



# Extraction behavior of cesium from nitric acid medium with calix[4]-bis[(4-*tert*-butyl-1,2-phenylene)-crown-6]

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## Abstract

Cesium, one of the heat-emitting fission elements contained in high active liquid waste, deserved separation. Calixbiscrown is a class of chemical compounds, promising in the cesium extraction. In this study, calix[4]-bis[(4-*tert*-butyl-1,2-phenylene)-crown-6] (CalixBBC for short) was synthesized by a multi-step scheme. The cesium extraction study was carried out using CalixBBC in two organic diluents such as chloroform and *o*-nitroanisole, which were used as electron-deficient and electron-rich surrogate dilutions, respectively. The effects of HNO<sub>3</sub> concentration, mixing time, temperature were investigated using a batch technique. Comparing with chloroform, *o*-nitroanisole was in favor of cesium extraction. Both extractions strongly relied on HNO<sub>3</sub> concentration in the range of 0.4–6.0 M. The pseudo-second-order model fitted the extractions well. Both extractions were spontaneous, exothermal processes. The foreigner metal ions showed little influence on the extraction. The stoichiometry of cesium and CalixBBC in the complex was 1:1.

**Keywords** Calix[4]biscrown · Cs(I) · Solvent extraction · Kinetics · Thermodynamics

## Introduction

Plutonium uranium reduction extraction process (PUREX) is often used to recover uranium and plutonium by using 30% tri-*n*-butyl phosphate/kerosene extraction system. Consequently a highly acidic and radioactive solution (commonly called Highly active liquid waste (HLW)) is produced. [1–3]. The resultant HLW contains various fission, transuranic, and activation isotopes such as the long-lived minor actinides MAs(III), rare earth metals REs(III), heat generators Cs(I) and Sr(II), noble metals, Mo(VI),

Tc(VII), Zr(IV), etc. Those metals deserve removal in view of final disposal, environment protection and human health. Although various techniques have been tested [4–15], industrial-scale separation of these metals is problematic so far.

With high energy gamma ray emission (661.9 keV), heat output (0.42 W/g) and relatively long half-life ( $t_{1/2} = 30.1$  years), Cs-137 is deleterious to the solidification matrix [16–20]. Cs-135 has a longer half-life ( $t_{1/2} = 2.3 \times 10^6$  years) than Cs-137 [21]. It is an important contributor to the long term radiological impact on the deep geological repository [22]. Especially the properties such as high mobility and solubility make cesium easily enter into organisms [23]. Undergoing ingestion and accumulation, cesium consequently enriches in the tissues and is hardly eliminated. The final results are likely genetic mutation, cancer and other disorders [24]. Thus the separation of cesium from HLW is of great engineering interests. So far some physical–chemical techniques are tested to separate cesium from aquatic solution such as adsorption [22], chemical precipitation [25], solvent extraction [26], and chromatography [21], etc. It is worth noting that the solvent extraction technique is promising owing to large

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handling capacity, continuous operation and high enrichment factor.

Calix[4]crowns mean the organic compounds composed of calix[4]arene and crown, which are conjuncted through phenolic oxygens. The  $\pi$  interaction and size-matching function make calix[4]crowns possess outstanding recognition performance toward alkali metal cations and other ions [27, 28]. Based on this calix[4]crowns show the potential application in the fields of selective electrodes [29], sensors [28], artificial allosterism [30], separation and purification [31]. Calix[4]crowns family can be further divided into two categories such as calix[4]monocrown and calix[4]biscrown in terms of the amount of polyether conjunct on the lower rim of the calix[4]arene molecule. Over the past decades calix[4]monocrown-6 in 1,3-alternate conformation gains considerable attention due to the high Cs(I)/Na(I) selectivity, which is significant in the post-treatment of spent nuclear fuel. In recent years the higher Cs(I)/Na(I) selectivity highlights 1,3-alternate calix[4]biscrown-6 [32, 33]. Various processes based on the calix[4]biscrown-6 like fission product extraction [34, 35] and caustic-side solvent extraction [36] are proposed to remove cesium from HLW. Although the Cs(I)/Na(I) selectivity reached an impressive value of 29,000 using calix[4]-bis-naphtho-crown-6 [33], the industrial scale separation of cesium is still problematic. One of the effective approaches to solve this is developing new extractant.

