Extraction equilibrium and thermodynamics of cesium with a new derivative of calix[4]biscrown

Ying Dai · Anyun Zhang

Abstract A new supermolecular recognition agent named *tetra-tert*-butyl-calix[4]-bis[(4-methly-1,2-phenylene-crown-6] (*Tert*ButylCalixC) was synthesized. Batchwise experiments of extraction of Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III) and Fe(III) from aqueous solution with *Tert*ButylCalixC/*o*-nitroanisole were carried out. Effects of HNO$_3$ concentration, contact time and temperature on the extraction behavior were examined. The equilibrium established within 30 min implied a fast extraction kinetics. The optimal operation temperature was 298 K. Stoichiometry of *Tert*ButylCalixC and Cs(I) by electrospray ionization mass spectrometry characterization revealed 1:1 molar ratio. It was observed that the extraction system of *Tert*ButylCalixC/*o*-nitroanisole was effective for selective removal of Cs(I), showing remarkable separation performance.

Keywords Calix[4]biscrown · High level liquid waste · Cesium · Solvent extraction · Composition

Introduction

Calix[4]crowns refer to the compounds in which calix[4]arenes are combined with crowns through the bridging of phenolic oxygens of calix[4]arenes. Due to their superior recognition ability toward alkali metal cations and other ions [1–6], calix[4]crowns have received increasing attention. Calix[4]crowns have been found to

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show the potential application in the fields of molecular sensors [7], ion selective electrodes [8], artificial allosteric systems [9], separation and purification [10–12]. According to the number of polyether bridging on the lower rim of a calix[4]arene molecule, calix[4]crowns can be divided into two types. One is calix[4]monocrown. The other is calix[4]biscrown. Both two types of calix[4]crowns, especially calix[4]crown-6 in 1,3-*alternate* conformation, are taken seriously due to their high selectivity for Cs(I)/Na(I) via matching size and π-interaction [13–15].

Due to the high selectivity for Cs(I)/Na(I), 1,3-*alternate* calix[4]biscrown-6 has been paid more attention than 1,3-*alternate* calix[4]monocrown-6 in recent years [16, 17]. Processes like fission product extraction [18, 19] and caustic-side solvent extraction [20, 21] using calix[4]biscrowns to selectively separate cesium from the highly active liquid waste (HLW) have been reported. The Cs(I)/Na(I) selectivity of calix[4]-bis-crown-6 could reach a level of 1,500. The selectivities of calix[4]-bis-benzo-crown-6 and calix[4]-bis-naphtho-crown-6 were more than 19,000 and 29,000, respectively. Although the calix[4]biscrown-6 derivative had remarkable Cs(I)/Na(I) selectivity, the Cs(I) extraction ability was not high. The distribution ratios of Cs(I) reported were not greater than 10 [22], which would result in the increment of extraction stage for better separation. However, in contrast to the extensive investigations on the host molecule of calix[4]arene, very little is known about *tetra-tert*-butyl-calix[4]arene.

Two major radioisotopes of cesium, ^{135}Cs ($t_{1/2} = 1.0 \times 10^5$ years) and ^{137}Cs ($t_{1/2} = 30$ years), can be produced from nuclear reactors. The two radioisotopes remain in HLW, the raffinate of PUREX which works for the recovery of uranium and plutonium from the spent nuclear fuel. Removal of ^{135}Cs and ^{137}Cs is necessary as their radioactivity brings adverse effect on environment and the treatment of HLW [23–25]. ^{137}Cs is also a heat generator

element and hampers the final vitrification of HLW [26]. As a β-emitter, ^{137}Cs can be applied in several industries [27, 28]. Efforts are on to separate cesium from HLW, but the effective separation is problematic. One problem is lack of an applicable extractant.

Tetra-tert-butyl-calix[4]arene containing *Tetra-tert*-butyl groups is a derivative of calix[4]arene. It might has more strong supramolecular recognition ability than calix[4]arene. Furthermore, *tetra-tert*-butyl groups make *tetra-tert*-butyl-calix[4]arene more lipophilic than calix[4]arene. This is of great beneficial to its dissolution in alkane diluents.

In the present work, a new calix[4]biscrown derivative, *tetra-tert*-butyl-calix[4]-bis[(4-methly-1,2-phenylene-crown-6] (*Tert*ButylCalixC), was synthezied by a cyclization reaction. Following *Tert*ButylCalixC was identified by proton nuclear magnetic resonance (^{1}H NMR), electrospray ionization mass spectrometry (ESI–MS), elemental analysis, and others. The solvent extraction of Cs(I) and other typical metals with *Tert*ButylCalixC/*o*-nitroanisole in the concentration range of 0.4 M to 6.0 M HNO_3 was carried out. The main factors affecting the extraction properties such as the HNO_3 concentration, contact time, and temperature were investigated. The extraction mechanism and properties of the tested metals were discussed.

