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# Effect of structure on extraction behavior of praseodymium with a series of unsymmetrical diglycolamides from hydrochloric acid

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Abstract: The extraction behavior of Pr(III) has been investigated using four kinds of unsymmetrical diglycolamide (DGA) extractants having different alkyl chain lengths, namely N,N'-dimethyl-N,N'-didodecyldiglycolamide (DMDDdDGA), N,N'-diethyl-N,N'-didodecyldiglycolamide (DEDDdDGA), N,N'-dibtyl-N,N'-didodecyldiglycolamide (DPDDdDGA) and N,N'-dibutyl-N,N'-didodecyldiglycolamide (DBDDdDGA). The effect of the alkyl chain of amidic N atoms in DGAs on the extraction ability of Pr(III) is discussed. The extraction of hydrochloric acid and Pr(III) from hydrochloric acid medium by DGAs in sulfonated kerosene, toluene and octanol was studied. The effect of extractant concentration and diluents on the distribution ratio (D) of Pr(III) was investigated to understand the extraction mechanism. Pr(III) and Fe(III) can be separated very well by DMDDdDGA and DBDDdDGA diluted by toluene in hydrochloric acid solution. IR spectra of extracted species of DGA–HCl and DGA–Pr(III) were recorded to study the structure of the extracted species.

*Keywords*: praseodymium (Pr); diglycolamide (DGA); rare earth; HCl; liquid–liquid extraction; distribution ratio.

# INTRODUCTION

In recent years, the rare earth elements (REE) have become increasingly important in advanced materials and technologies, such as laser materials, silicon solar cells, magnetic materials, catalysts, *etc.*<sup>1</sup> The separation and purification of rare earths have attracted wide attention. Therefore, the development of high-efficiency extractants for REE is of significant importance. Diglycolamides (DGAs) are a series of promising extractants in the separation of actinide and lanthanide.<sup>2</sup> In comparison with di(2-ethylhexyl)phosphoric acid (P204) and 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (P507), diglycolamides have some potential advantages. For example, diglycolamides are easy to synthesize and the degradation products are environmentally friendly.



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Diglycolamides as extractants for the extraction of REE were initially reported by Stephan *et al.*<sup>3,4</sup> Sasaki<sup>5</sup> and Peng<sup>6</sup> reported the extraction of lanthanum (La) with N,N,N',N'-tetrabutyldiglycolamide (TBDGA) from nitric acid medium. N,N,N',N'-Tetraoctyldiglycolamide (TODGA) has been widely reported due to its good extraction ability for actinides and lanthanides.<sup>7–9</sup>

Liquid–liquid solvent extraction and separation of REE from hydrochloric acid medium are very important in REE hydrometallurgy and have been reported by many researchers with many of extractants, *e.g.*, *N*,*N*,*N'*,*N'*-tetra(2-ethylhexyl)diglycolamide (T2EHDGA), TBDGA and *N*,*N'*-dibutyl-*N*,*N'*-di(1-methylheptyl)diglycolamide (DBD1MHDGA).<sup>10–12</sup> TODGA and T2EHDGA were used for the separation of <sup>90</sup>Y from <sup>90</sup>Sr in hydrochloric acid solution.<sup>13,14</sup> Cui *et al.*<sup>15</sup> reported the effect of diluents on the extraction behavior of rare earth elements with TBDGA from hydrochloric acid.

The alkyl substituents of diglycolamides have significant influence on extractability. The effect of extractant structure on the extraction behavior of lanthanide and actinide from nitric acid solution were reported.<sup>16,17</sup> However, only a few studies considered extraction in hydrochloric acid medium with diglycolamides.<sup>18</sup>

The purpose of this work was to examine the effect of alkyl substituents on REE extraction in hydrochloric acid medium. Four kinds of unsymmetrical digly-colamides, DMDDdDGA, DEDDdDGA, DPDDdDGA and DBDDdDGA were synthesized and the extraction properties of these structurally related extractants for Pr(III) from hydrochloric acid medium were investigated.

Iron is the main impurity in the rare earth products of chlorinated chloride, and it is difficult to completely remove it and obtain high purity REE. Therefore, we have also tested the separation performance of the designed extractants in the removal of iron from rare earth chloride.