In this paper, a new calix[4]biscrown derivative, calix[4]-bis[(4-*tert*-butyl-1,2-phenylene)-crown-6] (CalixBBC), was synthesized using a multi-step synthesis method. The extraction properties of Cs(I) were investigated as functions of HNO<sub>3</sub> concentration, mixing time, and temperature. The selectivity performance was explored. The extraction mechanism and the composition of the extracted species of Cs(I) with CalixBBC were qualitatively and quantitatively discussed using FT-IR and ESI-MS.

## Materials and methods

### Materials

Chemicals and reagents used in this study were of analytical grade, unless otherwise specified. Ruthenium nitrosyl nitrate solution containing 1.5 wt% of Ru(III) was purchased from the Strem Chemicals, USA. The other metal nitrates were received from the Minxing Co. Inc. China. CalixBBC was synthesized in lab. Solvents such as electron-donor *o*-nitroanisole and electron-deficiency chloroform were used as diluent in solvent extraction experiments.

### Apparatus

<sup>1</sup>H NMR spectra were collected using a Bruker in chloroform-*d* with TMS as internal standard. FT-IR spectra in the spectral range 600–4000 cm<sup>-1</sup> was obtained using a Thermo Nicolet. Samples were diluted with chromatographically pure dichloromethane which acted as film formation agent and dropped on the ZnSe crystal of attenuated total reflection accessory. ESI-MS spectra were recorded with a PerkinElmer SciexAPI 3000 (PerkinElmer, America) electrospray ionization mass spectrometry. The mass spectrometric measurements were recorded in positive ion mode using coupled with an ionic spray source. Elemental analysis was carried out with an X'Pert PRO X (PANalytical, Netherland). Metal ion concentrations were determined using a Varian AA 240 FS model atomic adsorption spectroscope.

### Synthesis

*Tetra-tert*-butyl-calix[4]arene and calix[4]arene were synthesized in lab according to the method described previously [33]. CalixBBC was synthesized as following.

#### Synthesis of bis[1,2-[2'(2''-hydroxyethoxy)ethoxy]]-4-*tert*-butylbenzene

In a three-neck flask, a 300 mL DMF solution of 2.0 g 4-*tert*-butyl-phenol and 16.0 g potassium carbonate was stirred at room temperature for 30 min, followed by addition of 4.5 g 2-(2-chloroethoxy)ethanol. The mixture was stirred at 78 °C for 2 d. After cooling to room temperature, the mixture was filtered and the residue was washed with 20 mL DMF twice. DMF was removed in vacuum, and the residue was extracted with 100 mL dichloromethane and 100 mL of water. The organic solvent was washed three times with water and dried with anhydrous magnesium sulfate. After filtration, dichloromethane was removed in vacuum to yield a transparent oil product. The analysis result of the thin layer chromatography proved that the purity of the crude product was enough to be used directly in the following sulfonation reaction.

#### Synthesis of Bis[1,2-[2'(2''-hydroxyethoxy)ethoxy]]-4-*tert*-butylbenzene di-*p*-toluenesulfonate

In a three-neck flask, a 7 mL THF solution of 2.3 g above crude product and 5 mL water containing 0.72 g sodium hydroxide was cooled down to below 0 °C, followed by the addition of a 10 mL THF solution containing 2.6 g *para* toluenesulfonyl chloride in 2 h. After 8 h, 15 mL

dichloromethane and 15 mL of 2 M sodium hydroxide solution were added. The organic phase was washed twice with diluted hydrochloric acid solution and washed to neutral pH with water. The organic phase was dried with anhydrous magnesium sulfate and removed in vacuum. Through purification with column chromatography (1:4 ethyl acetate-petroleum ether as eluent), 1.8 g transparent oil product was obtained. The yield of the two-step reaction above was considerable 41%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  relative to TMS) ppm: 1.285 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 2.405 (s, 6H,  $\text{CH}_3$ ), 3.764 (s, 8H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 4.030–4.052 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 4.078–4.171 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 6.785–6.792 (m, 3H,  $\text{ArHbenzo}$ ), 7.777–7.796 (d, 4H,  $\text{ArHOTs}$ ).

