements (III)

| $M^{3+}$ | log *K* | log $K_{\text{ex}}$ |
|---|---|---|
| $Nd^{3+}$ | 1.71 ± 0.05 | 1.86 ± 0.05 |
| $Sm^{3+}$ | 2.64 ± 0.04 | 2.79 ± 0.04 |
| $Gd^{3+}$ | 3.09 ± 0.08 | 3.24 ± 0.08 |
| $Dy^{3+}$ | 3.40 ± 0.09 | 3.55 ± 0.09 |
| $Er^{3+}$ | 3.34 ± 0.05 | 3.49 ± 0.05 |
| $Yb^{3+}$ | 3.52 ± 0.13 | 3.67 ± 0.13 |

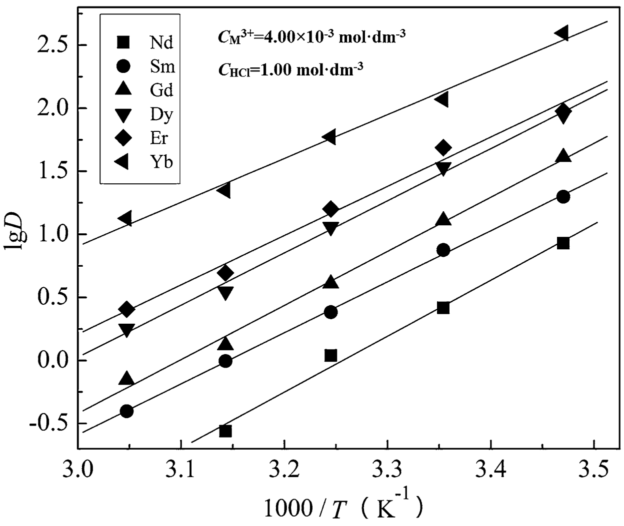

**Fig. 4** Effect of temperature on the extraction of different metals

**Table 2** Thermodynamic data of the extraction of different RE(III) with DBD1MHDGA (298 K)

| $M^{3+}$ | $\Delta_r H_m^0$ (kJ mol$^{-1}$) | $\Delta_r G_m^0$ (kJ mol$^{-1}$) | $\Delta_r S_m^0$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| $Nd^{3+}$ | −39.08 | −7.93 | −104.47 |
| $Sm^{3+}$ | −57.18 | −11.25 | −154.08 |
| $Gd^{3+}$ | −68.25 | −14.84 | −179.12 |
| $Dy^{3+}$ | −75.87 | −17.81 | −194.74 |
| $Er^{3+}$ | −67.20 | −16.73 | −169.28 |
| $Yb^{3+}$ | −75.17 | −17.70 | −192.76 |

### *3.5.1 Influence of acid concentration on the extraction of Dy(III) from the different ratios of kerosene/n-octanol*

The extraction efficiency for Dy(III) by DBD1MHDGA from different ratios of kerosene/n-octanol is shown in Fig. 6. The extraction capacity of DBD1MHDGA in different ratios of kerosene/n-octanol for Dy(III) increases in the order: kerosene/n-octanol ($V_{\text{kerosene}}{:}V_{\text{n-octanol}} = 7{:}3$) > kerosene/n-octanol ($V_{\text{kerosene}}{:}V_{\text{n-octanol}} = 8{:}2$) > kerosene/n-octanol ($\text{V}_{\text{kerosene}}{:}\text{V}_{\text{n-octanol}} = 9{:}1$). The distribution ratio increases with an increase in the n-octanol volume fraction. Since the solvation ability of n-octanol to the ionic compounds is better than that of kerosene, increasing the volume fraction of n-octanol is favored in the extraction process.

### *3.5.2 Influence of extractant concentration on the extraction capability of Dy(III) from different ratios of kerosene/n-octanol*

The extraction effect of Dy(III) with DBD1MHDGA from different ratios of kerosene/n-octanol was investigated.