### EXPERIMENTAL

## Materials

DMDDdDGA, DEDDdDGA, DPDDdDGA and DBDDdDGA were synthesized by a three-step method reported in a previous work.<sup>19</sup> The structures of the four extractants are shown in Fig. 1. DMDDdDGA, DEDDdDGA, DPDDdDGA and DBDDdDGA were characterized by <sup>1</sup>H-NMR, IR (Spectrum One NTS, PerkinElmer) and HPLC. The purities of these extractants were at least 98 %. The other chemical reagents used were of AR grade and used without further purification. Solutions of four extractants were prepared by dilution of DMDDdDGA, DEDDdDGA and DBDDdDGA with toluene or sulfonated kerosene. The Pr(III) and Fe(III) solutions were prepared by dissolving  $Pr_2O_3$  and  $Fe_2O_3$  (>99.9 %) in concentrated hydrochloric acid. Different concentrations of hydrochloric acid were prepared by dilution of concentrated hydrochloric acid solutions with distilled water.

## Extraction procedure

Liquid–liquid solvent extraction was performed by shaking 2 mL of organic phase with 2 mL of aqueous phase for about 30 min (to obtain equilibrium) in a water bath at a constant

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temperature. The two phases were then centrifuged and separated, and the concentration of Pr(III) in the aqueous phase was measured using an Arsenazo III visible spectrophotometric method. The metal ion concentration of the organic phase was obtained by subtracting the aqueous phase metal ion concentration from the initial concentration. The distribution ratio (*D*) was calculated as the ratio of the metal ion concentration in the organic phase to that in the aqueous phase. The experiments were conducted at 25 °C. In the extraction investigation of HCl, equal volumes of the organic and aqueous phases were equilibrated for 30 min followed by centrifugation. The HCl concentration in the organic phase was determined by the titration with standard sodium hydroxide solution using phenolphthalein as the indicator. The extraction experiment of Fe(III) was conducted using a similar method to that of Pr(III) described above. The concentration of Fe(III) in the aqueous phase was measured by the 1,10-phenanthroline visible spectrophotometric method.



#### **RESULTS AND DISCUSSION**

## Extraction of hydrochloric acid

Studies regarding the extraction of acid by extractants could be a significant contribution to a better understanding of the extraction mechanism. The extraction of HNO<sub>3</sub> by diglycolamides and malonamides derivatives have been widely reported.<sup>20–24</sup> However, few reports on the extraction of HCl by malonamides,<sup>25,26</sup> especially the extraction of HCl by diglycolamides, have been reported. Therefore, the effect of HCl concentration on the HCl concentration in the organic phase was investigated using sulfonated kerosene and toluene as diluents, (Figs. 2 and 3, respectively). In order to avoid third-phase formation, the HCl concentration was determined up to 4.0 M for DMDDdDGA and DEDDdDGA diluted with sulfonated kerosene, up to 4.5 M for DMDDdDGA and DBDDdDGA in sulfonated kerosene, up to 4.5 M for DMDDdDGA/toluene, and up to 5.0 M for the other three extractants in toluene.

As shown in Figs. 2 and 3, the hydrochloric acid concentration in the organic phase increased with increasing  $c_{\text{HCl}(aq)}$ . At low aqueous HCl concentration, the acid was practically not extracted. However, above a critical HCl concentration, the hydrochloric acid concentration in the organic phase increased sharply. This phenomenon is consistent with the observations reported for extraction of HCl by N,N'-dimethyl-N,N'-dioctyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA) in



Fig. 2. Extraction of hydrochloric acid with diglycolamides diluted with sulfonated kerosene;  $c_{\text{Ex}} = 0.20 \text{ mol dm}^{-3}$ .

Fig 3. Extraction of hydrochloric acid with diglycolamides diluted with toluene;  $c_{\rm Ex} = 0.20 \text{ mol dm}^{-3}$ .

