

Study of Solvent Extraction of Lanthanum with some Crown Ether Compounds

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ABSTRACT

Solvent extraction system of aqueous Lanthanum picrate with benzo-15-Crown-5 (B15C5) , 18-Crown-6 (18C6) , dibenzo-18-Crown-6 (B218C6) , dicyclohexyl-18-Crown-6 (Cy218C6) and dibenzo-24-Crown-8 (B224C8) dissolved in 1,2-DCE and other organic solvents. The lanthanum cation is extracted as 1:1 complex with B15C5, 18C6, B218C6 and Cy218C6, but as 2:1 L:M sandwich complex with B224C8. The effect of various parameters on the distribution ratio value of La (III) such as time of equilibrium and organic solvents are determined. The measurements are made using direct current polarography (DCP) and differential pulse polarography (DPP), using 0.1M-KCl as supporting electrolyte

INTRODUCTION

The extraction of the Lanthanide elements is a very broad subject. Interest has been shown in their group separation from their chemically different elements such as uranium and thorium. Due to the sensitivity of crown ethers to the size of ions they can be used in separating lanthanide elements from transition elements and from each other (1). It has been demonstrated that macrocyclic polyethers can behave as highly selective complexing agents for cations (2-6) and are of potential significance in the separation of ions using solvent extraction procedures. Solvent extraction methods can not only be applied in the separation of ions, but can also provide information concerning the nature of the complex. Possessing close formed between the ion and the ligand.

Similarity in the chemical properties, the elements of the lanthanide family is difficult in general to separate from each other (7). The crown ethers and the related macrocyclic ligands are known to recognize fairly strictly the size of the guest cation accommodated in cavity (8). In this work, lanthanum cation was extracted with B15C5, 18C6, B218C6, Cy218C6 and B224C8, the effect of different parameters on the distribution ratio value by using polarographic methods.

EXPERIMENTAL**Apparatus**

1. METROHM Polarecord E506 equipped with polarography stand E505, the requirements for a three-electrodes control system in polarography are that it consist of a dropping mercury electrode (DME) as working electrode is dipped electrolysis cell containing about 25 ml of solution. Saturated calomel into an electrode (SCE) as reference electrode and platinum wire as auxiliary electrode used for polarographic measurements.

2. pH meter, Expandable ion Analyzer EA940 (Orion Research).

3. Electrical shaker, Edmund Bühler 7400 Tübingen.

Chemicals and Reagents

All reagents and chemicals admit the following analytical grade. Crown ether compounds (Fig. 1) are obtained from Fluka Company. Lanthanum chloride was obtained from Riedle De Haenag Company. Picric acid was obtained from E. Merck. All organic solvents were obtained from Fluka, Ferak and Ajax companies. Water was doubly distilled deionized.

Extraction Procedure

Ten ml of aqueous solution of 3×10^{-3} M of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 5ml of (10 mg/ml) picric acid solution is transferred to a separate funnel, at pH 4.6, adjusted by the use of dilute HCl and NH_3 . 10ml of 0.1M crown ethers solution dissolved in 1, 2-DCE and others organic solvents, the mixtures were shaken vigorously on electrical shaker (200 min.^{-1}) for 30 min. at room temperature after shaking, the mixtures were allowed to stand for a period of time for phases separation. Concentration of the other lanthanum (III) is determined with direct current polarography (DCP) and differential pulse polarography (DPP).

Polarographic Measurement

A 25 ml of sample in organic phase and 0.1M of KCl as supporting electrolyte were transferred to the polarographic cell, after purge for 15 minutes with purified nitrogen (%99.99), the polarogram was recorded for residual current from (-0.6 to -2.0) V, the polarograms are then recorded under the following conditions: .

DCP

Dropping time (td), 1.4 Sec.

Scan rate, 2 mV/Sec.

Current range, 0.006-0.5 $\mu\text{A}/\text{mm}$

DPP Dropping time (td), 1.4 Sec.

Pulse amplitude (Dp), 80 mV

Scan rate, 2 mV/Sec.

Current range, 0.006-0.2 $\mu\text{A}/\text{mm}$

The distribution ratio value is calculated using the equation:

$$D = \frac{\text{Conc. of lanthanum ion in organic phase } C_{\text{org.}}}{\text{Conc. of lanthanum ion in aqueous phase } C_{\text{aq.}}} \quad \text{-----(1)}$$

Conc. of lanthanum ion in aqueous phase Caq.

