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## Synthesis of alkyl substituted dicyclohexano-18-crown-6 homologues for strontium extraction in HNO<sub>3</sub> media

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### Abstract

A series of dicyclohexano-18-crown-6 (DCH18C6) homologues containing different alkyl substituents were synthesized for a comparative study of the extraction ability towards strontium. The synthesis and the structure characterization of the intermediates and the products were detailed. The crown ether homologues were labeled as C<sub>X</sub>-DCH18C6 (X=3~7), where the X represents the number of the carbon atoms in the alkyl substituents. The extraction ability of the C<sub>X</sub>-DCH18C6 samples towards strontium in solvent extraction system was investigated. The substituent effect of the samples was discussed, and the factors affecting the separation such as solvent, acidity and initial metal concentration were examined.

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**Keywords:** DCH18C6; Dt-BuCH18C6; strontium separation; synthesis; high level liquid waste

### 1. Introduction

The treatment of radioactive waste is of great importance for the long-term development of nuclear energy. Every year, a large amount of high level liquid waste (HLLW) containing multiple hazardous fission products was generated during the reprocessing of spent fuels. Among which, strontium-90 is one

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of the typical long-lived ( $T_{1/2}=28.5$  years) nuclides and heat generators[1]. Separating such a fission product (FP) prior to vitrification is of great benefit for the volume reduction as well as the geological disposal of the radioactive waste[2]. To reach the goal, several methods including chemical precipitation[3], ion exchange[4], solvent extraction[5,6], adsorption[7], and extraction chromatography[8] have been developed. Considering the fact that radioactive liquid waste usually contains miscellaneous salt ions, selectivity to Sr(II) should be highlighted for the researches on separation methods. Hence, much efforts have been directed towards the exploration of effective extractants with specific affinity to Sr(II) .

Since the pioneering work of Pedersen[9,10], crown ether has attracted extensive interests of various research fields such as hydrometallurgy, catalysis, analytical chemistry, etc[11]. In recent years, it has been found that some eighteen-membered crown ethers, especially the dicyclohexano-18-crown-6 (DCH18C6) and its *tert*-butyl substituted derivative, exhibit favourable extraction ability and selectivity towards Sr(II) [12,13]. Using these macrocyclic ethers as extractants, the research on strontium separation from radioactive liquid waste has been greatly pushed forward. Horwitz et al. reported a novel strontium-selective chromatographic resin. By impregnating a 1-octanol solution containing DtBuCH18C6 into an inert polymeric support (XAD-7), a new kind of Sr-resin, which was called Sr-Spec (for Strontium Specific), was developed for the separation of Sr(II) in  $\text{HNO}_3$  solution[8,14]. Kumar et al. investigated the extraction of strontium by DCH18C6 in aliphatic alcohols as diluents. A mixture system containing 80% butanol-20% octanol was found to give optimal separation performance[15]. Meanwhile, practical separation process for strontium in radioactive liquid waste has also been developed. Zhang et al. reported a DtBuCH18C6 impregnated macroporous silica-based polymeric composite and proposed the SPEC process for chromatographic separation the Sr(II) in HLLW[16-18].

Substituents in the extractants can largely influence the binding strength to target ions. Evidences can be given by the different extraction ability of DCH18C6 and its derivative with *tert*-butyl substituents DtBuCH18C6. However, during the past two decades, few attentions have been paid to the researches related to substituent effect on separation of strontium by crown ethers. In this work, a series of DCH18C6 homologues containing different alkyl substituents were synthesized for a comparative study of the extraction ability towards strontium. Firstly, alkyl substituted aromatic counterparts were obtained through a typical electrophilic substitution reaction between secondary/tertiary alcohols and dibenzo-18-crown-6 (DB18C6). Then, catalytic hydrogenation of the benzene groups under proper condition resulted in the corresponding DCH18C6 homologues. The synthesis and the structure characterization of the intermediates and the products were detailed. The crown ether homologues were labeled as  $\text{C}_X\text{-DCH18C6}$  ( $X=3\sim7$ ), where the X represents the number of the carbon atoms in the alkyl substituents. The extraction ability of the  $\text{C}_X\text{-DCH18C6}$  samples towards strontium in solvent extraction system was investigated. The substituent effect of the samples was discussed, and the factors affecting the separation such as acidity in the aqueous phase and initial metal concentration were examined.

