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Extraction of Sm(III) and Nd(III) with *N,N,N',N'*-tetrabutyl-3-oxy-diglycolamide from hydrochloric acid

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Abstract: The behavior of Sm(III) and Nd(III) during extraction with *N,N,N',N'*-tetrabutyl-3-oxa-diglycolamide (TBDGA) in 70% kerosene–30 % *n*-octanol from hydrochloric acid was studied. The effects of temperature and the concentrations of hydrochloric acid and extractant on the distribution of the rare earth elements were investigated. The extraction mechanism was established and the stoichiometry of the main extracted species was confirmed to be $\text{SmCl}_3 \cdot 2\text{TBDGA}$ and $\text{NdCl}_3 \cdot 2\text{TBDGA}$ for Sm(III) and Nd(III), respectively. The extraction distribution ratio decreased with increasing temperature, which demonstrates that the extraction reaction is exothermic. The IR spectra of the loaded organic phase and free extractant were recorded and are discussed.

Keywords: 3-oxa-diglycolamide; hydrochloric acid; stoichiometry; lanthanides; distribution ratio.

INTRODUCTION

The rare earth elements have an important position in the exploration and preparation of new functional materials due to their electronic configuration and changeable radius of their atom and ion. Therefore, pure and simple rare earth elements are necessary.¹ Solvent extraction has been the main means in partition and purification of rare earth elements due to its rapid reaction rates and good separation effects.^{2,3}

Although tetrabutyl phosphate (TBP) has been used, 3-oxy-diglycolamides were selected as prospective extractants in this research project because they are widely used in nuclear fuel reprocessing. The products of radiolytic and hydrolytic degradation of amides are less detrimental to the extraction and separation processes than those of organic phosphorus extractants.^{4,5} The amide ligands are completely incinerable, which implies that secondary wastes generated during

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nuclear waste treatment could be significantly reduced.^{6,7} Moreover, they exhibited higher extractability than amides due to the soft ether oxygen atom.⁸ The extraction behavior of actinides and lanthanides with 3-oxy-diglycolamides from nitric acid medium has been reported.^{9–12} However, rare earth elements are usually recovered from hydrochloric acid medium. Therefore, it is important to study the extraction and separation of lanthanides with new extractants from hydrochloric acid medium. The extraction of lanthanides from hydrochloric acid media is very important for the hydrometallurgy and recycling process of lanthanides. To the best of our knowledge, there has only been one report¹³ of the extraction performances of lanthanides from HCl with amides.

The effect of diluents on the extraction behavior of the neutral extractant was reported in a previous paper.¹⁴ It was found that the extraction capacity was related to the polarity of the diluents. The extraction distribution ratios were lower in alkane and/or aromatic diluents than that in mixed diluents composed of a polar alcohol and an alkane. The extraction behavior of lanthanides with *N,N,N',N'*-tetrabutyl-3-oxa-diglycolamide (TBDGA) employing a 70 % kerosene–30 % *n*-octanol mixture as diluent from a hydrochloric acid system was investigated in this work. Kerosene and *n*-octanol were selected they are cheaper than other solvents.

EXPERIMENTAL

Reagents

N,N,N',N'-Tetrabutyl-3-oxo-diglycolamide (TBDGA) was laboratory synthesized in a three-step process.¹⁵ The final product was characterized by elemental analysis and IR and ¹H-NMR spectroscopy and the purity was higher than 98 %. The other employed chemical reagents were all of A.R. grade.

Preparation of the Sm(III) and Nd(III) solutions

Sm₂O₃ (1.7436 g) was dissolved in 20 mL of 12.66 mol·dm⁻³ HCl solution and the solution was then evaporated carefully to dryness. The residue was dissolved in 2 mL 12.66 mol·dm⁻³ HCl and diluted to 100 mL with distilled water. The obtained solution contained 0.100 mol·dm⁻³ Sm³⁺ and 0.25 mol·dm⁻³ HCl. A series of 4.00×10⁻³ mol·dm⁻³ Sm³⁺ solutions were then prepared by quantitative dilution. The Nd(III) solutions were prepared in a similar method.

Extraction of Sm(III) and Nd(III) with TBDGA

In the studies of the extraction distribution of Sm(III) and Nd(III), solutions of the desired concentration of TBDGA in 70 % kerosene–30 % *n*-octanol were employed after pre-equilibration with the respective acidities. Equal volumes of organic and aqueous phases were agitated for 30 min (enough for equilibrium) at 25 °C under the desired experimental conditions. The two phases were then centrifuged and assayed by taking known aliquots (0.05–0.10 mL) from the aqueous phase. The concentrations of Sm(III) or Nd(III) remaining in the sample were determined by the Arsenazo-III visible spectrophotometric method¹⁹ and those in organic phase were obtained by subtracting the aqueous concentrations from the total initial aqueous concentration of Sm(III) or Nd(III). The extraction distribution ratio (*D*) was cal-

culated as the ratio of the concentration of Sm(III) or Nd(III) in the organic phase to that in the aqueous phase.