RESULTS and DISCUSSION

Crown ethers showed selective extraction for metal ions in terms of the correspondence between the extracted ion crystal radii and the cavity size:

$$\frac{R_{ion}(\text{Å})}{R_{crown}(\text{Å})}$$

Table(1): Ratio values of diameters of holes, lanthanum cation to cavity size of crown ethers.

Cation	I.D(Å)	B15C5 1.95 Å	18C6 2.6 Å	B218C6 2.6 Å	Cy218C6 2.6 Å	B224C8 5.05 Å
La(III)	2.06	1.056	0.792	0.792	0.792	0.408

It is reasonable to predict that La³⁺ can be stronger complex and it is easily that B15C5 to fit a La³⁺ as well as 18C6, B218C6, and Cy218C6 (2.6 Å). While B224C8, (5.05 Å) is big for La³⁺. Figure(2) also show the linear relationship between distribution ratio (*log D*) and crown ether concentration (*log [Lo]*), which is in agreement with equation(9).

$$\log D = \log \frac{K_{ex} K_f K_a}{(1 - K_d)^n} + \frac{m}{2} \log [HA] + \log [Lo] \text{ ----- (2)}$$

Where *K_{ex}*, *K_f* and *K_a*=complex extraction, complex formation and complex dissociation respectively. Equation(2) shows that when the concentration of picric acid [HA] remains constant, the graph of *log D* against *log [Lo]* must give a straight line with slope *n*. From the *n* values the structure of extracted species can be elucidated. The slopes of graphs in Fig.(2) seem to indicate that the La(III) can forms 1:1 complex with B15C5,18C6, B218C6, and Cy218C6, but form a 1:2 sandwich complex with B224C8. The *n* values obtained from the slopes of the graphs seem to indicate the extraction species of La(III) which is La³⁺ [(crown ether)*n* (picrate)*m*], where crown ethers = B15C5,18C6, B218C6, Cy218C6, and B224C8, *n*=1, and *m*=3. As time of equilibration increases from 10 to 30 and 60 minutes, the *D* value will increase for La³⁺ as shown in table(2). The use of different organic solvents (nitrobenzene, 1,2-dichloroethane, chloroform, toluene and benzene) with 0.1M of crown ether, is shown in table (3). Shows that when the *D* increased with a increase of dielectric constant (*ε*) from La(III). Figure 3. represents the relation between *log ε* for organic solvents and *log D*, which gave a straight line approximately. Nitrobenzene was found to be the best for each of the ions, 1,2-dichloroethane was found as the second choice followed by chloroform, toluene and benzene showed very low ability for separating them.

Table 2 – Effect of time of equilibration D value from La(III) into 1,2-dichloroethane.

Time of equilibration	B15C5	18C6	B218C6	Cy218C6	B224C8
10 min.	30.66	8.61	8.34	10.20	0.88
30 min.	96.70	15.01	10.21	11.31	1.32
60 min.	100.03	15.13	20.33	12.81	1.63

Table 3- Values of distribution ratio with dielectric constant of organic solvents for a extracted individually of La(III) with 0.1M of crown ethers, 30 minutes.

Solvent	ϵ^*	B15C5	18C6	B218C6	Cy218C6	B224C8
Nitrobenzene	35.74	102.34	87.70	86.32	96.11	47.84
1,2-Dichloroethane	10.65	60.31	70.13	83.67	80.32	30.19
Chloroform	4.80	33.04	43.37	37.88	53.44	32.31
Toluene	2.38	21.05	24.40	19.90	21.31	14.30
Benzene	2.28	22.01	15.10	11.08	16.36	14.33

*Ref.(10).

