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Separation of Some Lanthanide (III) Ions by using 18-Crowns-6 Derivatives from Acidic Solution

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Abstract: The aim of this study is investigation of extraction ability of some lanthanide (III) ions; La^{3+} , Ce^{3+} , Pr^{3+} , Eu^{3+} and Er^{3+} , by using 18C-6, DB18C-6, DCH18C-6, DBP18C-6 as extractant in presence of trichloroacetic acid, from acidic solutions, in DMSO/water system. In this regard influence of trichloroacetic acid concentrations on stability and selectivity of extraction were studied. Experimental results showed that separation efficiency of mentioned ions with 18C6 and DCH18C6 in the presence of trichloroacetic acid, as counter anion, was improved and showed that is far more efficient than with DB18C6 and DBP18C6 or when nitric or acetic acid is used instead of trichloroacetic acid. Effective concentration of trichloroacetic acid was optimized and order of separation factors as $18\text{C}6 > \text{DCH}18\text{C}6 > \text{DB}18\text{C}6 > \text{DBP}18\text{C}6$, were found for each lanthanide ions. Also, obtained distribution coefficient values of lanthanide ions decreased with increasing atomic number of ions. The experimental conditions are presented and chemically structure effect of derivative crowns on separation efficiency will be discussed. Determination of lanthanide (III) ions were performed with ion chromatography techniques.

Key words: Separation, lanthanides, crown ethers, DMSO, trichloroacetic acid

INTRODUCTION

Due to importance of lanthanide complexes, in optical imaging of cells, medical diagnostics, contrast reagents in MRI, shift reagents in NMR (Bunzli and Piguet, 2002), as well as, their potential applications in fundamental and applied science (Gupta *et al.*, 2003) they are of interest in recent years. Ion exchange materials have found extensive application in view of their characteristics such as good selectivity. Moosavi *et al.* (2009) and Jayswal and Chudasama (2007) but In relation to selectivity, crown ethers have more excellent characteristics. Many of the applications of crown ether compounds are based on their complexing ability with various cations and hence, study of the stability of their complexes with metal cations and also the factors which affect their stability are important in many procedures such as separation, extraction, ion transport, chromatography and selectivity of analytical methods. It has been shown that the stability of lanthanide (III) complexes of crown ethers in solutions are distinctly changed and even in some cases prevented from formation of complexes and also thermodynamic behavior of some of these complexes have been reversed by changing the solvent, the flexibility of the crown ether ring and also by the counter ion (Liu *et al.*, 1993, 1998).

The ability of crown ethers were of special significance when new extraction processes were developed for extraction of radioactive elements from chemically complex solutions in the high level radioactive wastes, which contain significant amounts of lanthanide ions (Horwitz *et al.*, 1991). Extraction of the lanthanide elements can also serve as a model for studying extraction of the actinide elements. So, the design of selective macrocycle compounds is of both theoretical and applied significance for the development of radiochemistry. Wenji *et al.* (1983) examined different kinds of crowns, with 15 to 24 atoms in their rings, in the extraction of the lanthanides and actinides from nitrate solutions. They obtained best results for neodymium ($D = 0.615$) when 1 M DCH18C6 was used and salting out was carried out with 8 M NH_4NO_3 .

In earlier study, we have used a competitive spectrophotometric method to study the complexation of some derivative 18 membered crown ethers, 18-Crowns-6 (18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DCH18C6) and dibenzopyridino-18-crown-6 (DBP18C6) and murexide ligand with La^{3+} , Ce^{3+} , Pr^{3+} and Er^{3+} cations in DMSO to inspect the influence of various factors such as rigidity, substituent and ring size of the crown ethers and murexide concentration (Zolgharnein *et al.*, 2003). In the present study, we used

the 18C6, DB18C6, DCH18C6 and DBP18C6 to extract and separate the La^{3+} , Ce^{3+} , Pr^{3+} , Eu^{3+} and Er^{3+} cations in DMSO/water binary mixed solvent to inspect the influence of the TCA concentration as counter ion on the stability and selectivity of the complexes formed between these cations and macrocyclic ligands. The experimental conditions are presented and chemically structure effect of derivative crowns on separation efficiency will be discussed.

MATERIALS AND METHODS

This research project was conducted from February 2008 to April 2009 in Fule Cycle Research School in Esfahan and was sponsored by Nuclear Science and Technology Research Institute.

