

EXTRACTION OF RARE EARTHS BY OPEN CHAIN CROWN ETHER^①

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ABSTRACT

The extraction properties and regularity of rare earths by open chain crown ether 1, 11-di (8-quinoline)-3, 6, 9-trioxaundecane (noted as L) were investigated. And the effects of aqueous acidity, terminal group and organic acid group anion on the extractability of rare earths were examined respectively.

Key words: open chain crown ether extraction rare earths

1 INTRODUCTION

Many studies on the extraction of rare earth elements Re by macrocyclic crown ethers were reported^[1-3]. But little attention has been paid to the extraction behaviour of these elements towards the acyclic polyethers (or known as open chain crown ether). It was found that the extraction regularity for rare earths by macrocyclic crown ethers differs greatly from that of most of other extractants. This particular regularity of extraction should prove valuable in possible practical application, including the elaboration of extraction processes for the separation of rare earth ions. Open chain crown ether, which has no toxicity, costs less and is easy to synthesize, has a similar coordination characteristic to that of macrocyclic crown ether. About the coordination property of open chain crown ether, a "Terminal Group Concept" was proposed by Vogtle F^[4, 5], which suggested that the struc-

ture and property of terminal group in open chain crown ether has great influence on its coordination property for metal ions. Recently, some solid complexes of rare earth ions with glycols and their derivative have been isolated^[6-12]. It was therefore interesting to study the extraction property of open chain crown ether^[13]. In this paper, 1, 11-di (8-quinoline)-3, 6, 9-trioxaundecane was synthesized by replacing the two terminal hydroxyl in tetraethylene glycol with two 8-quinoline groups, and its extraction behaviour and regularity for rare earths were investigated.

2 EXPERIMENTAL

Rare earths standard solutions were prepared from the respective rare earth oxides of 99.9% or higher purity. Organic acid group anion stock solutions were obtained from the respective acids (Picrate acid is chemically pure, salicylate acid and trichloroacetic acid are analytically pure) by dissolving the solid

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acid in water, which were neutralized with a basic solution. Tetraethylene glycol was purified by a dry procedure with 5A molecular sieve and a distillation separation process under vacuum. Extractant L was synthesized according to the method described by Tummiler B^[14,15], and the product was evaluated with HNMR, IR and element analysis methods.

The extraction organic phases were prepared by diluting the open chain crown ether synthesized as above (hereafter L) with chloroform (A. R.), the concentration of L is 0.015 mol/L.

Extraction tests were carried out with phase ratio 1:1 in extraction tube. After equilibrium, the aqueous pH were measured with an Orion Research EA 940 ion meter. A certain portion of the aqueous phase was pipetted out, and the content of rare earth ion was estimated by Assenzo I spectrophotometry using a 751-G model spectrophotometer and the absorbance was measured at 670 nm, the concentration of picrate acid was determined by spectrophotometry at 355 nm. The organic phase concentrations of rare earth ion and picrate acid were then calculated by the method of difference.

3 RESULTS AND DISCUSSION

3.1 Comparison of Extractability of Re

The percentage extraction of rare earth ion (Pr^{3+}) by extractant L from picrate anion, salicylate anion and trichloroacetate anion aqueous phase solutions were determined respectively. Table 1 shows that the percentage extraction is different among the three kinds of organic acid group anion medium. Under the same pH condition, the extractability order for the different medium was found to be picrate

> salicylate > trichloroacetate. And this order is in agreement with that of their molecular volume.

Table 1 Comparison of extractability of rare earths by extractant L from different aqueous phase medium

anion	percentage extraction (pH)	
trichloroacetate	0 / 3.60	8 / 6.03
salicylate	0 / 4.48	14 / 5.36
picrate	33.5 / 5.23	61.5 / 6.09

Conditions: $\text{Pr}^{3+} = 2.5 \times 10^{-4}$ mol/L; $T = 25^\circ\text{C}$;

phase ratio 1:1; anion content: 0.01 mol/L

3.2 Effect of Acidity on the Extraction of Re

Fig.1 shows the variation of extraction percentage of rare earths with the aqueous initial pH for the systems containing 0.01 mol/L picrate anion or 0.02 mol/L salicylate anion in the aqueous phase respectively. It was found that no significant extraction for rare earth occurs when $\text{pH} < 4$, and the extraction percentage is greatly increased with the increasing pH when $\text{pH} > 4$. The extractability of rare earth in picrate anion medium is always higher than that in salicylate anion medium over the thorough pH range, which is in good agreement with the former result.

