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Extraction Property of *p-tert*-Butylsulfonylcalix[4]arene Possessing Irradiation Stability towards Cesium(I) and Strontium(II)

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Abstract: Solvent extraction behavior of *p-tert*-butylsulfonylcalix[4]arene (SC4A) towards Cs(I) and Sr(II) from aqueous solutions was studied with respect to the effects of contact time, pH value, SC4A concentration, nitrate concentration and temperature. The extraction of Na(I), K(I), Mg(II), Ca(II), Ba(II), Pb(II), Cd(II), Zn(II), Co(II), Ni(II), and Ce(III) was also investigated. It was demonstrated that SC4A can sequester both Cs(I) and Sr(II) efficiently from aqueous solutions. According to extraction experiments, Fourier transform infrared and ¹H nuclear magnetic resonance analysis of the metal-SC4A complex, authors proposed a possible mechanism involving formation of an adjustable cavity from two SC4A molecules for the complexation of one alkaline earth metal ion, and the size of the adjustable cavity changes depending on the ion within an appropriate range. Irradiation stability of the SC4A was tested, the results indicated that the main structure of SC4A remained unchanged when the temperature was below 400 °C, and SC4A maintains excellent extraction ability for Cs(I) and Sr(II) under an irradiation dose of $1.0 \times 10^4 - 1.1 \times 10^6$ Gy.

Keywords: calixarene; extraction; cesium; strontium; irradiation

1. Introduction

Substantial quantities of radioactive contaminants are generated each year from nuclear weapon tests, nuclear facilities, and reprocessing of spent fuels due to military and industrial activities. A significant amount of soil [1] and water [2] is contaminated by these contaminants in some districts, which poses great risks to the environment and human health. It is known that radioactive ¹³⁷Cs and ⁹⁰Sr, with half-lives of 30.1 and 28.9 years, respectively, are major contaminants. ¹³⁷Cs is an analog of potassium that is easily incorporated in living organisms [3], and ⁹⁰Sr can be introduced into the food chain, which seriously threatens human health [4]. They also have an adverse impact on ecology [5,6]. Thus, removal of radioactive contaminants from contaminated water has become a significant environmental matter in recent years. In addition, the removed ¹³⁷Cs and ⁹⁰Sr isotopes have potential application as gamma radiation sources for medical and industrial applications [7,8]. Accordingly, further research for feasible separation processes to recover Cs(I) and Sr(II) is required.

Solvent extraction has been proved to be one of the most effective partitioning and recovery techniques from the viewpoints of speed, simplicity and easiness of scaling up. This method has been used for the removal of Cs(I) and Sr(II) for long time. Thus, the selection of the extractants plays an important role in the extraction process, and can greatly affect the separation efficiency. In the past few decades, some conventional and newly developed extractants have been used to study solvent extraction of Cs(I) and Sr(II). Crown ethers, such as 4,5"-bis(*tert*-octylbenzo)dibenzo-24-crown-8 [9], dibenzo-21-crown-7 (DB21C7) [10],

and 4',4',(5')-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) [11]; calixarene-crown ethers, such as 1,3-alternate calix[4]arene-crown-6 conformers [12], calix[4]dibenzocrowns-6 [13], calix[4]arene-bis(naphthocrown-6) [14], 25,27-bis(isopropoxy) calix[4]-26,28-crown-6 (iPr-C[4]C-6) [15], calix[4]arene-bis-(*tert*-octylbenzo-crown-6) (BOBCalixC6) [16,17], and acryl-calix[4]-crown-6 [18]; and amide agents, such as *N*,*N*,*N*,*N*-tetraoctyl-3-oxapentanediamide (TODGA) [19], are potent extractants for separating Cs(I) or Sr(II) from acid solutions. Bis(2-propyloxy)calix[4]crown-6 (BPC6) [20], calix[4]arene-bis(crown-6-ethers) [21,22], and 4-*tert*-butyl-2-(α -methylbenzyl) phenol (*t*-BAMBP) [23] have shown excellent extraction ability for Cs(I) from aqueous solutions. In addition, di-2-ethyl hexyl phosphoric acid (D2EHPA) [24] has been proved to be feasible for the separation of Sr(II) from alkaline solutions. The abovementioned studies showed that crown ethers are generally selective for Sr(II), and calixarene-crown ethers are mainly selective for Cs(I). Extractants that are selective for both Cs(I) and Sr(II) in an aqueous solution have not been reported yet. Using a single extractant with high selectivity for both Cs(I) and Sr(II) can simplify the treatment of wastewater. Therefore, an agent with the ability to extract them efficiently is highly desired.