Reagent grade nitrate of lanthanides (all from Merck) were of the highest purity available and used without any further purification. Macrocycles 18C6, DB18C6, DCH18C6, DBP18C6; (Fig. 1a-d), were purchased from Merck. Reagent grade Dimethylsulfoxide (DMSO) and Trichloroacetic Acid (TCA) from Merck were also used. Test solutions for the extraction experiments were prepared by diluting the stock solution, which was a solution containing 1000 ppm of each lanthanide ions in 1 M HNO_3 . The stock solution was diluted with ultra pure deionized water and trichloroacetic acid added until the concentration of each metal ions became 100 ppm. Trichloroacetic acid with concentrations of 0.5, 1, 1.5, 2, 2.5 and 3 mol L^{-1} were used. The macrocycles concentration used in the extraction solutions was

0.05 mol L^{-1} ; the solvent used was DMSO. After the extraction and phase separation by 20 mL chloroform, back extraction with ultra pure deionized water was carried out.

Adsorption experiments were performed in 50 mL glass bottles containing 10 mL of different concentrations of each lanthanide ions and 10 mL of crowns solution to evaluate ion separation factor. To investigate the effect of trichloroacetic acid concentration different concentration of this acid were added to each bottle. The trichloroacetic acid concentration was determined by titration of the back extraction solutions with 0.1 M of NaHCO_3 solution. All batch experiments were carried out at ambient temperature ($25 \pm 2^\circ\text{C}$) and all the solutions were shaken on a magnetic stirrer for 5 min. The quantities of adsorbed ions were calculated by the difference of the initial and residual amounts of ions in solution divided by ion analysis.

The measure of the extraction efficiency of macrocycles represented by the distribution coefficient D in the whole extraction of 5 lanthanide ions. The degree of metal extraction and selectivity criterion showed by the separation factor D_1/D_2 , where D_1 and D_2 are the distribution coefficients of cation 1 and cation 2, respectively.

The determination of Lanthanides was performed utilizing an ion chromatograph system (Dionex, DX-100 USA). This instrument was equipped with a gradient pump module, a conductivity and UV-Vis detector and with the use of Dionex Ion Pac CS3 + CG3 column (sulfonic acid type), α -hydroxyisobutyric acid (a-HIBA) as an eluent and Arsenazo III as color forming reagents, was elaborated. The injection volume was 50 μL and three replicate injections were made for each sample.

RESULTS

Interesting results were obtained from the extraction experiments in the presence of trichloroacetic acid. It was found from new data that 18C6 and DCH18C6 extracted the lanthanide ions under these conditions; the extraction by DB18C6 and DBP18C6 was insignificant. Distribution factors of the total of 5 lanthanide ions as a function of trichloroacetic acid concentration in the extraction by 0.05 M 18C6 showed in Fig. 2. The curves for each of 5 cations shows a rising trend with increasing trichloroacetic acid concentrations. Figure 3 represent extraction of 5 lanthanides ions with DCH18C6. In Fig. 3, D factor in comparison shows the same trend as Fig. 2 except that maximums for all ions were diminished. Analogous curves were obtained for DB18C6 and DBP18C6. In Fig. 4 extraction of 5 cations with DB18C6 are displayed. Also in Fig. 4 as we can see decreasing trend of D factor by

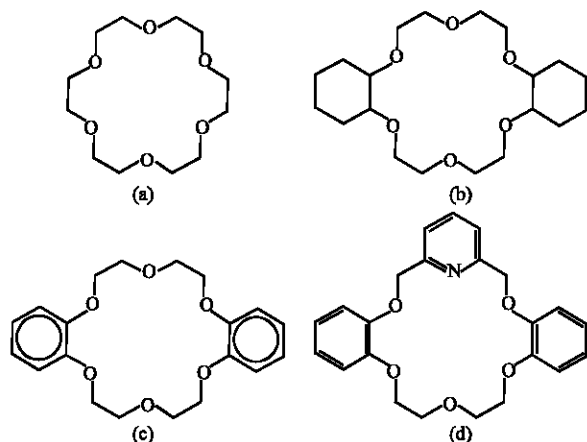


Fig. 1: Chemical structure of derivative 18 membered crown ether that used in this study; (a) 18-Crowns-6 (18C6), (b) dibenzo-18-crown-6 (DB18C6), (c) dicyclohexano-18-crown-6 (DCH18C6) and (d) dibenzopyridino-18-crown-6 (DBP18C6)