*n*-heptane.<sup>27</sup> The critical HCl concentration increased in the following order: DMDDdDGA < DEDDdDGA < DPDDdDGA < DBDDdDGA. The results also showed that the diluent plays an important role in the extraction of hydrochloric acid. The HCl concentration in organic phase was higher in sulfonated kerosene compared with toluene under the same conditions. Mowafy<sup>28</sup> and Gujar et al.<sup>18</sup> reported that the values of  $K_{\rm H}$  were 0.27±0.04 and 4.1±0.4 for TODGA extraction of HNO3 in benzene and n-dodecane, respectively. Both the results indicated that the acid extraction efficiency by diglycolamides was lower in the aromatic hydrocarbon compared with the aliphatic hydrocarbon. The structures of the extractants had a significant influence on acid extraction. The results showed that the extraction ability for HCl by diglycoamides increased in the following order: DMDDdDGA > DEDDdDGA > DPDDdDGA > DBDDdDGA. This phenomenon could be attributed to steric hindrance. Sharma et al.29 and Gujar et al.18 reported that the values of  $K_{\rm H}$  of T2EHDGA extraction of HNO<sub>3</sub> in *n*-dodecane were 1.72±0.20 and 1.8±0.3, which were lower than TODGA due to the branched alkyl group attached to nitrogen atom of T2EHDGA. This is consistent with the present conclusions.

In order to further understand the mechanism of extraction of HCl by the extractants, the IR spectra of free and extracted species after extraction of HCl with DMDDdDGA, DEDDdDGA, DPDDdDGA and DBDDdDGA were recorded and the spectra are shown in Fig. 4. The stretching vibration of carbonyl group of the extracted species was shifted from about 1647, 1643, 1643 and 1647 cm<sup>-1</sup> to 1632, 1632, 1630 and 1628 cm<sup>-1</sup> for DMDDdDGA, DEDDdDGA, DPDDdDGA, DEDDdDGA, DPDDdDGA and DBDDdDGA, respectively, which indicated that HCl was coordinated with the C=O group of the extractant. This is similar with the results reported previously.<sup>27</sup>



Fig. 4. IR spectra of the free extractant and extracted species in octanol. a) DMDDdDGA;
b) DMDDdDGA–HCl; c) DEDDdDGA; d) DEDDdDGA–HCl; e) DPDDdDGA;
f) DPDDdDGA–HCl<sup>-</sup>g) DBDDdDGA; h) DBDDdDGA–HCl.

## Influence of structure on the extraction of Pr(III)

The alkyl chain of the N substituent plays an important role in the extraction ability of the diglycolamides. The order of extraction ability of the diglycolamides for Pr(III) in sulfonated kerosene is DMDDdDGA > DEDDdDGA, DPDDdDGA > DBDDdDGA (Fig. 5). The decrease in the extraction ability of extractants with long alkyl chains could be explained by steric hindrance caused by the bulky substituents.<sup>5</sup> The extraction ability of the extractant with the smallest alkyl substituent, methyl group, was significantly higher than those of the other extraction agents, showing a better extraction ratio at lower acidity. Mowafy and Mohamed<sup>16</sup> also found that the distribution ratios of lanthanides decreased with increasing length of alkyl chains on the amide nitrogen atom.

As shown in Fig. 5, the extraction of Pr(III) from hydrochloric acid medium was investigated with four unsymmetrical diglycolamides, DMDDdDGA, DEDDdDGA, DPDDdDGA and DBDDdDGA, in sulfonated kerosene. At low

aqueous hydrochloric acid concentration, the distribution ratio (*D*) of Pr(III) was near to zero. When above a critical HCl concentration, the distribution ratios increase sharply with increasing HCl concentration. A third phase was observed at 3.5, 4.0, 5.0 and 5.5 M HCl for DMDDdDGA, DEDDdDGA, DPDDdDGA and DBDDdDGA after centrifugation, respectively. The critical aqueous concentration (*CAC*) of HCl for third-phase formation increased in the order: DMDDdDGA < DEDDdDGA < DPDDdDGA < DBDDdDGA; this order is in agreement with the length of alkyl chain on the amidic N atoms in the four extractants. If the length of substituent is shorter, the third phase forms more easily in hydrochloric acid medium.



Fig 5. Influence of alkyl substituent structure on the distribution of Pr(III) in sulfonated kerosene;  $c_{Pr(III)} = 1.00 \times 10^{-3}$  mol dm<sup>-3</sup>;  $c_{Ex} = 0.02$  mol dm<sup>-3</sup>.