### Synthesis of calix[4]-bis[(4-tert-butyl-1,2-phenylene)-crown-6]

Under nitrogen atmosphere, a mixture of 2.12 g calix[4]-arene and 4.8 g  $\text{Cs}_2\text{CO}_3$  was stirred for 2 h in 480 mL refluxed acetonitrile. Then 10 g bis[1,2-[2'-(2''-hydroxyethoxy)ethoxy]]-4-tert-butylbenzene di-*p*-toluenesulfonate was added. The mixture was refluxed for 15 d. After cooling to room temperature, the solvent was removed in vacuum. The residue was extracted using 100 mL dichloromethane. It was washed twice with diluted hydrochloric acid and washed to neutral pH with water. The organic phase was dried with anhydrous magnesium sulfate. After filtration, the organic solvent was removed in vacuum to give brown oil. Column chromatography was conducted with 1:4 of ethyl acetate-petroleum ether as eluent to give the designed product as a white solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  relative to TMS) ppm: 1.347 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 3.526–3.659 (m, 20H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 3.709–3.731 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 3.795 (s, 8H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 4.130–4.163 (m, 8H,  $\text{ArCH}_2\text{Ar}$ ), 6.672–6.710 (m, 6H,  $\text{ArHbenzo}$ ), 7.010–7.100 (m, 4H,  $\text{ArHcalix}$ ). ESI-MS: 1054.7  $[\text{M} + \text{NH}_4]^+$ . FT-IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  ( $\text{cm}^{-1}$ ) 2924; 2330; 1519; 1454; 1361; 1267; 1207; 1134; 1092; 1052; 928; 808; 764; 735; 634. Elemental analysis: Anal. Calcd. for  $\text{C}_{64}\text{H}_{76}\text{O}_{12}$ : C, 74.11; H, 7.39. Found: C, 75.01%; H, 7.85. The five-step synthesis scheme of CalixBBC was proposed and shown in Fig. 1.

### Solvent extraction

Liquid–liquid extraction experiments were carried out in duplicate. The detailed procedure was as following. First of all, organic phase containing  $8.0 \times 10^{-3}$  M CalixBBC was equilibrated by once contacting  $\text{HNO}_3$  solution of the needed concentration. Then equal volume of aqueous solution containing  $5.0 \times 10^{-4}$  M metal ions and the organic phase was mixed. The mixture was shaken at

120 rpm in a thermostatic water bath oscillator (MM-10, TAITEC, Japan). The two phases were disengaged by centrifugal for 5 min. Metal ion concentrations in the aqueous phase were determined. Distribution ratio ( $D$ ) was calculated out through the ratio of metal ion concentrations in organic phase and aqueous phase using Eq. (1).

$$D = \frac{C_i - C_a}{C_a} \quad (1)$$

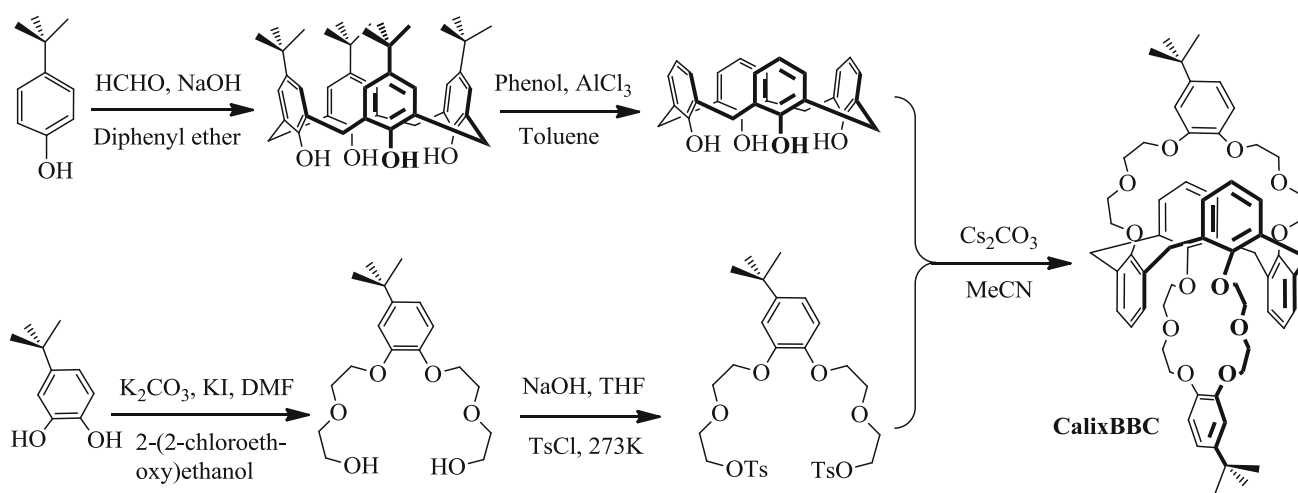
where  $C_i$  and  $C_a$  denote the metal ion concentration in aqueous phase before and after extraction (mg/L), respectively.