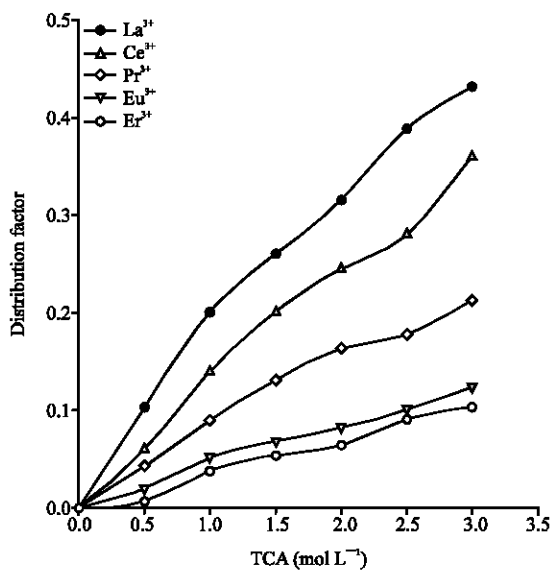


Fig. 2: Distribution factor of La^{3+} , Ce^{3+} , Pr^{3+} , Eu^{3+} and Er^{3+} as a function of Trichloroacetic Acid (TCA) concentration in the extraction of them by 0.05 M 18C6

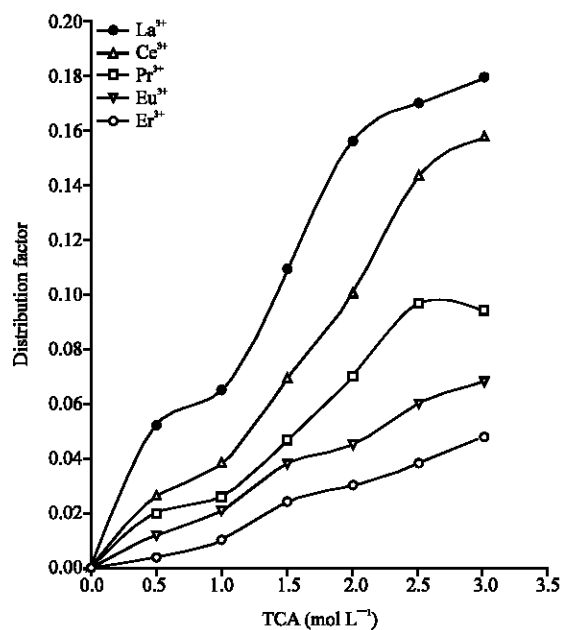


Fig. 4: Distribution factor of La^{3+} , Ce^{3+} , Pr^{3+} , Eu^{3+} and Er^{3+} as a function of TCA concentration for the extraction of them by 0.05 M DB18C6

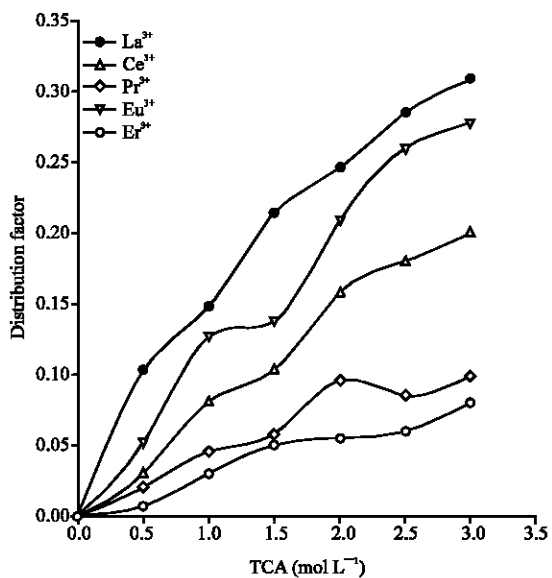


Fig. 3: Distribution factor of La^{3+} , Ce^{3+} , Pr^{3+} , Eu^{3+} and Er^{3+} as a function of TCA concentration in the extraction of them by 0.05 M DCH18C6.

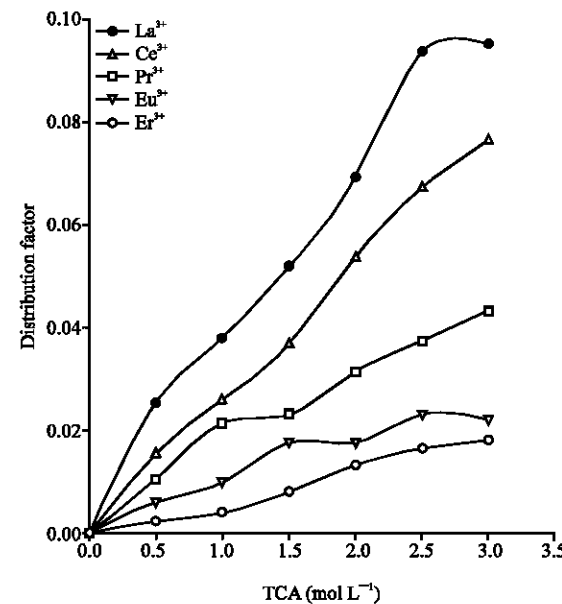


Fig. 5: Distribution factor of La^{3+} , Ce^{3+} , Pr^{3+} , Eu^{3+} and Er^{3+} as a function of TCA concentration for the extraction of them by 0.05 M DBP18C6