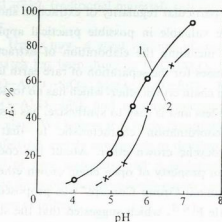


Fig.1 The variation of extraction percentage of rare earth with aqueous initial pH
curve 1—picrate; curve 2—salicylate

3.3 Comparison of Extraction for Organic Acid and Re by L and Tetraethylene Glycol

The difference between extractant L and tetraethylene glycol is in their terminal group. The former contains two 8-quinoline groups, which have certain extractability for organic acid in aqueous phase solution, and the later contains two hydroxyls. A comparison of extraction variation for picrate acid by L and tetraethylene glycol with different initial aqueous phase acidity was shown in Fig.2. The extraction percentage of picrate acid both by L and tetraethylene glycol increase with the decreasing pH, but the disparity between curve 1 and curve 2 which represented in Fig.2 is increased with the increasing acidity in aqueous phase, curve 1 is always over the curve 2. This indicates that the extractant L has stronger extractability for picrate acid than tetraethylene glycol, especially in a higher acidity solution. Fig.3 represents the variation of percentage extraction of rare earths with aqueous phase pH, where the extractants include open chain crown ether L and tetraethylene glycol (represented by curve 1 and curve 2 respectively). As compared with Fig.2, the rare earth extractability increases with the increasing pH of aqueous phase. Both extractants have close extractability for rare earth over the pH range from 5 to 6. This resemblance suggested that the extraction for rare earth ion with L is mainly due to the coordination between ether chain O atoms and rare earth ion over the pH range 5~6, which bears a resemblance to that with tetraethylene glycol. However, the rare earth extraction by the former is higher than that by the later when $\text{pH} > 6$, and is lower when $\text{pH} < 5$. Under a higher acidity condi-

tion, the decrease of rare earth extractability by L is due to the increasing extractability for organic acid by the terminal groups 8-quinoline in L. In neutral aqueous phase medium, because of the addition coordination between quinoline N atoms in L and rare earth ion, the extractability should be higher than that by tetraethylene glycol.

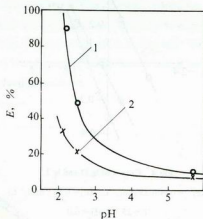


Fig.2 Extraction of picrate acid (*E*) by open chain crown ether

1—L; 2—E04

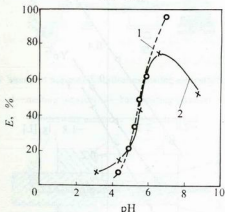


Fig.3 Extraction of rare earth by open chain crown ether

1—L; 2—E04

3.4 Effects of Concentration of L and Picrate on the Extraction of Rare Earths

Y, Pr (lighter rare earth element) and Yb (heavier rare earth element) were selected as the representation of rare earths to examine

the influence of concentration of L and picrate on the rare earth extraction at pH 6 respectively. Fig.4 and Fig.5 show the results, where

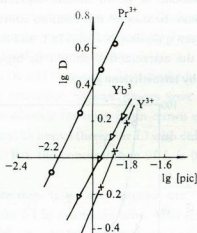


Fig.4 Curves of lg D and lg L

$[Re]^{3+} = 0.000,25 \text{ mol/L}$; $[L] = 0.015 \text{ mol/L}$

$T = 25^\circ\text{C}$; $\text{pH} = 6.0$

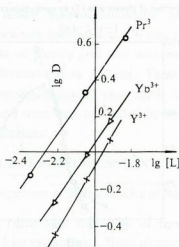


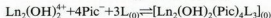
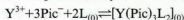
Fig.5 Curves of lg D and lg (Pic)

$Re = 0.000,25 \text{ mol/L}$; $T = 25^\circ\text{C}$

$[Pic] = 0.015 \text{ mol/L}$; $\text{pH} = 6.0$

lg D were plotted against lg L and lg (Pic) respectively (D is distribution ratio). Plots of lg D against lg L at constant pH and picrate concentration gave straight line of slope 1.8 for Y

and 1.5 for Pr, Yb lanthanide elements. Plots of lg D against lg (Pic) at constant pH and L concentration gave straight lines of slope 2.6 for Y and 2.0 for Pr, Yb approximately. Based on the rational of determining the composition of the extracted compounds in the systems studied here may be written as: $(Y(Pic)_3L_2)$ for Y and $(Ln_2(Pic)_4(OH)_2L_3)$ for Pr, Yb etc. lanthanide elements. Because extraction was carried out at pH 6, the rare earth ions may be hydrolyzed partially. These partially hydrolyzed rare earth ions should be extracted by L from neutral picrate anion medium, and then, their extraction reactions by open chain crown ether L from near neutral picrate anion medium can be represented by



3.5 Extraction Order for Lanthanides

The extraction distribution ratios for lanthanides (except for Pm) and Yttrium ions by L from picrate anion medium at constant pH 6 and temperature 25°C were determined. A plot of lg D vs lanthanides atomic number Z was shown in Fig.6. The curve is found to be similar to that reported by^[2,3]. Their extraction ordering is partially reverse order, with a maximum lying at Sm. The values of lg D increase from La to Sm, and then, decrease from Sm to Lu with an exception at Yb. No evident Tetral effect is observed from lg D-Z curve. The lg D value for Y falls near that for Tm and Er. These results suggested that the extraction of rare earth ions by open chain crown ether L is mainly due to the coordination between the O atoms in polyether chain and rare earth ions by ion-dipole interaction over the pH range 5 ~ 6. The action of terminal group 8-quinoline
(To be continued on page 101)