## Results and discussion

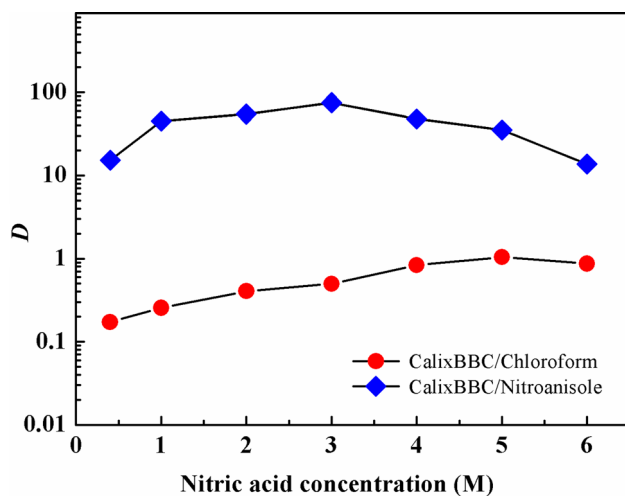
### Effect of $\text{HNO}_3$ concentration on the extraction

The spent nuclear fuel is usually dissolved in nitric acid solution, the concentration of which has decisive influence on the extraction performance. Thus the effect of  $\text{HNO}_3$  concentration in the range of 0.4–6.0 M on the Cs(I) extraction using CalixBBC/chloroform and CalixBBC/*o*-nitroanisole were investigated, respectively. The results are shown in Fig. 2.

As can be seen from Fig. 2, when chloroform was used as a diluent,  $D_{\text{Cs}}$  increased from 0.1 to 1.0 as  $\text{HNO}_3$  concentration increased from 0.4 to 5.0 M. Further increase in  $\text{HNO}_3$  concentration to 6.0 M lead the decrease in  $D_{\text{Cs}}$  to 0.8. When *o*-nitroanisole was used as diluent,  $D_{\text{Cs}}$  increased with  $\text{HNO}_3$  concentration increased in the range of 0.4–3.0 M.  $D_{\text{Cs}}$  decreased as  $\text{HNO}_3$  concentration increased to 6.0 M. The reason for the above phenomenons was as follows. When  $\text{HNO}_3$  concentrations were less than the concentration that the turning points happened, the recognition reactions between CalixBBC and Cs(I) were dominant. Once beyond the concentrations, the coordination reactions between CalixBBC and  $\text{HNO}_3$  were prior [35]. The optimum  $\text{HNO}_3$  concentration was determined as 5.0 M for CalixBBC/Chloroform and as 3.0 M for CalixBBC/*o*-Nitroanisole. The difference resulted from the distinct capacity of hydrogen bonds formation of *o*-nitroanisole and chloroform. Chloroform had stronger ability to form the hydrogen bond with  $\text{HNO}_3$  molecular. It worked like a buffer to counteract the increase of  $\text{HNO}_3$  concentration, and to delay the decrease in  $D_{\text{Cs}}$ . For CalixBBC/*o*-Nitroanisole, the maximum  $D_{\text{Cs}}$  of ca. 75 appeared at 3.0 M, which was meaningful as the corresponding optimal acidity was in agreement with acidity of the genuine HLW.



**Fig. 1** The five-step synthesis scheme of CalixBBC



**Fig. 2** The effect of HNO<sub>3</sub> concentration on the distribution ratio. [Cs(I)]<sub>0</sub> = 5.0 × 10<sup>-4</sup> M, [CalixBBC] = 8.0 × 10<sup>-3</sup> M, mixing time = 120 min, T = 298 K, phase ratio = 1. Uncertainties in *D* are estimated to be ± 5%

### Effect of mixing time on the extraction

The effect of mixing time in 120 min on the Cs(I) extraction was investigated. The results are shown in Fig. 3. It was found in Fig. 3a that in 20 min both  $D_{Cs}$  increased quickly as the mixing time increased. Afterward,  $D_{Cs}$  kept constant up to 120 min, showing extraction equilibrium, indicating equilibrium time of 20 min. The results mean both extractions were fast kinetics in nature. The results proved that diluents showed little influence on cesium transfer speed.