Calixarenes have been regarded as molecular platforms or building blocks for the construction of metal ion carriers, which is an attractive motif in coordination chemistry [25,26]. The extraction process of calixarenes for industrial applications is extremely important [27]. Classical CH₂-bridged calixarenes were studied in cations extraction and transport [28,29], and calixarene amide ionophores for strontium extraction were also researched [30]. In our present work, low-cost *p-tert*-butylsulfonylcalix[4]arene (SC4A), possessing the ability to extract Cs(I) and Sr(II) efficiently, was investigated. In order to research the selectivity of SC4A for the target ions and the combined form of the extracted complex, Na(I), K(I), Rb(I), Mg(II), Ca(II), Ba(II), Pb(II), Cd(II), Zn(II), Co(II), Ni(II), Ce(III), and Y(III) were also extracted with SC4A for comparison. Meanwhile, *p-tert*-butylthiacalix[4]arene (TC4A) and *p-tert*-butylsulfonylcalix[4]arene tetraacetate (SC4AOEt) were applied to extract Cs(I) or Sr(II) to examine the effects of the OH and SO₂ groups on the extraction. The composition of the complex, thermodynamic data for the extraction procedure, extraction mechanism, irradiation stability, and high-temperature resistance of SC4A were also researched.

2. Materials and Methods

2.1. Reagents

Alkali metals nitrates $M^{I}NO_{3}$ ($M^{I} = Na$, K, Rb, and Cs); alkaline earth nitrates $M^{II}(NO_{3})_{2}$ ($M^{II} = Sr$, Ba), $Ca(NO_{3})_{2} \cdot 4H_{2}O$, and $Mg(NO_{3})_{2} \cdot 6H_{2}O$; rare earth metal nitrates $M^{III}(NO_{3})_{3} \cdot 6H_{2}O$ ($M^{III} = Ce$ and Y); and heavy metals nitrates $Cd(NO_{3})_{2} \cdot 4H_{2}O$, $Zn(NO_{3})_{2} \cdot 6H_{2}O$, $Co(NO_{3})_{2} \cdot 6H_{2}O$, $Ni(NO_{3})_{2} \cdot 6H_{2}O$ and $Pb(NO_{3})_{2}$, were of analytical grade. Salt solutions in nitric acid medium were prepared by dissolving the required weights of the above nitrates in nitric acid solutions. Ultrapure water was used for preparation of nitrate solutions. The desired pH was achieved by injecting negligible volumes of HNO₃ or NaOH. An IS128 pH meter was used to measure the adjusted pH.

SC4A and its raw material, TC4A (Figure 1), were synthesized in our laboratory according to a previously reported procedure [31] with modification. In the general synthesis procedure of SC4A, 25 mL of acetic acid and 2.57 g (16.71 mmol) of NaBO₃· $4H_2O$ were added to a solution of 1.8 g (2.48 mmol) of TC4A in 30 mL of chloroform. After the mixture was stirred at 55 °C for four days, the product was extracted with chloroform (100 mL × 3). The extract liquor was dried with anhydrous magnesium sulfate for 2 h, and then filtered and evaporated. Then, the white SC4A powder was recrystallized from ethanol and dried under vacuum. SC4AOEt (Figure 1) was prepared following a reported procedure [32]. Detail synthesis procedures of TC4A (Figure S1), SC4A (Figure S2), and SC4AOEt (Figure S3), and characterization data of them are described in Supplementary Materials. Analytical grade chloroform was used as a diluent to dissolve SC4A, TC4A, and SC4AOEt for the extraction process.



Figure 1. Structures of (**a**) *p-tert*-butylsulfonylcalix[4]arene (SC4A); (**b**) *p-tert*-butylthiacalix[4]arene (TC4A); and (**c**) *p-tert*-butylsulfonylcalix[4]arene tetraacetate (SC4AOEt).

2.2. Extraction Procedure

Equal volumes (5 mL) of organic phase and aqueous phase containing the elements were mixed in a conical flask and horizontally shaken at 150 rpm for 60 min in a thermostated water bath maintained at 298 \pm 0.5 K unless otherwise stated. Sequentially, the two phases were centrifuged at 4000 rpm for 5 min. Then, the concentrations of the ions were measured using a Nexion 300Q model inorganic mass spectrometer (ICP-MS) (PerkinElmer, Boston, MA, USA). The distribution ratio ($D_{\rm M}$) of element M was calculated using the following equation:

$$D_{\rm M} = C_{\rm (o)}/C_{\rm (a)} \tag{1}$$

where $C_{(0)}$ and $C_{(a)}$ represent the equilibrium concentrations of the tested ions in the organic and aqueous phase, respectively.

The separation factors of Cs(I) and Sr(II) (SF_{Cs} and SF_{Sr}) to other ions were, respectively, calculated as follows:

$$SF_{\rm Cs/M} = D_{\rm Cs}/D_{\rm M} \tag{2}$$

$$SF_{\rm Sr/M} = D_{\rm Sr}/D_{\rm M} \tag{3}$$

2.3. Irradiation Procedure and Thermogravimetric Analysis

Irradiations of SC4A and SC4A/CHCl₃ were carried out at 25 ± 0.2 °C in air using a ⁶⁰Co radiation source (China institute of atomic energy, Beijing, China) with a total absorbed dose ranging from 1.0×10^4 to 1.1×10^6 Gy.