## 2. Experimental

### 2.1. Reagents and instruments

Dibenzo-18-crown-6 (DB18C6, 98+%) and palladium on activated carbon (Pd/C, 10%) were supplied by Alfa Aesar. The ruthenium catalyst for the hydrogenation was prepared following Pichler's method[19]. Deionized water (resistivity  $> 18 \text{ M}\Omega\text{-cm}$ ) was obtained from a Milli-Q water purification system.  $\text{Sr}(\text{NO}_3)_2$  (99+%) was purchased from Beijing Chemical Co. The stock solutions of Sr(II) was prepared by dissolving  $\text{Sr}(\text{NO}_3)_2$  in deionized water. The analytical grade chemicals, such as hydrazine

hydrate, ethanol, tetrahydrofuran (THF), chloroform, acetic acid and nitric acid, were commercially purchased and used without further purification.

$^1\text{H}$  NMR spectra were obtained on a JOEL JNM-ECA600 NMR spectrometer. Mass spectra were determined by Perkin-Elmer API3000 LC/MS/MS spectrometry system. Nicolet Nexus 470 FT-IR was used to record the infrared (IR) spectra in KBr matrix in the range  $4000\text{--}400\text{ cm}^{-1}$ . The concentration of strontium in nitric acid solution before and after extraction was measured by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (Thermo Jarrel Ash mod. IRIS Advantage).

## 2.2. Synthesis of the DCH18C6 homologues ( $\text{C}_X\text{-DCH18C6}$ , $X=3\text{--}7$ )

The DCH18C6 homologues substituted with different alkyl groups ( $\text{C}_X\text{-DCH18C6}$ ,  $X=3\text{--}7$ ) were synthesized according to a similar method. The synthesis of  $\text{C}_4\text{-DCH18C6}$  was described here for instance. 3.6 g (0.01 mol) dibenzo-18-crown-6 (DB18C6) was dissolved in 60 mL dichloromethane in a flask. 27 g ( $\sim 0.08$  mol) polyphosphoric acid (PPA) was added. Under vigorous stirring, a solution of 10 mL ( $\sim 0.1$  mol) *tert*-butanol in 20 mL dichloromethane was dropwise added (over 30 min). Then, the reaction was carried out under reflux for at least 2 h. After the reaction, deionized water was poured into the flask to hydrolyze the PPA. The organic phase was repeatedly washed to neutral and separated. After evaporating the solvent, white solid was collected. The crude product was purified by recrystallization in *n*-heptane with a yield of 90%.  $^1\text{H}$  NMR (300 MHz, *d*-DMSO):  $\delta$  6.92 (2H, s), 6.84 (4H, t), 4.09 (8H, d), 3.82 (8H, m), 1.23 (18H, s). IR (KBr) ( $\nu$ ,  $\text{cm}^{-1}$ ): 3095, 2955, 2863, 1603, 1590, 1530, 1454, 1364, 1268, 1205, 1137. MS:  $[\text{M}+\text{H}]^+$  473.17 (calc. value for  $[\text{C}_{28}\text{H}_{40}\text{O}_6 + \text{H}]^+$  473.29).

10 g of di-*tert*-butyl-diphenyl-18-crown-6 was dissolved in 100 mL *n*-butanol in a high-pressure reactor. 1.0 g Pichler ruthenium catalyst, after activation at  $110\text{ }^\circ\text{C}$  for 1 h, was dispersed in a small amount of solvent and added to the reactor. Nitrogen was injected for three times to exclude the air. Then, high-pressure hydrogen with the pressure of 9 MPa was pumped to replace the nitrogen. The mixture was heated to  $135\text{ }^\circ\text{C}$  under with a stirring speed of 500 rpm. After 10-hour reaction, the reaction solution was separated by filtration. The final reduction product was obtained with the evaporation of the solvent. Yield: 83% (isomer mixture).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.54 (8H, m), 3.52 (8H, m), 3.39 (4H, m), 1.69 (4H, m), 1.44(4H, m), 1.27 (4H, m), 1.12 (2H, m), 0.94 (18H, s). MS:  $[\text{M}+\text{Na}]^+$  507.49 (calc. value for  $[\text{C}_{28}\text{H}_{52}\text{O}_6 + \text{Na}]^+$  507.70).