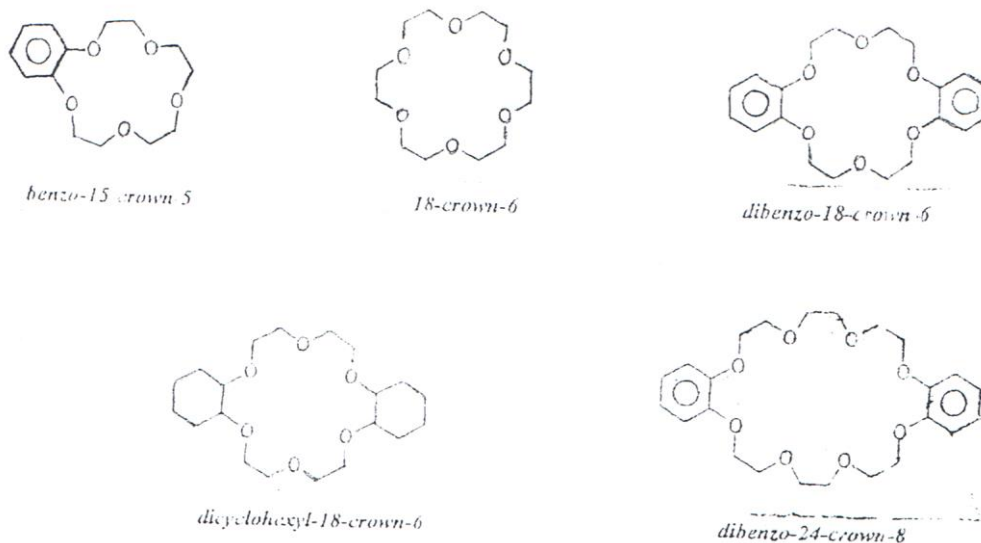


Figure 1. Structural formulas and nomenclature of typical crown ethers.

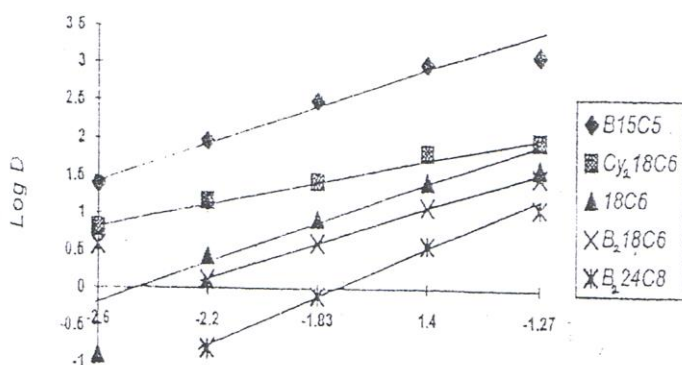


Figure 2: Extraction of aqueous lanthanum picrate 3×10^{-3} M with crown ethers in 1,2-dichloroethane.

	n
B15C5	1.28
Cy18C6	0.97
18C6	1.16
B ₂ 18C6	1.21
B ₂ 24C8	1.76

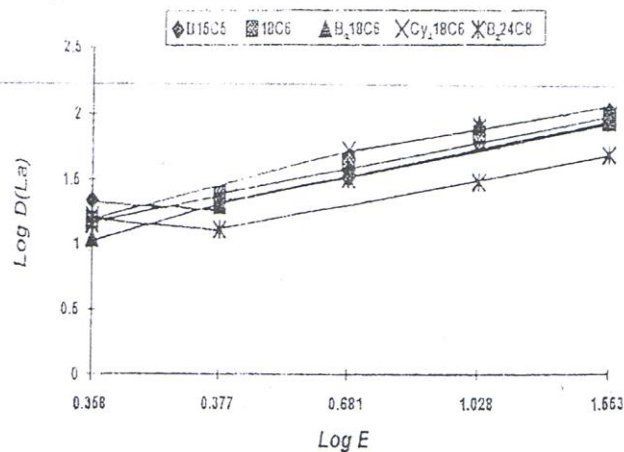


Figure 3: Effect of organic solvents on D value 0.1 M crown ethers in different solvent (organic phase). 10 mg picrate ion 3×10^{-3} M La^{3+} .

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دراسة الاستخلاص المذيبى لأيون اللانثانوم باستخدام
بعض مركبات الأيثرات التاجية

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الخلاصة

تم دراسة أنظمة الاستخلاص المذيبى لبكرات اللانثانوم في المحيط المائي بواسطة مركبات الأيثرات التاجية (بنزو-15-كراون-5 ، 18-كراون-6 ، ثنائي بنزو-18-كراون-6 ، ثنائي سايكلو هكساييل-18-كراون-6 و ثنائي بنزو-24-كراون-8) المذابة في 1 ، 2- ثنائي كلورو إيثان أو المذيبات العضوية الأخرى . من تحليل قيم الأندحارات تقترح النتائج المستحصلة أن أيون اللانثانوم يكون معقدات 1:1 مع بنزو-15-كراون-5 ، 18-كراون-6 ، ثنائي بنزو-18-كراون-6 و ثنائي سايكلو هكساييل-18-كراون-6 بينما يكون أيون اللانثانوم معقد ساندويج 2:1 مع ثنائي بنزو-24-كراون-8.

تم دراسة العوامل التي تؤثر على قيم نسب التوزيع لأيون اللانثانوم مثل زمن التوازن وتأثير قطبية المذيب العضوي ، طبقت تقنية بولاروغرافي التيار المباشر (DCP) وتقنية بولاروغرافي النبضي المشتق (التفاضلي) (DPP) باستخدام 1ر. مولاري – كلوريد البوتاسيوم كالكتروليت ساند