change of ligand. Figure 5 shows extraction of 5 lanthanides ions with DBP18C6. we can see least D factor for Fig. 5. It is interesting that the lanthanides distribution coefficients values decreased with increasing atomic number. Figure 6 which is a plot of Log D factor versus

Log Crown ethers concentrations, showed that the metal: crown ratio in complex for all cases is 1:1. Table 1 showed the numerical values of lanthanide ions separation factor

Table 1: Numerical values of lanthanide ions

Type of crown	Separation factor									
	La/Ce	La/Pr	La/Eu	La/Er	Ce/Pr	Ce/Eu	Ce/Er	Pr/Eu	Pr/Er	Eu/Er
18C6	1.43	2.22	4.0	5	1.56	2.8	3.50	1.8	2.25	1.25
DCH18C6	1.15	1.88	3.0	5	1.63	2.6	4.33	1.6	2.67	1.67
DB18C6	1.75	2.33	3.5	7	1.33	2.0	4.00	1.5	3.00	2.00
DBP18C6	1.33	2.00	4.0	--	1.50	3.0	--	2.0	--	--

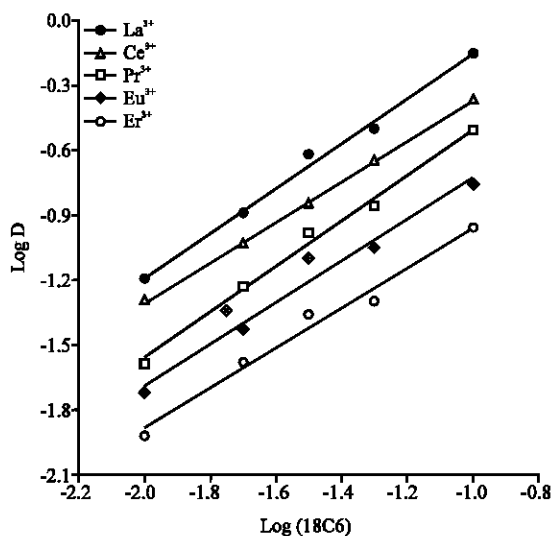


Fig. 6: Distribution factor of La³⁺, Ce³⁺, Pr³⁺, Eu³⁺ and Er³⁺ as a function of 18C6 concentration in the extraction of them in the presence of 2 M TCA

in DMSO/water system and in the presence of trichloroacetic acid and nitric acid solution.

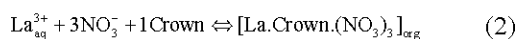
Also the trichloroacetic acid distribution in the lanthanides extraction were studied. We know that the extraction of the lanthanide ions in pure nitric or perchloric acid did not occur (Demin *et al.*, 2006). The trichloroacetic acid distribution between the two phases were not affected by the type and concentration of the macrocycles and the lanthanide metals concentration in the organic phase in the extraction process. In all cases, the trichloroacetic acid concentration in the organic phase was greater than the total lanthanide ions concentration.

DISCUSSION

As a general reaction for extraction of lanthanide ions, the extraction process represented as:



So, e.g., for La³⁺:



reaction constant of extraction process is:

$$K = \frac{[ML_nA_m]_{org}}{[M_{aq}^{n+}][A_{aq}^{-}]^n [L_{org}]^n} \quad (3)$$

and distribution constant is:

$$D = \frac{[ML_nA_m]_{org}}{[M_{aq}^{n+}]} \quad (4)$$

In this manner, the extraction constant became:

$$K_{extr} = \frac{D}{[A_{aq}^{-}]^n [L_{org}]^n} \quad (5)$$

Then, equation of a straight line showed by:

$$\text{Log} \left(\frac{D}{[A_{aq}^{-}]^n [L_{org}]^n} \right) = n \text{Log} L_{org} + \text{Log} K_{extr} \quad (6)$$

where, $L_{org} = L_{total} - m c_{org}$, $m = 3$ and c_{org} is the metal concentration in the organic phase. Here, $mc_{org} \ll L_{total}$.