To illuminate extraction kinetics in detail, the pseudo-first-order (Eq. 2) and pseudo-second-order (Eq. 3) kinetics equations were used to fit experimental data.

$$C_t = C_e \times (1 - e^{-k_1 t}) \quad (2)$$

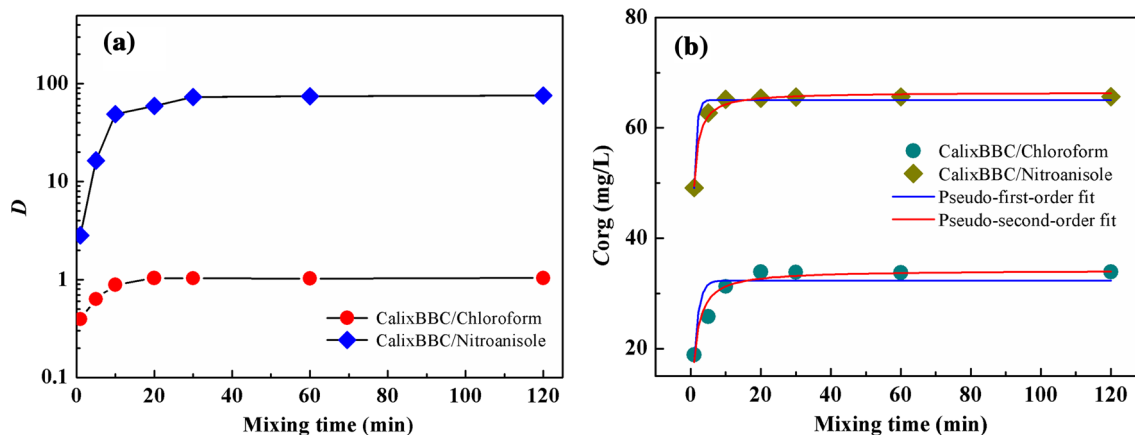
$$C_t = \frac{C_e^2 k_2 t}{1 + C_e k_2 t} \quad (3)$$

where  $k_1$  (min<sup>-1</sup>) and  $k_2$  (L mg<sup>-1</sup> min<sup>-1</sup>) represent extraction rate constants of pseudo-first-order and pseudo-second-order models, respectively;  $C_t$  (mg L<sup>-1</sup>) and  $C_e$  (mg L<sup>-1</sup>) are the extraction quantity at time  $t$  (min) and at equilibrium.

The extraction capacities as function of the mixing time were curve fitted using two kinetics model (shown in Fig. 3b) to calculate kinetic parameters and correlation coefficients ( $R^2$ ) (Table 1). It could be seen that the  $R^2$  values of the pseudo-second-order model were more approximate to 1.0 than those of the pseudo-first-order model, determining the better description of the pseudo-second-order model for both extractions. The result showed both extraction reactions are chemical in nature. The initial extraction rates,  $h$ , were calculated as 35.15 mg L<sup>-1</sup> min<sup>-1</sup> for CalixBBC/chloroform and 176.67 mg L<sup>-1</sup> min<sup>-1</sup> for CalixBBC/*o*-nitroanisole according to the equation of  $h = k_2 q_e^2$ .

### Effect of temperature on the extraction

An appropriate temperature determines the extraction efficiency and energy consumption. The cesium extraction distributions as functions of the temperature are shown in Fig. 4. It can be seen that a significant decrease in  $D_{Cs}$  using CalixBBC/*o*-nitroanisole from 74.26 to 23.27 and a slightly decrease in  $D_{Cs}$  using CalixBBC/chloroform when increasing the temperature from 298 to 318 K. Both decrease plots in cesium extraction performance were attributed to the heat release reaction in the nature of