Weighed quantities of SC4A were subjected to thermogravimetric analysis (TGA) in a nitrogen atmosphere using a TG/DTA6200 instrument (Seiko instruments inc, Tokyo, Japan) at a heating rate of $10 \, {}^{\circ}\text{C} \cdot \text{min}^{-1}$.

The structure of SC4A was analyzed using a Nicolet iS10 infrared (IR) spectrometer (Thermo Fisher, Waltham, MA, USA), Bruker DPX-400 nuclear magnetic resonance (¹H-NMR) spectrometer (Bruker, Karlsruhe, Germany), and Trace DSQ electrospray ionization mass spectrometry (ESI-MS) instrument (Thermo Fisher, Waltham, MA, USA).

3. Results and Discussion

3.1. Dependence of Extraction on Contact Time

To understand well the extraction performance of SC4A and TC4A, the effect of contact time on the extraction was investigated. Several ions including Cs(I), Sr(II), Na(I), K(I), Pb(II), Cd(II), Zn(II), Co(II), Ni(II) and Ce(III) were extracted at an initial pH of 6 (± 0.05) using 1.0×10^{-3} mol·L⁻¹ SC4A in CHCl₃ at different contact times. The results are displayed in Figure 2.



Figure 2. Dependence of the distribution ratio (*D*) of the tested elements onto SC4A with the change in contact time. Conditions: T = 298 K, [SC4A]_(o) = 1 × 10⁻³ M, [Metal]_(a) = 1 × 10⁻⁴ M, pH = 6 ± 0.05, shaking speed: 150 rpm.

As can be seen in Figure 2, the distribution ratios of Cs(I) (D_{Cs}) and Sr(II) (D_{Sr}) increased with an increase in contact time and were then maintained at approximately 27 and 20 after 15 and 20 min, respectively, which indicated that the extraction equilibrium had been reached. This was ascribed to the effective complexation of SC4A with Cs(I) and Sr(II). Meanwhile, Na(I), K(I), Pb(II), Zn(II), Co(II) and Ni(II) with distribution ratios less than 0.50 showed very poor or almost no extraction with SC4A. Moreover, when the extraction equilibrium was reached, the separation factors SF_{Cs} and SF_{Sr} to these metals were greater than 40. Although distribution ratios of 2.6 for Cd(II) and 4.4 for Ce(III) were observed, SF_{Cs} and SF_{Sr} to Cd(II) or Ce(III) were not less than 4.6. These data revealed that the influences of Cd(II) and Ce(III) on the selective extraction of Cs(I) or Sr(II) were not notable.

In order to get a complete understanding regarding to selectivity of SC4A for Cs(I) and Sr(II), further extraction were conducted on other alkaline earth metals Mg(II), Ca(II) and Ba(II), respectively, at the same extraction conditions. The results are listed in Table S1 (in Supplementary Materials). The distribution ratio for Mg(II), Ca(II) and Ba(II) are greater than 4, 48, and 17, respectively, when the extraction equilibrium was reached. The results showed that alkaline earth metals were favorable to the extraction of SC4A. The above discussion suggested high selectivity of SC4A for Cs(I) and Sr(II) can be explained by the Hard and Soft Acids and Bases (HSAB) rule [33]. The bridging SO₂ group of SC4A categorized as borderline acid that is sensitive to Cs(I) and alkaline earth metals incidentally.

3.2. Dependence of Extraction on pH

SC4A contains OH groups, and therefore its extraction abilities can be influenced by hydrogen ions or hydrogen-containing compounds through hydrogen bonding. To evaluate the impact of the pH, the extraction of the metals with SC4A at various pH values was investigated and the results are displayed in Figure 3. Separation factors SF_{Cs} and SF_{Sr} to other metals at different pH values were calculated and are listed in Table 1.



Figure 3. (a) Dependence of the distribution ratio (*D*) of the tested elements onto SC4A with a change in initial pH; and (b) relationship between log *D* and pH_e. Conditions: T = 298 K, [SC4A]_(o) = 1 × 10⁻³ M, [Metal]_(a) = 1 × 10⁻⁴ M, contact time = 120 min, shaking speed: 150 rpm.

Table 1. Separation I	Factor of Cs(I) a	nd Sr(II) to other m	etals at different initial	pH.
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Sonaration Factors		I	рН (±0.05)		
Separation Pactors	2	3	4	5	6
SF _{Cs/Na}	-	1.94	28.36	64.85	58.94
SF _{Cs/K}	9.14	25.89	24.71	77.90	115.4
SF _{Cs/Pb}	96.37	0.60	10.24	42.75	61.05
SF _{Cs/Ce}	21.51	0.10	1.37	3.94	6.28
SF _{Cs/Cd}	1.12	0.88	2.56	8.42	10.81
SF _{Cs/Zn}	-	160	162	>162	>162
$SF_{Cs/Co}$	-	-	121	>121	>121
SF _{Cs/Ni}	-	-	-	>10 ³	$>10^{3}$
SF _{Sr/Na}	-	1.35	8.36	42.25	44.17
SF _{Sr/K}	7.64	17.95	7.28	14.72	14.72
SF _{Sr/Pb}	80.60	0.42	3.02	38.07	45.74
SF _{Sr/Ce}	17.99	0.07	0.40	3.74	4.70
SF _{Sr/Cd}	0.94	0.61	0.76	7.59	8.10
SF _{Sr/Zn}	-	39.4	183	>183	>183
SF _{Sr/Co}	-	-	137	>137	>137
SF _{Sr/Ni}	-	-	-	>10 ³	>10 ³

Conditions: T = 298 K, [SC4A]_(o) = 1 × 10⁻³ M, [Metal]_(a) = 1 × 10⁻⁴ M, contact time = 60 min, shaking speed: 150 rpm.