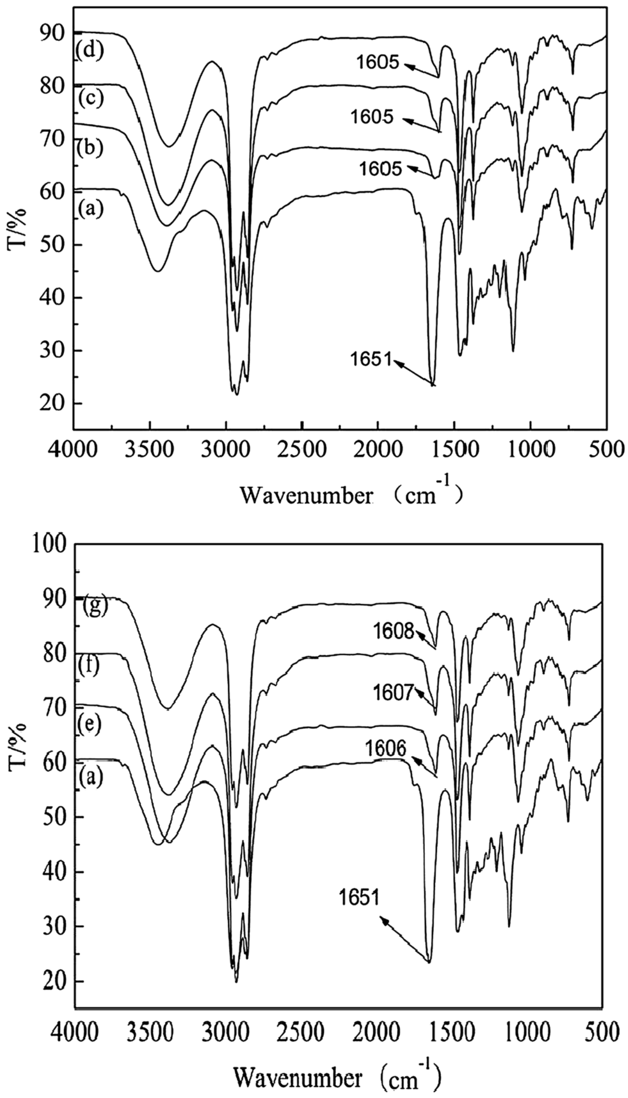

**Fig. 5** Infrared spectra of organic phase loaded rare earth ions. (*a*): DBD1MHDGA, (*b*): DBD1MHDGA-Nd, (*c*): DBD1MHDGA-Sm, (*d*): DBD1MHDGA-Gd, (*e*): DBD1MHDGA-Dy, (*f*): DBD1MHDGA-Er, (*g*): DBD1MHDGA-Yb

Figure 7 shows that the distribution ratio of rare earth elements increased as the DBD1MHDGA concentration increased. The line slopes are near 3, which shows that the extraction complex is $DyCl_3 \cdot 3DBD1MHDGA$.

The extraction constant of this equilibrium, $K$, and the constant of conditional equilibrium, $K_{ex}$, are obtained with the same computing method. The values are given in Table 3. In addition, n-octanol promotes the extraction of REEs from the HCl media.

### *3.5.3 Influence of temperature on the extraction capability of Dy(III) from different ratios of kerosene/n-octanol*

The influence of temperature on the extraction of Dy(III) from different ratios of kerosene/n-octanol has been studied.

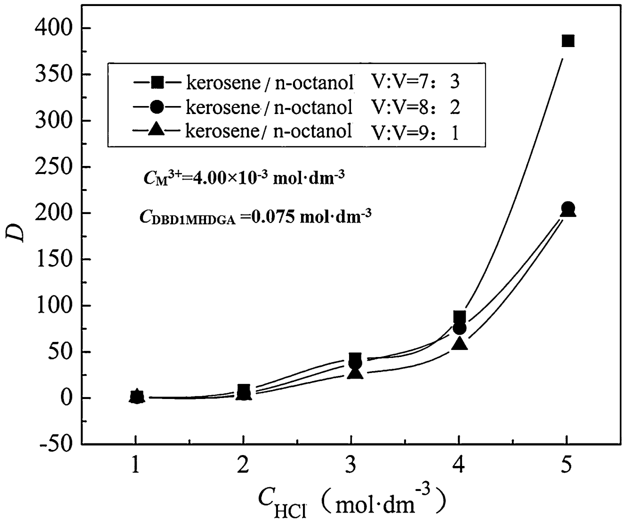

**Fig. 6** Influence of HCl concentration on the extraction capability of Dy(III) from different ratios of kerosene/n-octanol