Characterization of the extracted species

After the extracted species had been prepared, the TBDGA solution was shaken with a concentrated solution of SmCl₃ or NdCl₃, centrifuged and the organic phase separated. The organic solvent was removed and the IR spectra of the residue were recorded using an FTS-165 IR spectrometer in the range 400–4000 cm⁻¹. The scan times and the resolution were 60 and 2 cm⁻¹, respectively.

RESULTS AND DISCUSSION

Effect of HCl concentration

The effect of the concentration of HCl on the extraction behaviors of Sm(III) and Nd(III) with TBDGA are shown in Fig. 1. The distribution ratios of Nd(III) increased with increase in HCl concentration in the range of 1.00–5.00 mol dm⁻³. However, the distribution ratios of Sm(III) increased to a maximum value at about 3.5 mol dm⁻³ HCl and then slowly decreased with further increase in the HCl concentration. This phenomenon is different from that reported in nitric acid medium.¹² That the distribution of both Sm(III) and Nd(III) increases significantly under low acidity conditions may be due to the co-ion effect which plays a crucial role. The coordinated anions formed by lanthanide ions and chloride anions under high acidity could not be extracted, which resulted in the slow distribution decrease for Sm(III). It is inferred that the extraction distribution of Nd(III) may reach a maximum value above 5 mol dm⁻³ HCl, which will be investigated further in future work.

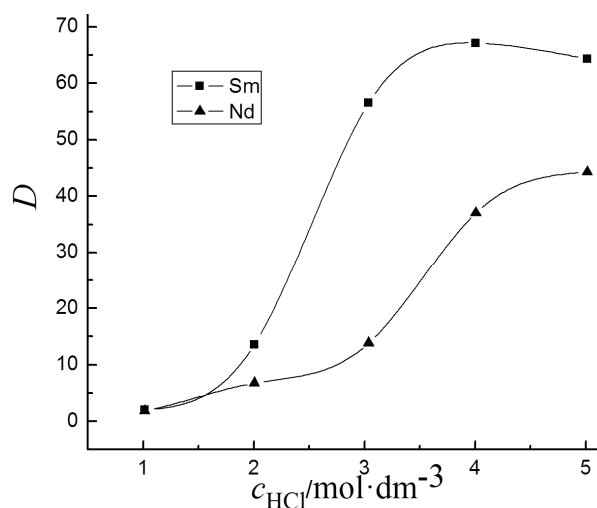
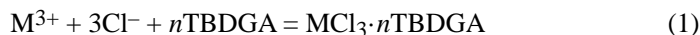


Fig. 1. Effect of the HCl concentration on the extraction distribution of Sm(III) and Nd(III). $c_{\text{M}^{3+}} = 4.00 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$; $c_{\text{TBDGA}} = 0.10 \text{ mol} \cdot \text{dm}^{-3}$.

Effect of TBDGA concentration

The chemical reaction involved during the extraction of metal ions from hydrochloric acid medium by TBDGA in 70 % kerosene–30 % *n*-octanol can be described as follows:



where *n* was determined by slope analysis method. The logarithm of the distribution ratio is plotted as a function of the logarithm of the initial concentration of TBDGA in Fig. 2. The distribution ratio increases with an increasing concentration of TBDGA.

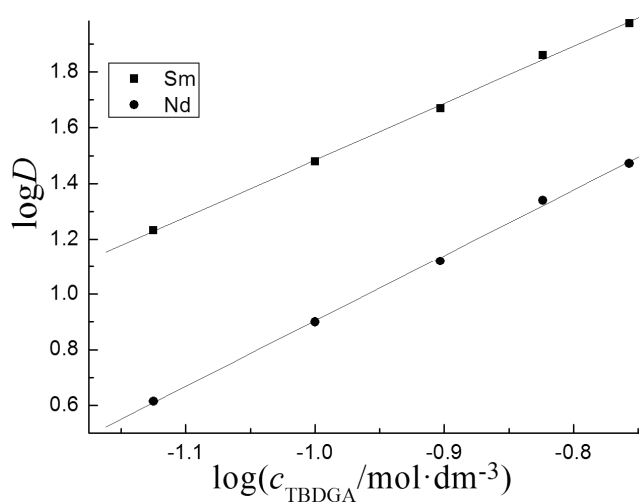


Fig. 2. Effect of the TBDGA concentration on the extraction distribution of Sm(III) and Nd(III). $c_{M^{3+}} = 4.00 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$; $c_{HCl} = 2.50 \text{ mol} \cdot \text{dm}^{-3}$.