# Dependence of extraction on the nature of the diluents

The diluents have a significant influence on the extraction behavior. The effect of diluents, octanol as polar diluent and toluene as nonpolar diluent, on the extraction behavior of Pr(III) with diglycolamides was studied in this work. As shown in Fig. 6, the distribution ratio of Pr(III) extracted by DEDDdDGA and DPDDdDGA in octanol increased linearly with increasing HCl concentration. Moreover, the extraction ability of DEDDdDGA was higher than that of DPDDdDGA, which could be explained by steric hindrance. However, Pr(III) was hardly extracted by DEDDdDGA and DPDDdDGA in toluene from HCl medium in the range of 1–5 mol dm<sup>-3</sup> (Fig. 6). This phenomenon is in agreement with the results of Cui *et al.* for the extraction of Gd(III), Dy(III), Er(III) and Yb(III) by TBDGA in toluene from HCl medium.<sup>15</sup>

Octanol–kerosene was also used as the diluent for diglycolamides in the extraction of lanthanide and actinide.<sup>11,30</sup> In order to understand the relationship between extraction ability and the polarity of diluents, octanol was mixed with sulfonated kerosene in different ratios to extract Pr(III), as show in Fig. 7. The distribution of Pr(III) fell sharply when a small amount of octanol was added into

sulfonated kerosene (5 %) and then  $D_{Pr(III)}$  remained almost unchanged with increasing volume fraction of octanol. However,  $D_{Pr}$  was close to 1.0 for DEDDdDGA and DPDDdDGA in octanol (Fig. 6). It was reported that  $D_{Gd}$  for TBDGA increased with increasing volume fraction of octanol (20–30 %).<sup>15</sup>  $D_{Pr}$  showed no change with a low volume fraction of octanol (0–25 %), while  $D_{Pr}$  could increase with a higher volume fraction of octanol. With a low volume fraction of octanol (0–25 %), the distribution ratio of Pr(III) remained unchanged with increasing polarity of the diluents.





The extraction of Pr(III) from hydrochloric acid medium with diglycolamide (DGA) in sulfonated kerosene could be described as:

$$\Pr_{(aq)}^{3+} + 3Cl_{(aq)}^{-} + nDGA_{(o)} \Longrightarrow \Pr{Cl_3} \cdot nDGA_{(o)}$$
(1)

where DGA=DMDDdDGA, DEDDdDGA, DPDDdDGA, DBDDdDGA.  
The conditional extraction constant (
$$K_{ex}$$
) is given by:

$$K_{ex} = \frac{[\Pr{Cl}_{3} \cdot nDGA]_{(o)}}{[\Pr^{3+}]_{(aq)}[Cl^{-}]_{(aq)}^{3}[DGA]_{(o)}^{n}}$$
(2)  
$$D = [\Pr{Cl}_{2} \cdot nDGA]_{(o)}/[\Pr^{3+}]_{(aq)}$$

$$K_{ex} = \frac{D}{[Cl^{-}]^{3}_{(aq)}[DGA]^{n}_{(q)}}$$
(3)

where the subscripts (aq) and (o) refer to the aqueous and organic phase, respectively.  $[PrCl_3 \cdot nDGA]_{(o)}$  is the concentration of the extracted species in the organic phase,  $[Pr^{3+}]$  is the total concentration of  $Pr^{3+}$  in the aqueous phase, *D* is distribution ratio of Pr(III). If  $[Cl^{-}]$  is kept constant, Eq. (3) could be rearranged into Eq. (4) after taking the logarithms:

$$\log D = \log K_{\text{ex}} + n\log[\text{DGA}]_{(0)} + 3\log[\text{Cl}^-]_{(\text{aq})}$$
(4)

Therefore, the stoichiometry of the extracted species was obtained from the slope of the linear fits of plot of log  $D vs. \log c_{\text{Fx}}$ .