As can be seen in Figure 3a, D_{Cs} and D_{Sr} increased along with the increase of the solution pH. D_{Cs} reached 27 at pH 6 and D_{Sr} reached 20 at pH 5, respectively. These implied the extraction abilities of SC4A in neutral or weak acidic solution to Cs(I) and Sr(II) are better than that in strong acidic solution. However, the distribution ratios of Na(I), K(I), Pb(II), Zn(II), Co(II) and Ni(II) were less than 0.4, indicating poor or almost no extraction with SC4A. Although the maximum distribution ratios for Cd(II) and Ce(III) were 2.55 and 4.90 respectively at pH 6, the $SF_{Cs/Cd}$, $SF_{Cs/Ce}$, $SF_{Sr/Cd}$, and $SF_{Sr/Ce}$ values under identical experimental conditions were 6.28, 10.81, 8.10, and 4.70, respectively, as can be seen in Table 1. This result indicated that SC4A had efficiently selective separation ability for Cs(I) or Sr(II), and the above mentioned coexistent metals may have no adverse impacts on the extraction and separation of the target ions. Experiments were not carried out at pH > 7 because

metal precipitation occurs at higher pH. Therefore, pH 6 was chosen as the optimum pH value for the following extraction experiments.

Since the extraction of Cs(I) or Sr(II) is pH dependent, it appears that the phenolic hydroxyl groups of SC4A have substantial contribution on the observed extraction ability. This can be confirmed by the results of log *D* versus equilibrium pH (pH_e), as shown in Figure 3b. The plot for Cs(I) and Sr(II) showed that the slopes are equal to 1.09 and 1.74, which indicated that 1 and 2 protons were released upon complexation, respectively.

3.3. Dependence of Extraction on SC4A Concentration

In order to determine the stoichiometry of the extracted complex containing Cs(I) and Sr(II), the effect of SC4A concentration on the extraction was investigated. Under fixed experimental parameters, varying the SC4A concentration in the organic phase altered the distribution ratio. As shown in Figure 4, the distribution ratios of Cs(I) and Sr(II) were enhanced as SC4A concentration increased, and a linear relationship was established between log *D* and log [SC4A]. Specifically, the plot of log D_{Cs} versus log [SC4A] showed a slope of 1.07, suggesting 1:1 stoichiometry of Cs(I) and SC4A. Similarly, another straight line with a slope of 1.78 was obtained for Sr(II), this value indicated the participation of two molecules of SC4A and one Sr(II) in the extracted complex.



Figure 4. Relationship between log *D* and log [SC4A]. Conditions: T = 298 K, pH = 6, [Metal]_(a) = 1 × 10⁻⁴ M, contact time = 60 min, shaking speed: 150 rpm.

3.4. Dependence of Extraction on Nitrate Concentration

In order to investigate the type of complex formed, either ionic complex by ionization of phenolic group or the ion-pair complex by co-extraction of nitrate ion, the effect of nitrate concentration on the extraction was investigated. SC4A can hardly extract Na(I), thus sodium nitrate was added to aqueous phase to obtain desired nitrate concentration. A plot of log *D* versus log Na[NO₃⁻] was constructed and shown in Figure 5. It can be seen that there is no significant effect of nitrate ion on extraction of Cs(I) and Sr(II). This result confirmed that the electroneutrality of the metal-SC4A complex was achieved by ionization of phenolic group(s) rather than the involvement of nitrate ion at the extraction conditions.



Figure 5. Relationship between log *D* and log Na[NO₃⁻]. Conditions: T = 298 K, pH = 6, [SC4A]_(o) = 1×10^{-3} M, $[Cs^+]_{(a)} = [Sr^{2+}]_{(a)} = 1 \times 10^{-4}$ M, contact time = 60 min, shaking speed: 150 rpm.

3.5. Dependence of Extraction on Temperature

In spite of a variety of studies on metal extraction thermodynamics [34], to the best of our knowledge, the thermodynamics for the extraction of Cs(I) and Sr(II) with SC4A have seldom been reported. They are important for understanding the nature of the extraction process and predicting the extraction rate. The extraction of Cs(I) and Sr(II) with SC4A was examined at different temperatures between 288 and 308 K. A plot of ln *D* versus 1/T was constructed, as shown in Figure 6.



Figure 6. Relationship between ln *D* and 1/T. Conditions: $[SC4A]_{(o)} = 1 \times 10^{-3}$ M, $[Meta]_{(a)} = 1 \times 10^{-4}$ M, pH = 6, contact time = 60 min, shaking speed: 150 rpm.