Experimental

Materials

All the chemicals and reagents used in the study were of analytical grade, unless otherwise specified. Ruthenium nitrosyl nitrate solution (1.5 wt% of Ru(III)) was procured from the Strem Chemicals, the United States of America. The other metal nitrates were purchased from the Minxing Co. Inc. China. Because the electron-deficiency solvents such as $CHCl_3$, CH_2Cl_2 and others usually can be effectively associated with calix[4]biscrown through hydrogen bonding, the available concentration of calix[4]biscrown in organic phase decreased. It makes the extraction ability of Cs(I) with calix[4]biscrown decreased significantly. An electron-donor organic solvent, *o*-nitroanisole provided by the Aladdin company, was therefore utilized as a diluent. *Tetra-tert*-butyl-calix[4]arene and bis[1,2-[2′(2″-hydroxy-ethoxy)ethoxy]]-4-methylbenzene di-*p*-toluenesulfonate used for the synthesis of *Tert*ButylCalixC was prepared.

Considering the toxicity of *o*-nitroanisole, all experiments were performed in an airtight glovebox, while an antigas mask was utilized to health protection.

A calix[4]biscrown supermolecular derivative, *tetra-tert*-butyl-calix[4]-bis[(4-methly-1,2-phenylene-crown-6] (*Tert*ButylCalixC), was prepared quantitatively synthesized through an improved experimental method.

Apparatus

^{1}H NMR spectrum was recorded in an Avance DMX500 (Bruker, Switzerland) spectrometer. Mass spectra was obtained with a PerkinElmer SciexAPI 3000 (PerkinElmer, America) electrospray ionization mass spectrometry. Elemental analysis was carried out with an X'Pert PRO X (PANalytical, Netherland). The metal ion concentration was determined by using a Varian AA 240 FS model atomic adsorption spectroscope.

Preparation of *Tert*ButylCalixC

*Tert*ButylCalixC was synthesized according to a classical method [29]. Under a condition of N_2 *tetra-tert*-butyl-calix[4]arene (1) and Cs_2CO_3 were mixed in acetonitrile and stirred at reflux for 2 h. Then bis[1,2-[2′(2″-hydroxy-ethoxy)ethoxy]]-4-methylbenzene di-*p*-toluene sulfonate (2) was added dropwise and the mixture was stirred at reflux for 20 days. After cooling, the solvent was removed in vacuo. Chloroform was added and the mixture was neutralized by dilute hydrochloric acid solution. The organic layer was separated and dried over magnesium sulfate. The filtered solution was concentrated under vacuo and the residue was purified by column chromatography [SiO_2, petroleum ether-ethyl acetate (25:1)] to yield *Tert*ButylCalixC. ^{1}H NMR (300 MHz, $CDCl_3$, δ relative to TMS) ppm: 1.23 (s, 36H, C(CH_3)$_3$), 2.30 (s, 6H, CH_3), 2.86–3.68 (m, 24H, OCH_2CH_2O), 3.97 (s, 8H, ArCH_2Ar), 3.96–4.02 (m, 8H,OCH_2CH_2O), 6.66–6.79 (m, 6H, ArH-benzo), 7.02 (s, 8H, ArHcalix). MS (ESI) m/z: 1,177.9 [M + H]$^+$. Elemental analysis found: 75.25 % for C, 8.46 % for H. calcd: 75.48 % for C, 8.22 % for H. Figure 1 shows the scheme of synthesis of *Tert*ButylCalixC.