As shown in Fig. 8, the distribution ratio (D) of Pr(III) increased linearly with increasing concentration of the diglycolamide. The slopes of the plots were  $3.34\pm0.11$  for DMDDdDGA,  $2.94\pm0.12$  for DEDDdDGA,  $1.02\pm0.06$  for DPDDdDGA and 1.09±0.07 for DBDDdDGA. One extractant molecule was coordinated with Pr(III) ion in the extracted species for DPDDdDGA and DBDDdDGA, and three for DMDDdDGA and DEDDdDGA. This means that the main Pr(III) species extracted by each of the four extractants from hydrochloric acid medium were Pr(DMDDdDGA)<sub>3</sub>Cl<sub>3</sub>, Pr(DEDDdDGA)<sub>3</sub>Cl<sub>3</sub>, Pr(DPDDdDGA)Cl<sub>3</sub> and Pr(DBDDdDGA)Cl<sub>3</sub>, respectively. The stoichiometries of extracted species were different with different extractants. The stoichiometries of extracted species for DPDDdDGA and DBDDdDGA were nearly one. This phenomenon is similar to the stoichiometries of the extracted species for extraction of Ln(III) with TBDGA diluted with octane in 4.0 mol dm<sup>-3</sup> HCl medium.<sup>15</sup> It was reported that steric hindrance of diglycolamides have a significant impact on the stoichiometry of the extracted species.<sup>18</sup> DMDDdDGA and DEDDdDGA have a short alkyl chain substituent, and hence, their steric hindrance is lower compared with those of DPDDdDGA and DBDDdDGA. Therefore, the number of ligand molecules around the Pr(III) ion for DMDDdDGA and DEDDdDGA was greater than for DPDDdDGA and DBDDdDGA. On the other hand, the acid concentration of the aqueous phase also has an impact on the stoichiometries of the extracted species.<sup>16</sup> Thus, the hydrochloric acid concentration may also be a reason leading to different stoichiometries of the extractants.



Fig. 8. Dependence of Pr(III) extraction on the concentration of diglycolamides in sulfonated kerosene;  $c_{Pr(III)} = 1.00 \times 10^{-3}$  mol dm<sup>-3</sup>.

The IR spectra of DMDDdDGA, DEDDdDGA, DPDDdDGA and DBDDdDGA diluted by octanol were investigated before and after extraction of Pr(III) from hydrochloric acid medium (Fig. 9). Compared with the free diglycolamides, the stretching vibration of the carbonyl group of the extracted species were shifted from about 1647, 1643, 1643 and 1647 cm<sup>-1</sup> to 1624, 1616, 1614 and 1614 cm<sup>-1</sup>, respectively, *i.e.*, the shifts were about 30 cm<sup>-1</sup>. The similar results were reported by Mowafy and Mohamed<sup>10</sup> and Zhang *et al.*<sup>19</sup> As shown in Fig. 4, the stretching vibration of carbonyl group shifted about 13 cm<sup>-1</sup> after extraction of HCl, which is far less than that after extraction of Pr(III). This indicated that the shift in the C=O stretching vibration peak was caused by C=O groups coordinated with Pr(III) instead of HCl. Therefore, these data illuminate



Fig 9. IR spectra of the free extractant and extracted species diluted by octanol. a) DMDDdDGA; b) DMDDdDGA–Pr(III); c) DEDDdDGA; d) DEDDdDGA–Pr(III); e) DPDDdDGA; f) DPDDdDGA–Pr(III); g) DBDDdDGA; h) DBDDdDGA–Pr(III).

that the Pr(III) ion is mainly coordinated to the oxygen of the carbonyl group of the unsymmetrical diglycolamide extractants.

# Separation of Fe(III) from Pr(III)

The distributions of Fe(III) and Pr(III) in hydrochloric acid medium with both DMDDdDGA and DBDDdDGA in toluene are given in Fig. 10. The D<sub>Fe(III)</sub> for both extractants slowly increased with the HCl concentration until a concentration of 2.0 mol dm<sup>-3</sup> was reached and then significantly increased with increasing HCl concentration in the range of 2.0 to 3.0 mol dm<sup>-3</sup>. This phenomenon is similar to the extraction of Fe(III) by TBDGA in toluene from hydrochloric acid medium.<sup>31</sup> DMDDdDGA has a higher extraction ability toward Fe(III) than DBDDdDGA, which may be attributed to the alkyl steric hindrance. It is noteworthy that the distribution ratios of Pr(III) for both extractants were nearly zero under the studied concentrations of hydrochloric acid.



Fig 10. Extraction distribution ratio of Pr(III) and Fe(III) in toluene;  $c_{\text{Ex}} = 0.2$ mol dm<sup>-3</sup>;  $c_{\text{Pr(III)}} = 5.0 \times 10^{-3}$  mol dm<sup>-3</sup>;  $c_{\text{Fe(III)}} = 5.0 \times 10^{-3}$  mol dm<sup>-3</sup>.