As can be seen in Figure 6, increasing the extraction temperature resulted in an obvious decrease in D_{Cs} and D_{Sr} , indicating that the extraction reaction is exothermic. Therefore, increasing the operation temperature in the experimental conditions adversely affected the extraction.

It could be determined from Figures 3–5 that the extracted species of Cs(I) and Sr(II) with SC4A are Cs·SC4A and Sr·2SC4A, respectively, the extraction equilibrium of Sr(II) is similar to that reported in the literature [35], and can be expressed as follows:

$$\mathrm{Sr}^{2+}_{(a)} + 2\mathrm{H}_4\mathrm{L}_{(o)} \rightleftharpoons \mathrm{Sr} \cdot 2\mathrm{H}_3\mathrm{L}_{(o)} + 2\mathrm{H}^+_{(a)}$$
 (4)

where H_4L and $Sr \cdot 2H_3L$ are free SC4A and Sr-SC4A complex.

The conditional extraction equilibrium constant, K_{ex1} , in Reaction (4) is described as:

$$K_{\text{ex}} = [\text{Sr} \cdot 2\text{H}_3\text{L}]_{(0)} [\text{H}^+]^2{}_{(a)} / ([\text{Sr}^{2+}]_{(a)} [\text{H}_4\text{L}]^2{}_{(0)})$$
(5)

The distribution coefficient D_{Cs} is defined as:

$$D_{\rm Sr} = [{\rm Sr} \cdot 2{\rm H}_3 {\rm L}]_{(0)} / [{\rm Sr}^{2+}]_{(a)}$$
(6)

According to Equations (5) and (6), the relationship between the distribution ratio and the extraction constant can be described as:

$$\ln D_{\rm Sr} = \ln K_{\rm ex} + 2\ln \left[{\rm H}_4 {\rm L} \right]_{\rm (o)} - 2\ln \left[{\rm H}^+ \right]_{\rm (a)} \tag{7}$$

Thus, the change in the enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°) during the extraction procedure can be calculated using the Arrhenius law and the Gibbs–Helmholtz equation:

$$d \ln K_{\rm ex}/dT = \Delta H^{\circ}/(RT^2)$$
(8)

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{9}$$

Then, $\ln D_{Cs}$ can be calculated using the following equation:

$$\ln D_{\rm Sr} = -\Delta H^{\circ} / (\rm RT) - 2\ln[\rm H^+]_{(a)} + 2\ln[\rm H_4L]_{(o)} + \Delta S^{\circ} / \rm R$$
(10)

Similar to the calculation of $\ln D_{Sr}$, $\ln D_{Cs}$ can be expressed as (the calculation of $\ln D_{Cs}$ in Supplementary Materials):

$$\ln D_{\rm Cs} = -\Delta H^{\circ} / (\rm RT) - \ln [\rm H^+]_{(a)} + \ln [\rm H_4 L]_{(o)} + \Delta S^{\circ} / \rm R$$
(11)

The values of ΔH° and ΔS° were determined from the slope and intercept respectively as shown in Figure 6. The values of ΔH° , ΔS° and ΔG° of the system were summarized in Table 2. The ΔH° was negative indicating that the extraction of Cs(I) or Sr(II) with SC4A was an exothermic process. The negative values of ΔS° suggested a decrease in degree of freedom of the system as the metal ions are restricted by complex formation. ΔG° was negative, indicating that the reaction is spontaneous.

Table 2. Thermodynamic parameters of the solvent extraction.

Conditions		Cs(I)			Sr(II)	
Temperature	ΔH° (kJ· mol $^{-1}$)	ΔS° (kJ· mol $^{-1}$ K $^{-1}$)	ΔG° (kJ· mol $^{-1}$)	ΔH° (kJ· mol $^{-1}$)	ΔS° (kJ· mol $^{-1}$ K $^{-1}$)	ΔG° (kJ· mol $^{-1}$)
288 K			-3.49			-6.44
293 K			-3.03			-4.85
298 K	-29.29	-0.09	-2.56	-80.38	-0.26	-3.51
303 K			-2.09			-2.08
308 K			-1.62			-0.69

Conditions: $[SC4A]_{(o)} = 1 \times 10^{-3} \text{ M}$, $[Metal]_{(a)} = 1 \times 10^{-4} \text{ M}$, pH = 6, contact time = 60 min, shaking speed: 150 rpm.

3.6. Function of Groups and Coordination Feature

It is known that small modifications in the structures of calixarenes can generate a significant change in distribution coefficients, and lead to distinctly different extraction behaviors [36]. Morohashi [37] reported that the sulfonyl oxygen and adjacent phenol moieties of *p*-tetramethyl-butylsulfonylcalix[4]arene take part in coordination to metal ions. SC4A has a structure similar to that of *p*-tetramethyl-butylsulfonylcalix[4]arene with four OH groups and SO₂ groups.