## 2.3. Extraction of strontium in $\text{HNO}_3$ media

Solvent extraction of strontium was performed in 5 mL glass vials with stoppers. The organic phase was prepared by dissolving the  $\text{C}_X\text{-DCH18C6}$  into different solvents including chloroform, *n*-butanol / *n*-octanol (80/20), and 30% TRPO-Kerosene. The concentration of each extractant in organic phase was 0.1 mol/L. The aqueous phase containing  $5 \times 10^{-3}$  mol/L Sr(II) was prepared in  $\text{HNO}_3$  media with different acidity (2 mol/L or 5 mol/L). After pre-equilibrium, the organic phase was violently agitated with an equal volume of aqueous phase in a thermostatic water bath at  $25.0 \pm 0.1\text{ }^\circ\text{C}$  for 20 min. Then, the mixture was centrifuged and both the organic and aqueous phases were collected. Deionized water was utilized to wash the organic phase for the elution of Sr(II). Both the concentrations of Sr(II) in organic and aqueous phase was measured by ICP-AES. The distribution ratio (D) is defined as the ratio of concentration of Sr(II) in organic phase to that in aqueous phase.

## 3. Results and discussions

### 3.1. Synthesis of the alkyl-substituted DCH18C6 derivatives

The DCH18C6 derivatives bearing different alkyl substituents were synthesized through a two-stage procedure. Fig. 1 shows the synthetic route. Firstly, substituents with different length of aliphatic chains were introduced onto the benzene groups of dibenzo-18-crown-6 (DB18C6). This is a typical electrophilic substitution reaction. DB18C6 was activated by the PPA catalyst, and secondary or tertiary alcohol was employed as electrophiles to attack the benzene groups. By-products can be totally avoided by carefully controlling the reaction conditions, especially the temperature during the hydrolysis of PPA at the end of the reaction. Then, catalytic hydrogenation was performed to transfer the benzene groups to cyclohexyl groups, which was a demanding reaction because of the steric hindrance of the bulky substituents. Harsh reaction conditions including high pressure and high temperature were involved. Due to the moderate catalytic activity and the poor-sensitivity to poisons, ruthenium powder was chosen as the catalyst, which enabled the complete hydrogenation of the substrate and a minimum amount of side products.

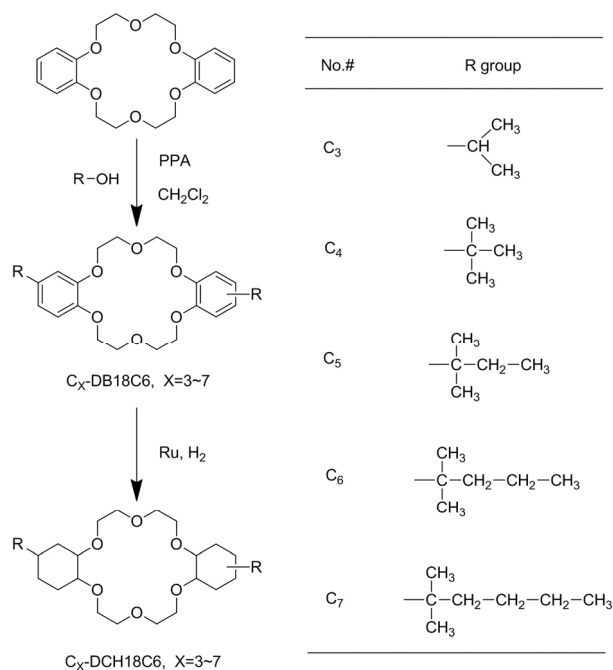


Figure 1. Synthesis route of the alkyl substituted dicyclohexano-18-crown-6

### 3.2. Solvent effect on extraction ability of strontium

Solvent effect on the extraction ability of the DCH18C6 homologues towards Sr(II) was investigated. Organic phases were prepared by dissolving the different extractants into chloroform, 30% TRPO-kerosene and *n*-butanol / *n*-octanol (80/20) with the concentration of 0.1 mol/L (Phase ratio=1). The aqueous phase was 5.0 mol/L nitric acid solution containing Sr(II) ion with the initial concentration of  $5.0 \times 10^{-3}$  mol/L. The result in Fig. 2 shows that solvent has obvious influence to the extraction ability of the C<sub>X</sub>-DCH18C6 (X=3~7) extractants. The highest distribution coefficient (~40.6) was achieved in chloroform system for the 6-carbon substituted crown ether. Meanwhile, *n*-butanol / *n*-octanol (80/20) was also a favorable solvent system that deserves consideration for application. Poorest extraction ability was obtained in 30% TRPO-kerosene system. Comparing the results in the same organic phase, it could