The separation factors of Fe(III) and Pr(III), which are defined as the ratio of  $D_{\text{Fe(III)}}$  to  $D_{\text{Pr(III)}}$ , with DMDDdDGA and DBDDdDGA diluted with toluene in HCl medium are given in Table I. The separation factor ( $\beta_{Fe-Pr}$ ) of Fe(III) and Pr(III) increased with increasing HCl concentration and a maximal value for DMDDdDGA and DBDDdDGA was observed at the studied maximum concentration, 3.0 mol dm<sup>-3</sup> HCl. The  $\beta_{\text{Fe-Pr}}$  of DMDDdDGA was higher than that of DBDDdDGA.

TABLE I. The separation factors of Fe(III) to Pr(III) under different hydrochloric acid concentrations

Separation factor	$c_{ m HCl}$ / mol dm <sup>-3</sup>			
	1.5	2.0	2.5	3.0
$\beta_{\rm Fe-Pr(DMDDdDGA)}$	6.32	36.2	270	2185
$\beta_{\rm Fe-Pr(DBDDdDGA)}$	2.91	13.1	71.4	423

Reusability is an important consideration when choosing an extractant. Thus, the back extraction of Fe(III) with pure water by DMDDdDGA and DBDDdDGA using toluene as diluents was investigated. The first stripping rates of Fe(III) from the organic phase were greater than 95 %. High  $\beta_{\text{Fe-Pr}}$  values and stripping rates show that there are good prospects for using these extractants in the separation and purification of Pr(III).

## CONCLUSIONS

In this works, four unsymmetrical extractants, DMDDdDGA, DEDDdDGA, DPDDdDGA and DBDDdDGA, were synthesized and their extraction ability of Pr(III) in HCl medium was studied. The structure of the alkyl group adjacent to the N atom of extractant molecule has a great impact on the extraction ability of Pr(III). The order of extraction ability of diglycolamides for Pr(III) in sulfonated kerosene is DMDDdDGA > DEDDdDGA, DPDDdDGA > DBDDdDGA. A small alkyl group is beneficial to the extraction. The main extracted species for diglycolamides were  $Pr(DMDDdDGA)_3Cl_3$ ,  $Pr(DEDDdDGA)_3Cl_3$ ,  $Pr(DPDDdDGA)Cl_3$  and  $Pr(DBDDdDGA)Cl_3$ , respectively.

The extraction capacity for Pr(III) is weak in the low acidity range, while the extraction capacity for Fe(III) is relatively strong. Thus, in a certain acidity range, a good separation could be achieved.

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#### ИЗВОД

## УТИЦАЈ СТРУКТУРЕ НА ЕКСТРАКЦИЈУ ПРАЗЕОДИМА ИЗ РАСТВОРА ХЛОРОВОДОНИЧНЕ КИСЕЛИНЕ РАЗЛИЧИТИХ НЕСИМЕТРИЧНИХ ДИГЛИКОЛАМИДА

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Испитивана је екстракција Pr(III) помоћу четири типа несиметричних дигликоламида (DGA) који се разликују у дужини алкилног низа, као што су N,N'-диметил-N,N'--дидодецилдигликоламид (DMDDdDGA), N,N'-диетил-N,N'-дидодецилдигликоламид (DEDDdDGA), N,N'-дипропил-N,N'-дидодецилдигликоламид (DPDDdDGA) и N,N'-дибутил-N,N'-дидодецилдигликоламид (DBDDdDGA). Дискутован је утицај алкилног остатка на N-амидном атому DGA на ефикасност екстракције Pr(III) јона. Испитивана је ефикасност екстракције смеше хлороводоничне киселине и Pr(III) јона из раствора у којима се хлороводонична киселина налази у смеши са сулфонованим керозином, толуеном или октанолом помоћу DGA. Испитиван је утицај концентрације екстрактанта и растварача на дистрибуциони однос (D) Pr(III) јона, да би се објаснио екстракциони механизам,. Нађено је да се Pr(III) и Fe(III) јони могу успешно раздвојити помоћу DMDDdDGA и DBDDdDGA који се налазе у раствору који садржи хлороводоничну киселину у смеши са толуеном. Испитивана је структура DGA-HCl и DGA-Pr(III) екстрактованих врста на основу поређења њихових IR спектара.

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