Solvent extraction studies

All extraction experiments were conducted batch wise in duplicate. Prior to an extraction experiment, the organic phase with 8.0×10^{-3} M of *Tert*ButylCalixC in *o*-nitroanisole was preconditioned via one contact with equal volume of nitric acid solution without metal ions. Equal volume (5.0 cm^3) of the aqueous phase containing 5.0×10^{-4} M of Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III) and Fe(III) ions and the organic phase were shaken at 120 rpm for the required time in a conical flask. The phases were allowed to settle down and centrifuged for disengagement. Errors in the measurement of the concentration of the tested metals by the atomic adsorption spectroscope in aqueous phase was within ±0.5 %. The distribution ratio (D) was calculated by taking the ratio of equilibrium concentration of metal ion in the organic phase

Fig. 1 Synthesis of *tetra-tert-*
butyl-calix[4]-bis[(4-methly-
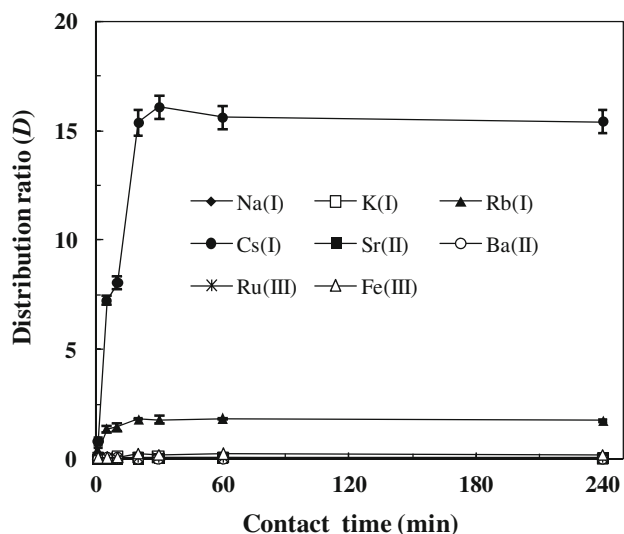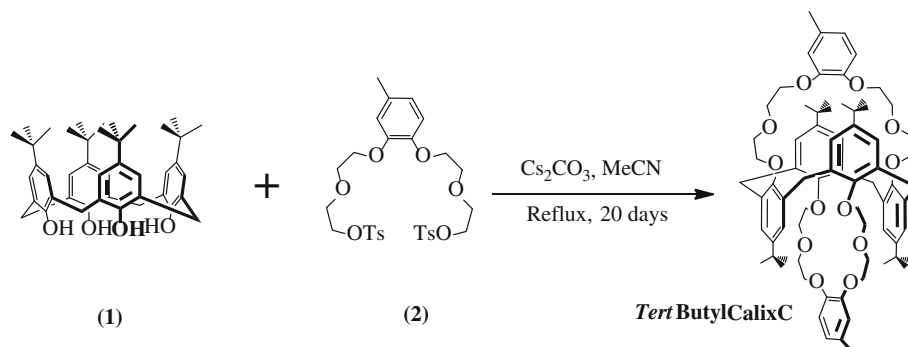1,2-phenylene-crown-6]
(*Tert*ButylCalixC)

(1)   **(2)**   ***Tert*ButylCalixC**

Fig. 2 The effect of contact time on the distribution ratio of the tested metals. $[HNO_3]_{(a)} = 4.0$ M, $[Tert\text{ButylCalixC}]_{(a)} = 8.0 \times 10^{-3}$ M, $[\text{Metals}]_{(a)} = 5.0 \times 10^{-4}$ M, $T = 298$ K, Phase ratio = 1:1

Table 1 D_{Cs} of *Tert*ButylCalixC and some typical calix[4]biscrowns

Compounds	D_{Cs}
*Tert*ButylCalixC	16.09
Calix[4]-bis-crown-6	4.54
Calix[4]-bis-benzo-crown-6	4.54
Calix[4]-bis-naphtho-crown-6	5.47
Calix[4]-bis-*tert*-octyl-benzo-crown-6	4.22

the investigation on the effect of contact time on extraction is meaningful. These typical fission and nonfission elements, Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III) and Fe(III) were extracted by *Tert*ButylCalixC/*o*-nitroanisole for different contact time at 4.0 M HNO_3 medium. The results are shown in Fig. 2.

It was found that the increase in contact time in 30 min increased D_{Cs} quickly. Values of D_{Cs} were 0.82 at 1 min, 7.26 at 5 min, 8.06 at 10 min, 15.39 at 20 min and 16.09 at 30 min, respectively. A further increase in contact time up to 240 min had a negligible effect on D_{Cs} which kept at a constant value ca. 15.61. The nature of fast extraction dynamic was proved. The explanation for this was that the process of recognition of *Tert*ButylCalixC toward Cs(I) was fast and the resultant complex was transferred into the organic phase quickly. For the other tested elements, only Rb(I) had a similar extraction dynamic process with Cs(I) and the distribution ratio of Rb(I) at equilibrium was nearly 1.86. Na(I), K(I), Sr(II), Ba(II), Ru(III) and Fe(III) ions showed almost no extraction due to the weak complexation.