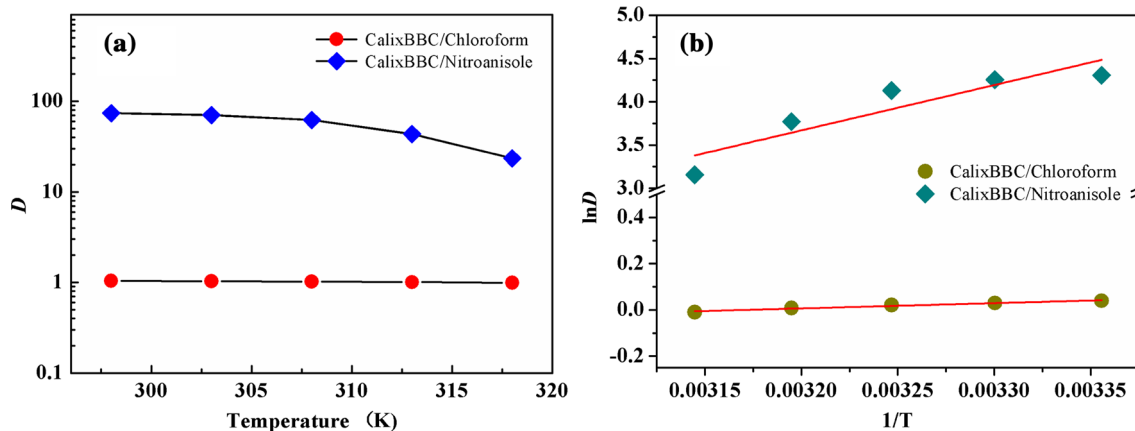


**Fig. 3 a** The effect of mixing time on the distribution ratio.  $[Cs(I)]_0 = 5.0 \times 10^{-4}$  M,  $[CalixBBC] = 8.0 \times 10^{-3}$  M,  $T = 298$  K, phase ratio = 1,  $[HNO_3] = 5.0$  M for CalixBBC/chloroform,

$[HNO_3] = 3.0$  M for CalixBBC/o-Nitroanisole. Uncertainties in  $D$  are estimated to be  $\pm 5\%$ . **b** Curve fitted using pseudo-first-order and pseudo-second-order model

**Table 1** Kinetic parameters of the extraction of Cs(I)

Diluent	Pseudo-first-order model			Pseudo-second-order model			
	$k_1$ ( $\text{min}^{-1}$ )	$C_e$ ( $\text{mg L}^{-1}$ )	$R^2$	$k_2$ ( $\text{L mg}^{-1} \text{min}^{-1}$ )	$h$ ( $\text{mg L}^{-1} \text{min}^{-1}$ )	$C_e$ ( $\text{mg L}^{-1}$ )	$R^2$
Chloroform	0.78	32.32	0.729	0.03	35.15	34.23	0.927
o-Nitroanisole	1.4	65.03	0.965	0.04	176.67	66.46	0.990



**Fig. 4 a** The effect of temperature on the distribution ratio.  $[Cs(I)]_0 = 5.0 \times 10^{-4}$  M,  $[CalixBBC] = 8.0 \times 10^{-3}$  M, mixing time = 120 min, phase ratio = 1,  $[HNO_3] = 5.0$  M for CalixBBC/chloroform,

$[HNO_3] = 3.0$  M for CalixBBC/o-nitroanisole. Uncertainties in  $D$  are estimated to be  $\pm 5\%$ . **b**  $\ln D$  versus  $1/T$

cesium complex. The results indicated that increasing temperature were not in favor of cesium extraction.

The thermodynamic parameters for the cesium extraction were observed using basic thermodynamics relations as following:

$$\ln D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

where  $R$  is the ideal gas constant ( $8.314 \text{ J/mol/K}$ ),  $T$  is the temperature in Kelvin (K),  $\Delta S^\circ$ ,  $\Delta H^\circ$  and  $\Delta G^\circ$  are changes in entropy ( $\text{J mol}^{-1} \text{K}^{-1}$ ), enthalpy ( $\text{KJ mol}^{-1}$ ) and Gibb's free energy ( $\text{KJ mol}^{-1}$ ). The straight fit of  $\ln D$  versus  $1/T$  gives the linear equation, which can deduce the values of  $\Delta S^\circ$  and  $\Delta H^\circ$  from the slope and the intercept. The resultant parameters are listed in Table 2.