Figure 8 shows the plots of lg$D$ versus 1000/$T$. The change in enthalpy ($\Delta H$), the change in Gibbs free energy ($\Delta G$), and the change in entropy ($\Delta S$) can thus be obtained with Eqs. (20) and (21). The values are given in Table 4.

It can be seen that $\Delta H$ is smaller than zero, indicating that the extraction of Dy(III) in the kerosene/n-octanol system is an exothermic reaction.

The back extraction of rare earth elements was carried out with water. The back extraction efficiency from the organic phase was up to 98 %, which shows that the stripping of rare earth ions studied is easy.

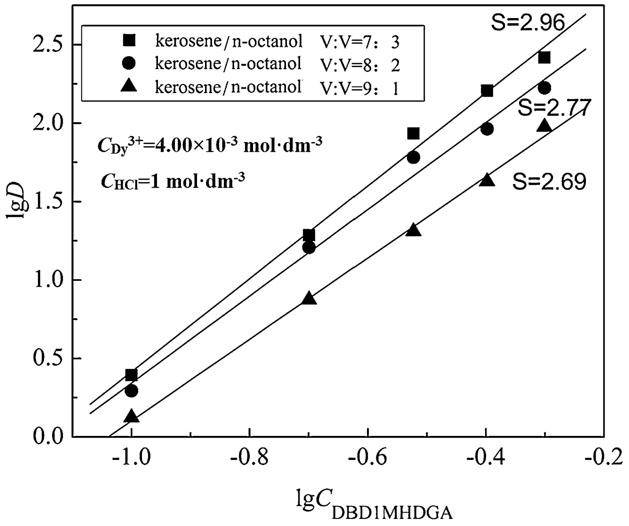

**Fig. 7** Influence of extractant concentration on the extraction capability of Dy(III) from different ratios of kerosene/n-octanol

**Table 3** Data of log*K* and log$K_{ex}$ of the extraction of Dy(III) with DBD1MHDGA

| Diluents Kerosene/n-octanol | *V*:*V* = 7:3 | *V*:*V* = 8:2 | *V*:*V* = 9:1 |
|---|---|---|---|
| log*K* | 3.40 ± 0.09 | 3.11 ± 0.10 | 2.66 ± 0.06 |
| log$K_{ex}$ | 3.55 ± 0.09 | 3.26 ± 0.10 | 2.81 ± 0.06 |

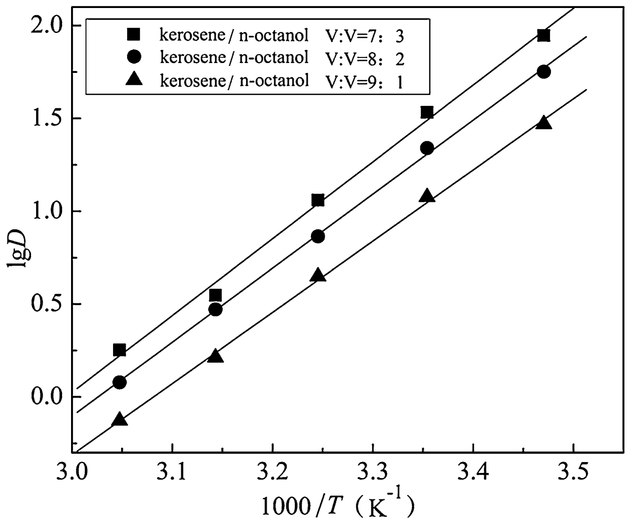

**Fig. 8** Influence of temperature on the extraction capability of Dy(III) from different ratios of kerosene/n-octanol

**Table 4** Thermodynamic data of the extraction of Dy(III) with DBD1MHDGA in different ratios of kerosene/n-octanol (298 K)

| Diluents Kerosene/n-octanol | $\Delta_r H_m^0$ (kJ mol$^{-1}$) | $\Delta_r G_m^0$ (kJ mol$^{-1}$) | $\Delta_r S_m^0$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| *V*:*V* = 7:3 | −75.87 | −17.80 | −194.73 |
| *V*:*V* = 8:2 | −76.31 | −18.61 | −193.52 |
| *V*:*V* = 9:1 | −73.43 | −16.04 | −192.48 |