Comparing with extraction systems based on other calixbiscrowns, the *Tert*ButylCalixC/*o*-nitroanisole system had a good cesium extraction ability. The maximum distribution ratio of Cs(I) in the *Tert*ButylCalixC/*o*-nitroanisole extraction system reached round 16 which is significantly greater than distribution ratios in literatures [22]. The distribution ratios of *Tert*ButylCalixC and some typical calix[4]biscrown derivatives in the extraction of Cs(I) are listed in Table 1.
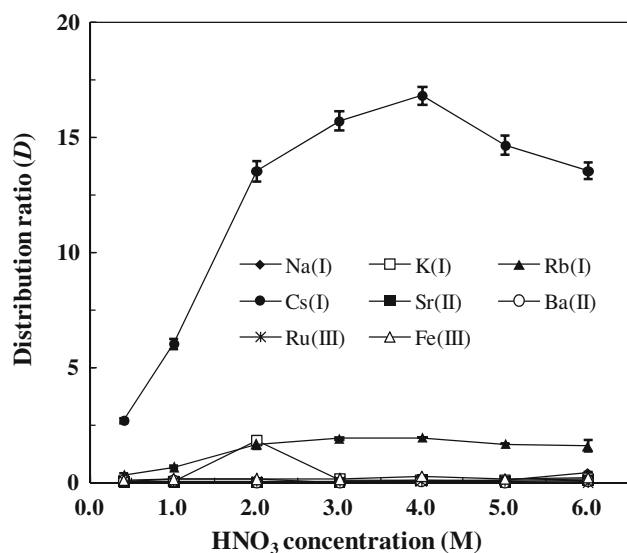
and that in the aqueous phase after extraction. The equation for D was listed by Eq. (1).

$$D = \frac{C_{(o)}}{C_{(a)}} \quad (1)$$

where $C_{(o)}$ and $C_{(a)}$ denote the equilibrium concentration of the tested metals in organic phase and aqueous phase after extraction, respectively.

Separation factor of Cs(I) to the other tested metals, $SF_{Cs/M}$, was figured out by Eq. (2).

$$SF_{Cs/M} = \frac{D_{Cs}}{D_M} \quad (2)$$

Results and discussion

Effect of contact time on the extraction

Datum about distribution ratios at different contact time is useful for the determination of equilibrium as well as for a better separation at non equilibrium if needed. Therefore

Fig. 3 Effect of HNO$_3$ concentration on the distribution ratio of the tested metals. [*Tert*ButylCalixC]$_{(o)}$ = 8.0 × 10^{-3} M, [Metals]$_{(a)}$ = 5.0 × 10^{-4} M, Contact time = 240 min, T = 298 K, Phase ratio = 1:1

Fig. 4 The dependent of the relative intensity of reaction A and B on the HNO$_3$ concentration

It could be concluded that under the experimental conditions the *Tert*ButylCalixC/*o*-nitroanisole system had high ability to selectively extract Cs(I). The equilibrium of extraction of *Tert*ButylCalixC/*o*-nitroanisole toward Cs(I) reached in 30 min.

Effect of HNO$_3$ concentration on the extraction

Highly active liquid waste, the raffinate of PUREX process, contains a high amount of nitric acid. Hence, it is necessary to investigate the effect of HNO$_3$ concentration on the solvent extraction with *Tert*ButylCalixC/*o*-nitroanisole. The evaluation experiment was carried out and 240 min of shake time was utilized to make the extraction equalized. The results are shown in Fig. 3.

As can be seen, the distribution ratio of Cs(I) (D_{Cs}) increased from 2.68 to 16.82 with increasing HNO$_3$ concentration from 0.4 to 4.0 M. The reason for this was that the reaction A (Fig. 4) was dominant in extraction system. D_{Cs} decreased from 16.82 to 13.55 with increasing HNO$_3$ concentration from 4.0 to 6.0 M. The reason for this behavior was that the coordination reaction B (Fig. 4) between HNO$_3$ and *Tert*ButylCalixC was the main reaction which decreased the effective quantity of *Tert*ButylCalixC for Cs(I) extraction. The coordination reaction resulted from oxygen atoms in crown ether moieties, which had strong affinity toward nitric acid through hydrogen bonding.