**Table 2** Thermodynamic parameters of the extraction of Cs(I)

Diluent	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )				
			298 K	303 K	308 K	313 K	318 K
Chloroform	- 5.98	- 1.89	- 0.097	- 0.074	- 0.053	- 0.02	- 0.026
<i>o</i> -Nitroanisole	- 108.58	- 43.48	- 32.25	- 32.79	- 33.33	- 33.87	- 34.42

It can be seen from Table 2 that the extraction toward Cs(I) with CalixBBC/chloroform and CalixBBC/*o*-nitroanisole were processes of entropy decrease. The reason was that spatial position became more orderly after Cs(I) bound with CalixBBC. Negative values of  $\Delta H^\circ$  implied the extraction toward Cs(I) were exothermic processes. Cs(I) extraction behaviors were spontaneous in consideration of the negative values of  $\Delta G^\circ$ .

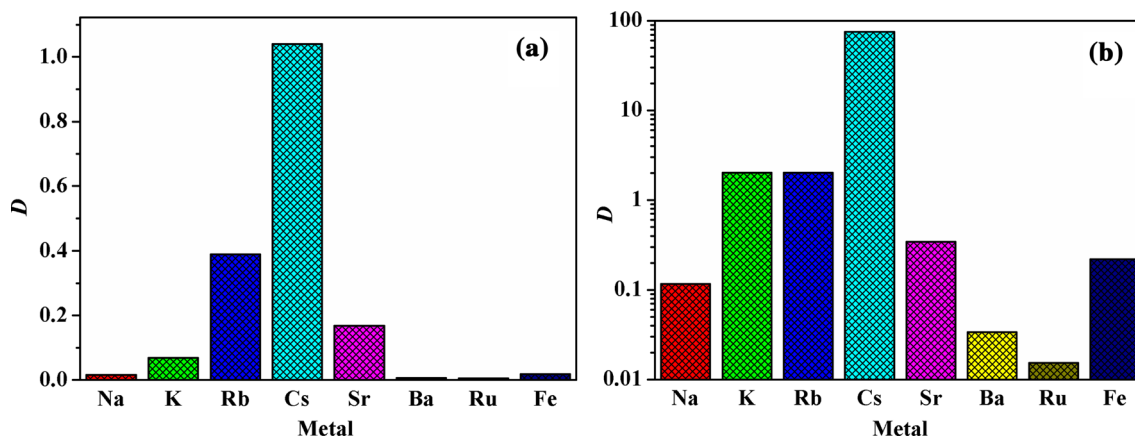
### Selectivity

Cesium ion selectivity is important due to the complex composition in the HLW system. Thus, the effects of Na(I), K(I), Rb(I), Sr(II), Ba(II), Ru(III) and Fe(III) were investigated. The results are shown in Fig. 5. It was found that both extraction systems had outstanding cesium selectivity.  $D_{\text{Cs}}$  were remarkably greater than  $D$  values of other metals. Rb(I) could be extracted by both extraction system owing to the most closer radius to cesium. Other metals were hardly extracted. The high selectivity was resulted from the *para*-position benzene ring in the molecular structure of CalixBBC, which offered  $\pi$ -electron orientation [37].