## 4 Conclusion

A novel diglycolamide, DBDIMHDGA, was synthesized. In the range of hydrochloric acid concentration studied, the distribution ratio of the extraction of rare earth elements with DBD1MHDGA increased with hydrochloric acid concentration. When the concentration of HCl is over 3 mol dm$^{-3}$, the distribution ratio increased sharply. The sequence of the extraction ability of rare earth ions with DBDIMHDGA was in the order: Nd(III) < Gd(III), Er(III) < Dy(III) < Sm(III) < Yb(III), which shows that this extractant has a better affinity for heavier lanthanides.

The distribution ratio increases with the extractant concentration. The slope analysis indicated that the extraction chemical reactions proceeded as follows:

$$\mathrm{Nd^{3+} + 3Cl^- + 2DBD1MHDGA_{(o)} = NdCl_3 \cdot 2DBD1MHDGA_{(o)}}$$

$$\mathrm{M^{3+} + 3Cl^- + 3DBD1MHDGA_{(o)} = MCl_3 \cdot 3DBD1MHDGA_{(o)}}$$

M = Sm, Gd, Er, Dy, Yb.

The experiments involving the temperature effect indicated that the extraction reaction is an exothermic process. Increasing temperature had a negative effect on the extraction efficiency. IR spectra suggested that the extractant, DBD1MHDGA, coordinated with rare earth ions through the oxygen of the carbonyl group.

## References

1. M.E. Nasab, A. Sam, S.A. Milani, Determination of optimum process conditions for the separation of thorium and rare earth elements by solvent extraction. Hydrometallurgy **106**, 141–147 (2011). doi:10.1016/j.hydromet.12.014
2. D.A. Renata, A.M. Carlos, Study on separation of heavy rare earth elements by solvent extraction with organophosphorus acids and amine reagents. Miner. Eng. **61**, 82–87 (2014). doi:10.1016/j.mineng.2014.03.015
3. S. Radhika, K.B. Nagaphani, K.M. Lakshmi, Solvent extraction an separation of rare-earths from phosphoric acid solutions with TOPS 99. Hydrometallurgy **110**, 50–55 (2011). doi:10.1016/j.hydromet.2011.08004
4. B.C. McLellan, G.D. Corder, A. Golev, S.H. Ali, Sustainability of the rare earths industry. Proc. Environ. Sci. **20**, 280–287 (2014). doi:10.1016/j.proenv.2014.03.035
5. Q. Jia, S.S. Tong, Z.Y. Li et al., Solvent extraction of rare earth elements with mixtures of sec-octylphenoxy acetic acid and bis(2,4,4-trimethylpentyl) dithiophosphinic acid. Sep. Purif. Technol. **64**, 345–350 (2009). doi:10.1016/j.seppur.2008.10.024
6. C.Z. Li, C.F. Yao, S.B. Wang, Z.X. Jia, C.F. He, D. Zhao, G.S. Qin, W.P. Qin, $Tm^{3+}/Ho^{3+}$ co-doped fluorotellurite microstructure fiber for 2.1 μm lasing. Chin. J Lumin **37**, 74–80 (2016). doi:10.3788/fgxb20163701.0074
7. P.Z. Hu, L.J. Qian, H.L. Wang et al., Extraction of uranium(VI) and thorium(IV) from nitric acid solution by N,N,N′,N′–tetraoctylglutaricamide. Sep. Sci. Technol. **49**, 1521–1526 (2014). doi:10.1080/01496395.885531
8. H. Tong, Y.L. Wang, W.P. Liao et al., Synergistic extraction of Ce(IV) and Th(IV) with mixtures of Cyanex 923 and organophosphorus acids in sulfuric acid media. Sep. Purif. Technol. **118**, 487–491 (2014). doi:10.1016/j.seppur.2013.07.039
9. W.H. Duan, P.J. Cao, Y.J. Zhu, Extraction of rare earth elements from their oxides using organophosphorus reagent complexes with $HNO_3$ and $H_2O$ in supercritical $CO_2$. Rare Earths **28**, 221–226 (2010). doi:10.1016/S1002-0721(09)60084-3
10. M.M. Tian, Q. Jia, W.P. Liao, Studies on synergistic solvent extraction of rare earth elements from nitrate medium by mixtures of 8-hydroxyquinoline with Cyanex 301 or Cyanex 302. J. Rare Earths **31**, 604–608 (2013). doi:10.1016/S1002-0721(12)60328-7
11. R. Surampally, N.K. Batchu, L.K. Mannepalli et al., Studies on solvent extraction of Dy(III) and separation possibilities of rare earths using PC-88A from phosphoric acid solutions. J. Taiwan Inst. Chem. Eng. **43**, 839–844 (2012). doi:10.1016/j.jtice.2012.04.009