To examine the effects of OH groups and SO₂ groups on extraction ability toward Cs(I) and Sr(II), TC4A containing sulfur atoms instead of SO₂ groups, and SC4AOEt containing OCH₂COOC₂H₅ groups rather than OH groups (Figure 1) were also employed to the extraction of Cs(I) and Sr(II) at various pH values. The results are listed in Table 3.

Conditions		D _{Cs}			D _{Sr}	
pH (±0.05)	SC4A	TC4A	SC4AOEt	SC4A	TC4A	SC4AOEt
2	0.13	0.07	0.07	0.04	0	0.25
3	1.60	0.06	0.09	0.39	0	0.28
4	4.86	0.04	0.10	5.49	0.01	0.30
5	19.32	0.02	0.12	20.04	0	0.31
6	27.62	0.04	0.17	20.67	0	0.35

Table 3. Distribution ratio of metals with a change in pH.

Conditions: T = 298 K, $[SC4A]_{(0)} = [TC4A]_{(0)} = [SC4AOEt]_{(0)} = 1 \times 10^{-3}$ M, $[Metal]_{(a)} = 1 \times 10^{-4}$ M, contact time = 60 min, shaking speed: 150 rpm.

According to Table 3, TC4A can hardly extract Cs(I) or Sr(II), indicating interaction between soft sulfur atoms of TC4A and Cs(I) or Sr(II) is not favorable. SC4A displayed better extraction ability, since the lone pair electrons of the sulfonyl oxygen can coordinate to Cs(I) and Sr(II). Meanwhile, it can be seen that SC4AOEt displayed weak extraction ability. The observed gap in extraction ability of SC4A and SC4AEt are likely due to the ionization potential of OH groups of SC4A.

To well understand the binding location of Cs(I) and Sr(II), SC4A-Cs(I) and SC4A-Sr(II) complexes were obtained by drying the organic phases in air after extraction. Their IR spectra are presented in Figure 7. It can be seen that the characteristic absorptions at 3412 cm^{-1} in the IR spectrum of SC4A are attributed to OH stretching, while that of the SC4A-Cs(I) and SC4A-Sr(II) complexes were observed at 3346 and 3352 cm⁻¹, respectively. The OH stretching bands of the extracted species were shifted to lower frequencies, which implied that hydroxyl groups were coordinated with metal ions. Previously examined complexes of *p-tert*-butylcalix[5]arene hexacarboxylic acid ligand with Cu(II) ion [38] showing that C=O stretching band of ligand-Cu(II) changed intensely and positively. In this experiment, the absorption bands at 1313 and 1156 cm⁻¹ correspond to asymmetrical and symmetrical sulfonyl stretching vibrations of SC4A, respectively. Obviously, in IR spectrum of SC4A-Cs(I) and SC4A-Sr(II) complexes, and the increased relative intensities (see green indicatrix) of asymmetrical sulfonyl vibration stretching to symmetrical sulfonyl vibration stretching, indicated that SO₂ groups were coordinated with the metal ion. O=S=O stretching bands were shifted to higher frequencies compared to the free SC4A, denoting the complexation of the SC4A with metal ion as well. The changes in peak position of sulfonyl vibrations of SC4A-metal complexes are not spectacular may be due to metal concentration was too small.

¹H-NMR spectrum is a powerful tool to analyze the conformation of calixarene derivatives. In the ¹H-NMR spectra of SC4A-Cs(I) and SC4A-Sr(II) complexes in Figure S4 (in Supplementary Materials), the downfield shift of the aromatic protons signal confirming the involvement of phenoxy oxygen atoms in complexation with metal ions [39]. This is consistent with the formation of the complex in which the metal is located within the hydrophilic cavity of SC4A surrounded by phenoxy and sulfonyl oxygen atoms. Furthermore, in ¹H-NMR spectrum of SC4A-Sr(II) complex, the appearance of the two signals in the region of ArH protons indicates the cation is restricted upon cavity of SC4A [40]. SC4A-Cs(I) complex did not cause notable changes in the ¹H-NMR except peak shift. This may because the size of the Cs(I) ion, which is larger than the Sr(II) ion, does not fit in the cavity of SC4A.



Figure 7. IR spectra (KBr) of SC4A and extracted species: (a) SC4A; (b) SC4A-Cs(I) complex; and (c) SC4A-Sr(II) complex. Conditions: T = 298 K, [SC4A]_(o) = 1×10^{-3} M, [Metal]_(a) = 1×10^{-4} M, contact time = 60 min, pH = 6, shaking speed: 150 rpm. SC4A-Cs(I) complex and SC4A-Sr(II) complex were dried in air.