### Investigation on the extraction mechanism

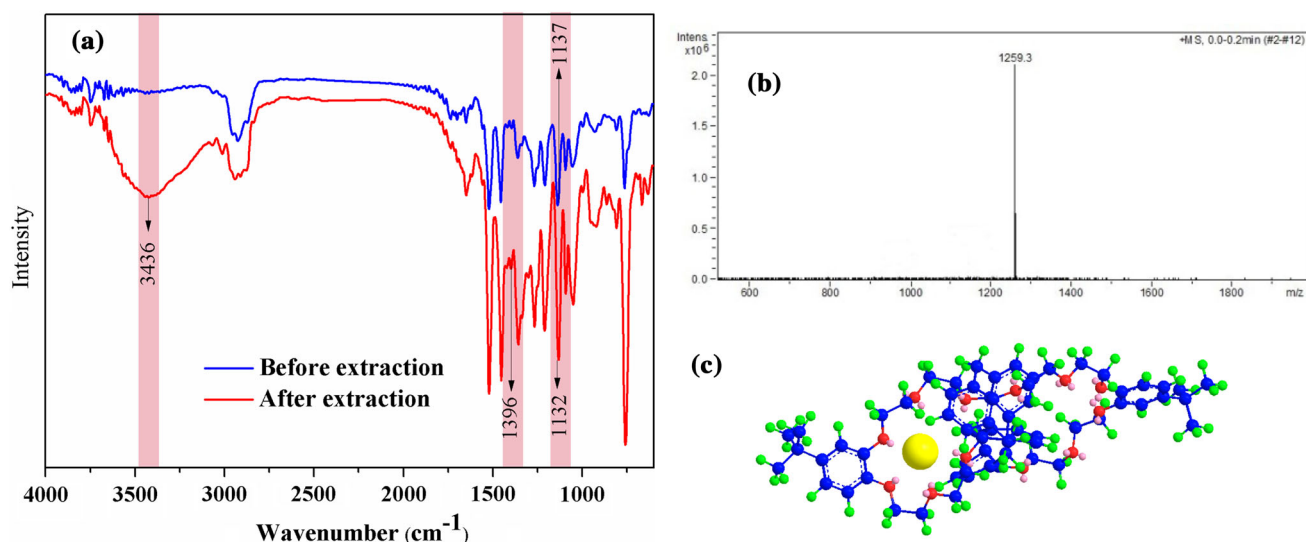
Virgin and cesium-loaded organic solvents were analyzed by FT-IR spectroscopy. The two spectra were recorded and plotted in the same scale on the intensity axis. The FT-IR spectra in Fig. 6a reveal the changes in the adsorption bands of the character groups of CalixBBC. After action with Cs<sup>+</sup>, C–O–C vibration absorption of 1137 cm<sup>-1</sup> in free CalixBBC shifted to the lower frequency of 1132 cm<sup>-1</sup>. The shift was due to Cs(I) attachment. It indicated that oxygen atoms in ether moieties involved in Cs(I) extraction. The weak adsorption peak at 1396 cm<sup>-1</sup> proved the presence of free NO<sub>3</sub><sup>-</sup>, which made the extraction complex be electric neutrality. There was a strong and wide adsorption peak at 3424 cm<sup>-1</sup>, presenting H<sub>2</sub>O existence in the coordination formation.

The cesium-loaded organic solvent was analyzed by flow injection ESI–MS. The ESI–MS spectrum in Fig. 6b showed the ionic peak after extraction. The *m/z* at 1259.3 presented a strong peak, which could be determined as the ionic peak of [M + Cs + 5H<sub>2</sub>O]<sup>+</sup>. The result demonstrated 1:1 mononuclear complex formed. However the 1:2 binuclear complex of [M + 2Cs]<sup>2+</sup> and [M + 2Cs – H]<sup>+</sup> were not found. The reason was that the electrostatic



**Fig. 5** Effect of coexisting metals on the extraction. [Metals] =  $5.0 \times 10^{-4}$  M, [CalixBBC] =  $8.0 \times 10^{-3}$  M, mixing time = 120 min,  $T = 298$  K, phase ratio = 1, [HNO<sub>3</sub>]<sub>(a)</sub> = 5.0 M in chloroform,

[HNO<sub>3</sub>]<sub>(b)</sub> = 3.0 M in *o*-nitroanisole. Uncertainties in  $D$  are estimated to be  $\pm 5\%$



**Fig. 6** **a** FT-IR spectra of CalixBBC before and after extraction, **b** ESI-MS spectrum of CalixBBC after extraction, **c** 1:1 Type of mononuclear complex of CalixBBC and CsNO<sub>3</sub> drawn with the software of ChemBio3D Ultra

repulsion between the two cesium ions and an induced conformation change made one CalixBBC molecule not able to bind two cesium ions. [38]. Five H<sub>2</sub>O molecules were bound with CalixBBC molecular, which was agreement with the FT-IR result. Therefore, the possible complex mechanism is proposed and shown in Fig. 6c.

## Conclusions

In this study, calix[4]-bis[(4-*tert*-butyl-1,2-phenylene)-crown-6] was firstly synthesized. The extractions of cesium were conducted using CalixBBC in chloroform and *o*-nitroanisole, respectively. Comparing with chloroform, *o*-nitroanisole is in favor of cesium extraction. The optimum HNO<sub>3</sub> concentrations were determined as 5.0 M for CalixBBC/chloroform and as 3.0 M for CalixBBC/*o*-nitroanisole. Both extraction behaviors were fast kinetics, spontaneous, exothermal processes. The foreigner metal ions such as Na(I), K(I), Rb(I), Sr(II), Ba(II), Ru(III) and Fe(III) showed little influence on the cesium extraction. FT-IR and ESI-MS characterization results proved the formation of 1:1 mononuclear complex between Cs(I) and CalixBBC.

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