12. H. Huang, S.D. Ding, N. Liu et al., Extraction of trivalent americium and europium from nitric acid solution with a calixarene-based diglycolamide. Sep. Purif. Technol. **123**, 235–240 (2014). doi:10.1016/j.seppur.2013.12.039
13. J. Ravi, T. Prathibha, K.A. Venkatesan et al., Third phase formation of neodymium (III) and nitric acid in unsymmetrical N,N-di-2-ethylhexyl-N′,N′-dioctyldiglycolamide. Sep. Purif. Technol. **85**, 96–100 (2012). doi:10.1016/j.seppur.2011.09.053
14. G.X. Sun, M. Liu, Y. Cui et al., Synthesis of N,N′-dimethyl-N,N′-dioctyl-3-oxadiglycolamide and its extraction properties for lanthanides. Solvent Extr. Ion Exch. **28**, 482–494 (2010). doi:10.1080/07366299.2010.480932
15. S. Yuji, T. Shoichi, Extraction of actinides(III), (IV), (V), (VI), and lanthanides(III) by structurally tailored diamides. Solvent Extr. Ion Exch. **20**, 21–34 (2002). doi:10.1081/SEI-100108822
16. E.M. Nasab, Solvent extraction separation of uranium(VI)and thorium(IV) with neutral organophosphorus andamine ligands. Fuel **116**, 595–600 (2014). doi:10.1016/j.fuel.2013.08.043
17. D.D. Dicholkar, P. Kumar, P.K. Heer et al., Synthesis of N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) and its steam thermolysis-nitrolysis as a nuclear waste solvent minimization method. Ind. Eng. Chem. Res. **52**, 2457–2469 (2013). doi:10.1021/ie302603q
18. D. Magnusson, B. Christiansen, J.P. Glatz et al., Demonstration of a TODGA based extraction process for the partitioning of minor actinides from a PUREX raffinate. Solvent Extr. Ion Exch. **27**, 26–35 (2009). doi:10.1080/07366290802544726
19. J. Ravi, K.A. Venkatesan, M.P. Antony et al., Tuning the diglycolamides for modifier-free minor actinide partitioning. J. Environ. Chem. Eng. **1**, 690–695 (2013). doi:10.1007/s10967-012-1905-9
20. V. Chavan, V. Thekkethil, A.K. Pandey et al., Assembled diglycolamide for f-element ions sequestration at high acidity. React. Polym. **74**, 52–57 (2014). doi:10.1016/j.reactfunctpolym.2013.10.011
21. E.A. Mowafy, D. Mohamed, Extraction behavior of trivalent lanthanides from nitric acid medium by selected structurally related diglycolamides as novel extractants. Sep. Purif. Technol. **128**, 18–24 (2014). doi:10.1016/j.seppur.2014.03.005
22. S.L. Gwang, U. Masahito, M. Kouji et al., Separation of major impurities Ce, Pr, Nd, Sm, Al, Ca, Fe, and Zn from La using bis(2-ethylhexyl)phosphoric acid (D2EHPA)-impregnated resin in a hydrochloric acid medium. Sep. Purif. Technol. **71**, 186–191 (2010). doi:10.1016/j.seppur.2009.11.020
23. Y. Cui, Y.Q. Wang, M.P. Pang et al., Effect of diluents on the extraction and separation of Fe(III) and Cu(II) from hydrochloric acid solutions using N,N,N′,N′-tetrabutyl succinamide. Hydrometallurgy **152**, 1–6 (2015). doi:10.1016/j.hydromet.2014.11.012