The plots of $\log D$ vs. \log TBDGA for both Sm(III) and Nd(III) gave slopes of about 2, which suggests that the stoichiometries of the extracted species were $\text{SmCl}_3 \cdot 2\text{TBDGA}$ and $\text{NdCl}_3 \cdot 2\text{TBDGA}$. Thus, the chemical reactions can be expressed as follows:



The apparent equilibrium constants for Sm(III) and Nd(III), K_{ex1} and K_{ex2} , respectively, are:

$$K_{\text{ex1}} = \frac{c_{\text{SmCl}_3 \cdot 2\text{TBDGA}}}{c_{\text{Sm}^{3+}} c_{\text{TBDGA}}^2 c_{\text{Cl}^{-}}^3 \gamma_{\text{M}^{3+}} \gamma_{\text{Cl}^{-}}^3} \quad (4)$$

$$K_{\text{ex2}} = \frac{c_{\text{NdCl}_3 \cdot 2\text{TBDGA}}}{c_{\text{Nd}^{3+}} c_{\text{TBDGA}}^2 c_{\text{Cl}^-}^3 \gamma_{\text{M}^{3+}} \gamma_{\text{Cl}^-}^3} \quad (5)$$

where $\gamma_{\text{Sm}^{3+}}$, $\gamma_{\text{Nd}^{3+}}$ and γ_{Cl^-} are the activity coefficients of Sm^{3+} , Nd^{3+} and Cl^- , respectively.

The total concentration of Sm(III) and Nd(III) in aqueous phase can be written:

$$c_{\text{M}} = c_{\text{M}^{3+}} (1 + \beta_1 c_{\text{Cl}^-}) \quad (6)$$

where β_1 is the coordination constant of metal ions with Cl^- . It is much more difficult for Cl^- to coordinate with Sm^{3+} and Nd^{3+} than with a water molecule. Therefore, Eq. (6) can be simplified as:

$$c_{\text{M}} \approx c_{\text{M}^{3+}} \quad (7)$$

The distribution ratio (D) is given by:

$$D = \frac{c_{\text{M}^{3+}(\text{o})}}{c_{\text{M}^{3+}}} = \frac{c_{\text{MCl}_3 \cdot n\text{TBDGA}}}{c_{\text{M}^{3+}}} \quad (8)$$

Hence, K_{ex} can be written as:

$$K_{\text{ex}} = \frac{D}{c_{\text{Cl}^-}^3 c_{\text{TBDGA}(\text{o})}^n \gamma_{\text{M}^{3+}} \gamma_{\text{Cl}^-}^3} \quad (9)$$

The values of $\gamma_{\text{M}^{3+}}$ and γ_{Cl^-} , calculated according to the Debye–Hückel Formula,¹⁶ were 0.9011 and 0.9659, respectively. The values of $\log K_{\text{ex}}$ calculated from Eq. (9) are 2.30 ± 0.12 for Sm^{3+} and 1.82 ± 0.05 for Nd^{3+} .

Effect of temperature on the extraction distribution ratio of Sm(III) and Nd(III)

The effect of temperature on the extraction equilibrium is given in Fig. 3. The distribution ratio decreased with increasing temperature, which demonstrated that the extraction reaction is an exothermic process. The change in enthalpy, ΔH , in each case was evaluated using the Van't Hoff Equation:

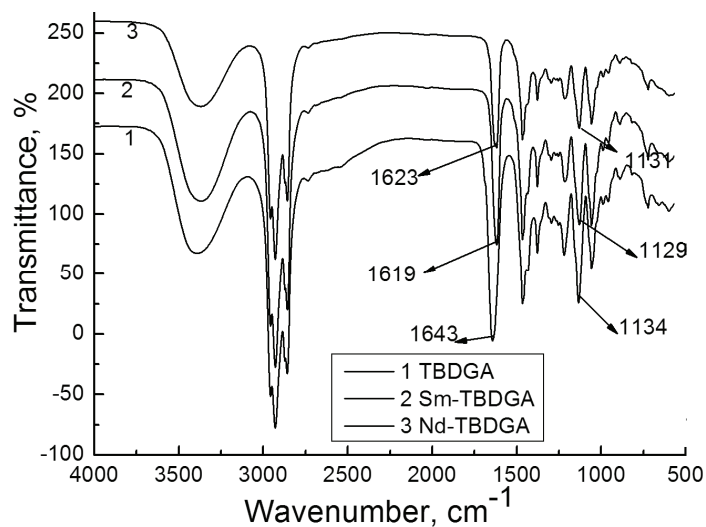
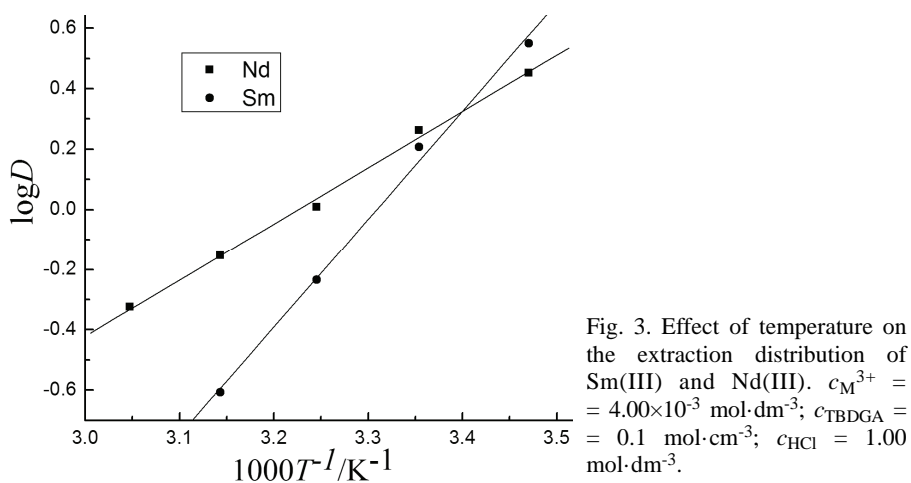
$$\left[\frac{\partial \log D}{\partial (1/T)} \right]_p = \frac{-\Delta_r H_m^\theta}{2.303R} \quad (10)$$

The values of enthalpy change obtained for the extraction of Sm(III) and Nd(III) were -68.54 and -35.70 kJ mol^{-1} , respectively. These values indicate that the extraction reaction is enthalpy favored.¹⁷

Spectroscopic studies of the extracted species

The IR spectrum of TBDGA and the extracted species are shown in Fig. 4. Compared with the free extractant, the C=O stretching vibration of the extracted

species were shifted to lower frequencies, to 1619 cm^{-1} for Sm(III) and to 1623 cm^{-1} for Nd(III). These results are consistent with the observation by Sasaki of the complex of Eu(III) with *N,N,N',N'*-tetra(*n*-octyl)-3-oxy-diglycolamide (TODGA),¹⁸ In addition, the C–O stretching band at 1134 cm^{-1} in spectrum of TBDGA was shifted slightly after extraction.¹⁵ The above results indicate that the three oxygen atoms of the two carbonyl groups and alkoxy group are all coordinated with Sm(III) and Nd(III) in the extracted species; in other words, TBDGA is a tridentate ligand.



CONCLUSIONS

Sm(III) and Nd(III) can be extracted effectively from hydrochloric acid solution using TBDGA in 70 % kerosene–30 % *n*-octanol. The extractability of TBDGA for Sm(III) was higher than that for Nd(III). The distribution ratio increased with increasing concentration of HCl at low concentrations. The values of *D* increased with increasing TBDGA concentration. The stoichiometries of the extracted species can be described as $\text{SmCl}_3 \cdot 2\text{TBDGA}$ and $\text{NdCl}_3 \cdot 2\text{TBDGA}$. The extraction reactions are exothermic, and increasing temperature has a negative impact on the extraction process. From IR spectroscopy, it could be concluded that TBDGA forms tridentate complexes with Sm(III) or Nd(III) through its three oxygen atoms of carbonyl group and alkoxy group.

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ИЗВОД

ЕКСТРАКЦИЈА Sm(III) И Nd(III) ИЗ ХЛОРОВОДОНИЧНЕ КИСЕЛИНЕ ПОМОЋУ
N,N,N',N'-ТЕРАБУТИЛ-3-ОКСИ-ДИГЛИКОЛАМИДА

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Испитана је екстракција Sm(III) и Nd(III) из хлороводоничне киселине помоћу N,N,N',N'-терабутил-3-окси-дигликоламида (TBDGA) у раствору 70 % керозина–30 % *n*-октанола. Истражен је утицај концентрације хлороводоничне киселине, концентрације екстранта и температуре на дистрибуцију ових ретких земаља. Установљен је екстракциони механизам и потврђена је стехиометрија основних екстрахованих врста: $\text{SmCl}_3 \cdot 2\text{TBDGA}$ за Sm(III) и $\text{NdCl}_3 \cdot 2\text{TBDGA}$ за Nd(III). Дистрибуциони однос екстракције се смањује са повећањем температуре, указујући да је реакција екстракције егзотермна. Снимљени су и дискутовани инфрацрвени (IR) спектри органске фазе и слободног екстранта.

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