Furthermore, D_{Cs} were obviously greater than D of the other metals in the range of 0.4 M to 6.0 M HNO$_3$
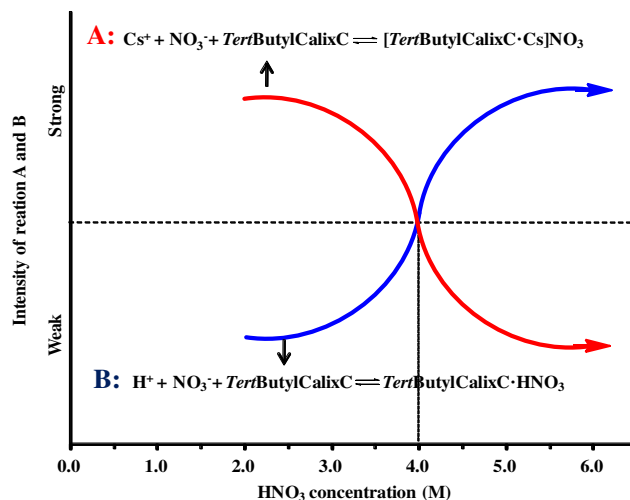
concentration. For all the other metals, only Rb(I) was slightly extracted with a maximum distribution ratio of 1.94 because the properties of Rb(I) was the most close to them of Cs(I). Therefore good selectivity for Cs(I) over the other metals was affirmed. The process of good selectivity for Cs(I) could be described as follows. When a *Tert*ButylCalixC molecule was surrounded by Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III) and Fe(III) ions, the *Tert*ButylCalixC molecule only accepted Cs(I) by an oxygen-rich cycle due to the similar size. The accepted Cs(I) ion was fixed in the oxygen-rich cycle by lone pair electrons of oxygen atoms. Then the resultant complex was transferred into the organic phase by dissolution.

Separation factors of Cs(I) to the other metals at the evaluated HNO$_3$ concentration were worked out and shown in Table 2.

According to above results, it was concluded that the extraction system based on the new compound *Tert*ButylCalixC had selective extraction ability toward Cs(I). Other metals such as Na(I), K(I), Rb(I), Sr(II), Ba(II), Ru(III) and Fe(III) ions almost had no influence on the selectivity. The optimum HNO$_3$ concentration for the extraction was 4.0 M which was close to the acidity of actual HLW.

Effect of temperature on the extraction

To understand the thermodynamic behavior, the extraction of Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III), and Fe(III) with the *Tert*ButylCalixC/*o*-nitroanisole system in 4.0 M HNO$_3$ was conducted at temperatures of 298, 303, 308, 313, and 318 K. The relevant results are shown in Fig. 5.

Table 2 Separation factors (SF) of Cs(I) to other metals at different HNO$_3$ concentration

HNO$_3$ Concentration (M)	$SF_{Cs/Na}$	$SF_{Cs/K}$	$SF_{Cs/Rb}$	$SF_{Cs/Sr}$	$SF_{Cs/Ba}$	$SF_{Cs/Fe}$	$SF_{Cs/Ru}$
0.4	213	74.5	8.02	77.5	207	31.4	642
1.0	49.5	188	9.16	154	929	51.8	253
2.0	110	7.36	8.17	646	>929	116	298
3.0	>110	257	8.23	1,153	>929	121	354
4.0	1,106	148	8.64	163	>929	66.1	414
5.0	189	184	8.76	423	>929	99.2	546
6.0	33.2	98.9	8.54	162	>929	68.4	>546

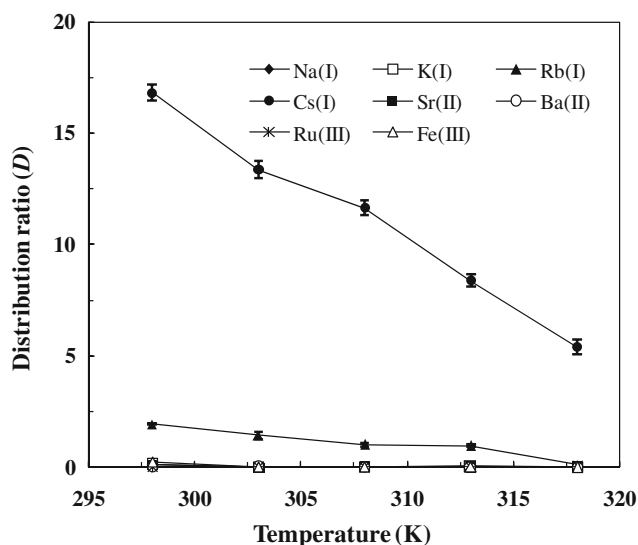**Fig. 5** Effect of temperatrue on the distribution ratio of the tested metals. [HNO$_3$]$_{(a)}$ = 4.0 M, [TertButylCalixC]$_{(o)}$ = 8.0 × 10^{-3} M, [Metals]$_{(a)}$ = 5.0 × 10^{-4} M, Contact time = 240 min, Phase ratio = 1:1