By a plot of $(D/[A_{aq}^{-}]^n)$ versus L_{org} for the extraction of lanthanide ions mixture with four crown ethers (Fig. 6), the n value for the extracted complex, from the slope of the linear plot were obtained. Each plot has one slope, which indicates that a 1 : 1 complexes is formed. Thus the metal: crown ether ratio in the extracted complex in all cases is 1:1 which in this regard supports previous work result. In addition to the slope method, also the stoichiometry of the complexes of these elements were examined in our previous work (Zolgharnein *et al.*, 2003) by the mole ratio method. As we reported there, the stability of the La³⁺, Ce³⁺, Pr³⁺, Eu³⁺ and Er³⁺ complexes with the various 18-crowns-6 in DMSO increases in the order La³⁺ > Ce³⁺ > Pr³⁺ > Eu³⁺ > Er³⁺. This order in stability is fairly small when compared with the specificity displayed by the groups IIA ions. Since the best fit of metal ion to ligand cavity is a prime necessary for complex stability. La³⁺ ion with an ionic radius of 1.061 Å should fit nicely inside the cavities of 18-crowns with radii of 1.3-1.6 Å (Ohyoshi, 1985; Jain and Gupta-Bahaya, 1992). The other cations with smaller radii are too loose for the cavities of the 18 membered ring. Therefore weaker complexes were expected. The fact that the trivalent lanthanide ions have radii comparable to Na⁺ and Ca²⁺ leads to the expectation that lanthanide ions would also form stable complexes with 18-crowns. There

are at least two factors that may account for the lack of high stability constants in lanthanide complex formation. First, the radii decreases by only ca. 0.2 Å from La³⁺ to Er³⁺. This is much less than the differences in radii among the ions of groups IA and IIA. Second, using dimethylsulfoxide as the solvent removes difficulties associated with metal ion hydrolysis, but the solvent may specifically interact with metal complexes (Pizer and Selzer, 1983). Extension of these ideas to lanthanide ions suggest that because of their higher coordination number (Bunzli *et al.*, 1982; Habeschuss and Spedding, 1980), lanthanide complexes may interact significantly with the solvent. Comparison of the evaluated distribution coefficient for different 18-crown-6 with lanthanide ions, follow the order 18C6 > DCH18C6 > DB18C6 > DBP18C6.

This sequence of order except for DBP18C6 has been reported before only for potassium ion (Tawarah and Ababneh, 1997), transition metal ions (Alizadeh and Shamsipur, 1993), thallium ion (Parham and Shamsipur, 1993) and alkali metal ions (Frensdorff, 1971; Izatt *et al.*, 1976). Information about the complexation of DBP18C6 is rare (Tawarah and Ababneh, 1997; Shamsipur and Zolgharnein, 2001). The presence of three aromatic moieties in this macrocycle substantially reduced the affinity of the donor atoms toward the lanthanide ions. Introducing the pyridyl unit in to the ring decreases both the flexibility and interaction of the macrocycle with lanthanide ions. This may be due to the pyridino nitrogen not being able to donate to the inner d orbital of lanthanide ions; on the other hand, these cations are so strongly solvated that considerably more energy must be expended in the desolvation step. The contribution of the solvent-complex and even solvent-ligand interactions on the stability of the resulting complexes cannot be ignored. Since, the two main parameters for specificity and affinity of complexation of metal ions with these macrocycles are size and solvating power. Literature review (Izatt *et al.*, 1976, 1985, 1991; Zhu and Izatt, 1990; Alizadeh and Shamsipur, 1993; Frensdorff, 1971; Kashanian and Shamsipur, 1989), clearly shows both two trends for complexation of 18-membered crowns with various metal ions group. These order are 18C6 > DCH18C6 > DB18C6 > DBP18C6 for macrocycles and group IA > group IIA > lanthanide (III) ions. So this trend for similar ionic size cations is Na⁺ (Frensdorff, 1971; Izatt *et al.*, 1976), > Ca²⁺ (Demin *et al.*, 2006), > La³⁺ (Pedersen, 1967; Zolgharnein *et al.*, 2003), for all 18-membered crowns.

The conclusion of this research shows that the 18-crowns-6 and DCH18C6 in presence of trichloroacetic acid extract the lanthanide ions and separate them from each other. These macrocyclic ligands also promote the isolation and recovery efficiency of extraction of the

lanthanide ions, in particular when phosphorus and binary extractants are used (Nishihama *et al.*, 2002; Egorova *et al.*, 2005; Zhu *et al.*, 1996).

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