24. H.T. Chang, M. Li, Z.G. Liu, Y.H. Hu et al., Study on separation of rare earth elements in complex system. J. Rare Earths **28**, 116–119 (2010). doi:10.1016/S1002-0721(10)60270-0
25. F. Xie, T.A. Zhang, D. David et al., A critical review on solvent extraction of rare earths from aqueous solutions. Miner. Eng. **56**, 10–28 (2014). doi:10.1016/j.mineng.2013.10.021
26. S.S. Tong, X.W. Zhao, W.H. Zhou, Solvent extraction study of rare earth elements from chloride medium by mixtures of sec-nonylphenoxy acetic acid with Cyanex301 or Cyanex302. Hydrometallurgy **100**, 15–19 (2009). doi:10.1016/j.hydromet.2009.09.006
27. S. Dutta, P.K. Mohapatra, V.K. Manchanda, Separation of 90Y from 90Sr by a solvent extraction method using N,N,N′,N′-tetraoctyl diglycolamide (TODGA) as the extractant. Appl. Radiat. Isot. **69**, 158–162 (2011). doi:10.1016/j.apradiso.2010.09.016
28. Y. Cui, J.H. Yang, G. Yang et al., Effect of diluents on extraction behavior of rare earth elements with N,N,N′,N′-tetrabutyl-3-oxy-glutaramide from hydrochloric acid. Hydrometallurgy **121–124**, 16–21 (2012). doi:10.1016/j.hydromet.2012.04.013
29. G. Yang, D. Ma, Study of 3-oxa-glutaramide extractting rare earth metals from hydrochloric acid system. Thesis, University of Jinan (2010)
30. P.N. Pathak, L.B. Kumbhare, V.K. Manchanda, Structural effects in N,N-dlalkyl amides on their extraction behavior toward uranium and thorium. Solvent Extr. Ion Exch. **19**, 105–126 (2011). doi:10.1081/SEI-100001377
31. E. Hosten, H.E. Rohwer, Complexation reactions of uranyl with arsenazo III. Anal. Chim. Acta **355**, 95–100 (1997). doi:10.1016/S0003-2670(97)81616-9
32. S.P.K. Donald, H.K. Kean, C.Y.J. Chan, The application of the pitzer equations to 1–1 electrolytes in mixed solvents. Solut. Chem. **14**, 635–651 (1985). doi:10.1007/BF00646056
33. S. Manohar, J. Ananthaswamy, G.J. Atkinson, Application of Pitzer equations for quaternary systems: sodium chloride-sodium nitrate-sodium acetate-water and potassium chloride-potassium nitrate-potassium acetate-water at 25 °C. Chem. Eng. Data. **37**, 459–463 (1992). doi:10.1021/je00008a019
34. A. Shimada, T. Yaita, H. Narita et al., Extraction studies of lanthanide(III) Ions with N, N′-dimethyl-N,N′-diphenylpyridine-2,6-dicarboxyamide (DMDPhPDA) from nitric acid solutions. Solvent Extr. Ion Exch. **22**, 147–161 (2004). doi:10.1081/SEI-120030392
35. M. Anitha, M.K. Kotekar, D.K. Singh et al., Solvent extraction studies on rare earths from chloride medium with organophosphorous extractant dinonyl phenyl phosphoric acid. Hydrometallurgy **146**, 128–132 (2014). doi:10.1016/j.hydromet.2014.03.015