Thus, the mechanism of the extraction of Cs(I) with SC4A is illustrated in Figure 8a. The sulforyl and phenol moiety of SC4A take part in coordination to Cs(I) ion in the extraction process. For the 2:1 (SC4A:Sr) complex, its coordination feature in the extraction process arouses our interest due to the excellent extraction ability of SC4A towards alkaline earth metals such as Mg(II), Ca(II) and Ba(II). The feature of crown ether-Sr(II) complex had been obtained according to X-ray structural studies [41]. Unfortunately, structures of the extracted species in the organic phase could not be obtained. In order to further examine the formation of the SC4A-Sr(II) complex, the extractions of alkaline earth metals Mg(II), Ca(II) and Ba(II) with SC4A were conducted. The relationship of log D and log [SC4A] is illustrated in Figure S5 (in Supplementary Materials). The stoichiometry of these extracted complexes determined using the slope analysis method revealed a 2:1 molar ratio of SC4A to the metals even though the ionic radii of Mg(II), Ca(II) and Ba(II) are 57, 100, and 135 pm, respectively [42]. On the basis of the above discussion, it was further deduced that two SC4A molecules formed an adjustable cavity for complexation of one alkaline earth metal ion, and the size of the adjustable cavity changes depending on the ion within an appropriate range. This coordination feature is similar to the sandwich complex of Cs(I) with 18-crown-6 [43]. The possible mechanism of the extraction of Sr(II) with SC4A is illustrated in Figure 8b. During the extraction process, an adjustable cavity that can capture alkaline earth metal with different radii is expected to be formed.



Figure 8. (a) Extraction mechanism of Cs(I) with SC4A from aqueous solution; (b) Extraction mechanism of Sr(II) with SC4A from aqueous solution.

3.7. Effect of Irradiation

3.7.1. Irradiation Stability and Thermal Stability of SC4A

Irradiation stability and thermal stability are important properties of extractants for radioactive elements. Therefore, SC4A was subjected to irradiation and thermogravimetric analysis. Detailed irradiation parameters are listed in Table 4.

Table 4. Irradiation parameters of the SC4A sample
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Irradiated Samples	Dose Rate (Gy/min)	Irradiation Dose (Gy)
А	0	0
В	30	1.0×10^4
С	30	$1.0 imes10^5$
D	50	$5.0 imes 10^5$
E	75	$1.1 imes 10^6$

Photographs of SC4A samples before and after irradiation are presented in Figure 9. SC4A was white initially, but its color changed gradually to buff when the irradiated dose was higher than 5.0×10^5 Gy.



Figure 9. The photograph of SC4A samples before and after irradiation, irradiated dose: (**A**) 0 Gy; (**B**) 1.0×10^4 Gy; (**C**) 1.0×10^5 Gy; (**D**) 5.0×10^5 Gy; and (**E**) 1.1×10^6 Gy.

The IR spectra of SC4A samples irradiated under different doses are presented in Figure S6 (in Supplementary Materials). It can be seen that the IR spectra of irradiated samples B and C remained the same as that of sample A, while a weaker absorbed peak appeared in that of sample D at 1728.2 cm⁻¹ owing to the appearance of a C=O group, for which the flex vibration zone ranges from 1870 to 1650 cm^{-1} [44], and its intensity increased at a higher irradiated dose of 1.1×10^6 Gy as shown in the spectrum of sample E.

MS spectrum data are an important tool to examine the decomposition of a material. To determine whether the SC4A decomposed in the experiment conditions, samples were analyzed via ESI-MS. The MS spectra of these samples are presented in Figure S7 (in Supplementary Materials). The main molecular peaks for samples were at 847.2, 847.3, 847.3, 847.2, and 847.3, respectively, showing that there were no discernible changes in the MS spectra. This indicated that there was no group loss even under an irradiation dose of 1.1×10^6 Gy.

TGA measurements of all samples were carried out from 50 to 600 $^{\circ}$ C. The results are displayed in Figure S8 (in Supplementary Materials). For un-irradiated sample A, it can be seen that at a temperature

range of 80–120 °C, there was 4% weight loss due to evaporation of water. The main stage on thermal degradation curves from 400 to 420 °C was assigned to the loss of the *p-tert*-butyl functional groups and the SO₂ groups of SC4A. In this stage, the weight loss of the sample was approximately 60%, which was close to the theoretical value of 57% of the molecular weight of the *p-tert*-butyl and SO₂ groups. The second stage from 420 to 550 °C was due to the breakage of the SC4A rings. The weight loss curves of irradiated samples were similar to that of sample A with the exception of sample E. It was irradiated at 1.1×10^6 Gy, which probably resulted in structural changes of trace impurities, and thus its residuals were more abundant than those of other samples.

The SC4A samples before and after irradiation were also evaluated by UV-visible spectroscopy and ¹H-NMR spectrum, and the results are presented in Figures S9 and S10, respectively (in Supplementary Materials). In the UV/vis spectroscopy, all the samples exhibited an absorption band with absorption maxima at 245 and 309 nm. No notable changes were observed in the UV/vis spectroscopy and ¹H-NMR spectrum.

Based on MS, TGA, UV/vis and ¹H-NMR analyses, it can be concluded that the SC4A remained unchanged under an irradiation dose of 1.1×10^6 Gy. The appearance of the negligible peak at 1728 cm⁻¹ in the IR spectra of samples D and E was probably due to structural changes of trace impurities caused by intense irradiation.