be seen that the distribution ratio of Sr(II) was evidently different for the C<sub>X</sub>-DCH18C6 (X=3~7) extractants with different length of the aliphatic chain. Basically, the extractants with longer substituents show better extraction ability towards Sr(II).

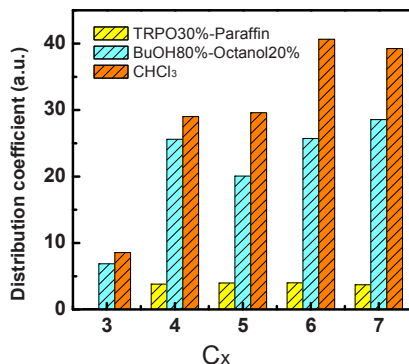
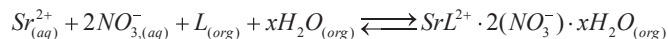


Figure 2. Effect of organic solvent on the C<sub>X</sub>-DCH18C6's extraction behavior. [Sr(II)] = 5.0 × 10<sup>-3</sup> mol/L, phase ratio=1, [HNO<sub>3</sub>] = 5.0 mol/L, [C<sub>X</sub>-DCH18C6] = 0.1 mol/L.

### 3.3. Effect of acidity on extraction ability of strontium

It has been demonstrated that HNO<sub>3</sub> participates in the complexation between strontium ions and crown ether extractants. The interaction between Sr(II) and crown ether extractant can be represented by the following equation [15],



where L refers to the ligand group of the extractant, the subscripts (aq) and (org) indicate the aqueous phase and organic phase, respectively. Therefore, the acidity of the aqueous phase can significantly affect the extraction performance of 2+the extractants. Fig. 3 shows the extraction behavior of the crown ether homologues in the *n*-butanol/*n*-octanol (80/20) system towards Sr(II) in HNO<sub>3</sub> solution with different acidity. It can be seen that under conditions of higher acidity (5mol/L HNO<sub>3</sub>), the extractants exhibit much better extraction ability.

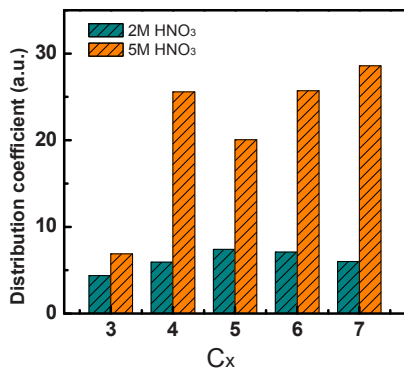


Figure 3. Effect of the nitric acid concentration on the C<sub>X</sub>-DCH18C6's extraction behavior in *n*-butanol/*n*-octanol (80/20). [Sr(II)] = 5.0 × 10<sup>-3</sup> mol/L, phase ratio=1, [C<sub>X</sub>-DCH18C6] = 0.1 mol/L.

#### 4. Conclusion

In this study, five kinds of dicyclohexano-18-crown-6 (DCH18C6) derivatives substituted by aliphatic chain with different length were synthesized. The two-stage synthetic route was detailed and the structures of the products were characterized. The extraction behavior of the crown ethers towards Sr(II) in nitric acid media was comparatively studied. Influencing factors including the chain length of the substituents, solvent, and acidity of the aqueous phase were investigated. The result showed that the highest distribution ratio was obtained when using chloroform as organic phase. Substituents with longer carbon chains benefited the extraction ability of the crown ether extractants. Higher concentration of HNO<sub>3</sub> in aqueous resulted in a better extraction of Sr(II). This series of the crown ether extractants, we believe, might find applications in the separation of strontium as well as some other metal ions in the future.

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