Extractions of Cs(I) and Sr(II) with irradiated SC4A samples were examined. The results are listed in Table 5. They showed that D_{Cs} remained approximately invariant when the irradiated dose was between 0 and 1.0×10^5 Gy and then increased when the irradiated dose was higher than 1.0×10^5 Gy. This may be due to the lone pair electrons of oxygen in the ketone group, which can enhance the extraction ability of SC4A for Cs(I). Meanwhile, no notable change in D_{Sr} was observed when the irradiated dose was less than 1.1×10^6 Gy. It can be concluded that SC4A retained good extraction ability for Cs(I) and Sr(II) after irradiation at 1.1×10^6 Gy.

Table 5.	The effect	of irradiated	extractants	on D_{Cs}	and D_{Sr}
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Irradiation Dose (Gy)	0	$\textbf{1.0}\times\textbf{10}^{4}$	$\textbf{1.0}\times\textbf{10}^{\textbf{5}}$	$\textbf{5.0}\times \textbf{10}^{\textbf{5}}$	$\textbf{1.1}\times\textbf{10^6}$
D _{Cs}	27.62	27.48	27.42	28.37	31.27
$D_{\rm Sr}$	20.74	20.18	21.14	21.54	20.94
01		0	4		

Conditions: T = 298 K, $[SC4A]_{(o)} = 1 \times 10^{-3}$ M, $[Metal]_{(a)} = 1 \times 10^{-4}$ M, pH = 6, contact time = 60 min, shaking speed: 150 rpm.

3.7.2. Irradiation Stability of SC4A/CHCl₃

Irradiation stability of SC4A/CHCl₃ was investigated in the present study. First, SC4A/CHCl₃ was irradiated with varying doses (200 Gy·min⁻¹), and then 1.0×10^{-3} mol·L⁻¹ irradiated SC4A/CH₃Cl was employed to extract Cs(I) or Sr(II) from an aqueous phase of equal volume. The D_{Cs} and D_{Sr} values under different irradiation doses are listed in Table 6. The values of D_{Cs} and D_{Sr} are almost constant until the irradiation dose reached 5.0×10^5 Gy. The results indicate that SC4A/CH₃Cl was hardly impaired by irradiation.

Table 6. The effect of irradiated extraction system on D_{Cs} and D_{Sr} .

Irradiationdose (Gy)	0	$\textbf{1.0}\times\textbf{10}^{4}$	$\textbf{1.0}\times\textbf{10}^{\textbf{5}}$	$\textbf{5.0}\times \textbf{10}^{\textbf{5}}$	$1.1 imes 10^{6}$
D _{Cs}	27.59	26.92	27.55	20.67	16.27
D_{Sr}	20.86	21.13	20.62	15.36	11.51

Conditions: T = 298 K, [SC4A]_(o) = 1 × 10⁻³ M, [Metal]_(a) = 1 × 10⁻⁴ M, pH = 6, contact time = 60 min, shaking speed: 150 rpm.

A process for extraction of Cs(I) and Sr(II) from aqueous solutions using SC4A was studied. The results are promising in the sense that SC4A can sequester both Cs(I) and Sr(II) from radioactive contaminated aqueous waste. The stoichiometry of metal with respect to SC4A was determined to be 1:1 (Cs:SC4A) and 1:2 (Sr:SC4A). From the thermodynamic data, the extraction process was found to be exothermic. A possible extraction mechanism involves formation of an adjustable cavity from two SC4A molecules for the complexation of one Sr(II) ion, and the size of the adjustable cavity changes depending on the ion within an appropriate range. Furthermore, SC4A exhibited superior thermal and irradiation stability. The main structure of SC4A remained unchanged when the irradiation dose was lower than 1.1×10^6 Gy. The distribution ratios of Cs(I) and Sr(II) remained above 27 and 20, respectively, under an irradiation dose of 1.0×10^4 to 1.1×10^6 Gy. In addition, SC4A/CHCl₃ showed efficient extraction ability when the irradiation dose was less than 5.0×10^5 Gy.

Supplementary Materials: The following are available online at www.mdpi.com/2076-3417/6/8/212/s1, Figure S1: Synthesis of *p-tert*-butylthiacalix[4]arene, Figure S2: Synthesis of *p-tert*-butylsulfonylcalix[4]arene, Figure S3: Synthesis of *p-tert*-butylsulfonylcalix[4]arene tetraacetate, Figure S4: ¹H-NMR of SC4A and extracted species, Figure S5: Dependence of the distribution ratio (*D*) of Mg(II), Ca(II), Ba(II) onto SC4A with a change in [SC4A], Figure S6: The IR of SC4A for different irradiated dose, irradiated dose, Figure S7: The MS spectra of SC4A before and after irradiation, Figure S8: TG curves of SC4A before and after irradiation, Figure S9: The UV-visible spectra of SC4A before and after irradiation, Figure S10: The ¹H-NMR spectrogram of SC4A before and after irradiation, Table S1: The distribution ratio (*D*) of Mg(II), Ca(II) and Ba(II) onto SC4A with the change in contact time.

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Conflicts of Interest: The authors declare no conflict of interest.

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