As shown in Fig. 5, D_{Cs} sharply decreased at higher temperatures, which indicated that extraction of Cs(I) in this system was an exothermic process. Other metals showed negligible extraction in the evaluated temperature range except for Rb(I), which presented similar tendency with Cs(I). It is known that both Rb(I) and Cs(I) are alkali metals and their ionic radius are close. This makes it possible that as TertButylCalixC recognizes Cs(I) ion, the size of Rb(I) might also match with cavity of TertButylCalixC. It resulted in the effective recognition of TertButylCalixC for Rb(I) when Cs(I) was extracted. The solvent extraction behavior of Rb(I) with TertButylCalixC was therefore similar to that of Cs(I). Thermodynamics parameters of the extraction reaction such as Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were calculated by Arrhenius law

$\mathrm{d}\ln D/\mathrm{d}T = \Delta H°/(RT^2)$ and Gibbs free energy $\Delta G° = \Delta H° - T\Delta S°$. The corresponding results are listed in Table 3. The negative $\Delta G°$ of Cs(I) extraction at all evaluated temperature confirmed the feasibility of the process and spontaneous nature. The decrease of the value of $\Delta G°$ with increasing temperature indicated that the recognition of TertButylCalixC toward Cs(I) was weaker. The negative value of $\Delta H°$ (−43.2 kJ·mol^{-1}) of Cs(I) extraction confirmed the extraction reaction was exothermic. The negative value of $\Delta S°$ (−121.28 J mol^{-1} K^{-1}) of Cs(I) extraction reflected a decrease in randomness. For Rb(I), the negative value of $\Delta H°$ (−94.84 kJ mol^{-1}) and $\Delta S°$ (−309.94 J mol^{-1} K^{-1}) also denoted the extraction was exothermic and a decrease in randomness. All of these results showed that in HNO$_3$ solution, Cs(I) and Rb(I) had similar extraction properties due to close ionic radius and electric structure.

The discussion of the extraction mechanism

Electrospray ionization mass spectrometry is regarded as a powerful method for chemical stoichiometry determination. To investigate the extraction mechanism, an extraction experiment identical to the extraction above was performed except the aqueous phase only contained Cs(I). The separated organic phase was then characterized by ESI–MS. The result is shown in Fig. 6.

The peak of 1,194.0 was determined as the complex of [TertButylCalixC·NH$_4$]$^+$. The strongest mass peak at 1,309.0 indicated the formation of 1:1 mononuclear complex, [TertButylCalixC·Cs]$^+$. The mass peak at 1,443.2 was considered to be [TertButylCalixC·2Cs]$^{2+}$, proving the existence of the 1:2 binuclear complex. However, the extent of formation of the 1:2 binuclear complex was a hundred-fold less than formation of the 1:1 mononuclear complex. The results demonstrated that 1:1 mononuclear complex accounted for the mechanism of extraction. Since calix[4]biscrown-6 had the same complex behavior [29], it

Table 3 Thermodynamic parameters of the solvent extraction of Cs(I) and Rb(I) with *Tert*ButylCalixC/*o*-nitroanisole

Metal ion	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta H°$ (KJ mol^{-1})	$\Delta G°$ (KJ mol^{-1})				
			298 K	303 K	308 K	313 K	318 K
Cs(I)	−121.28	−43.2	−6.99	−6.53	−6.29	−5.54	−4.46
Rb(I)	−309.94	−94.84	−1.64	−0.90	−0.05	0.09	5.61

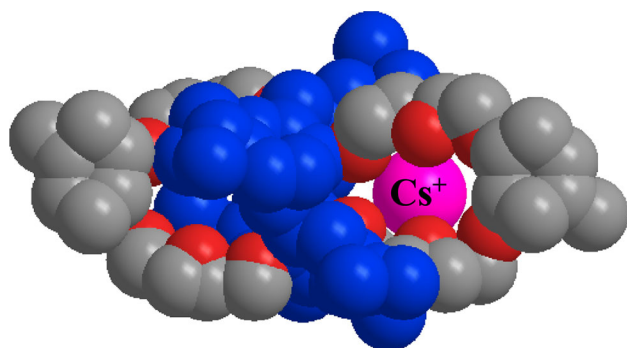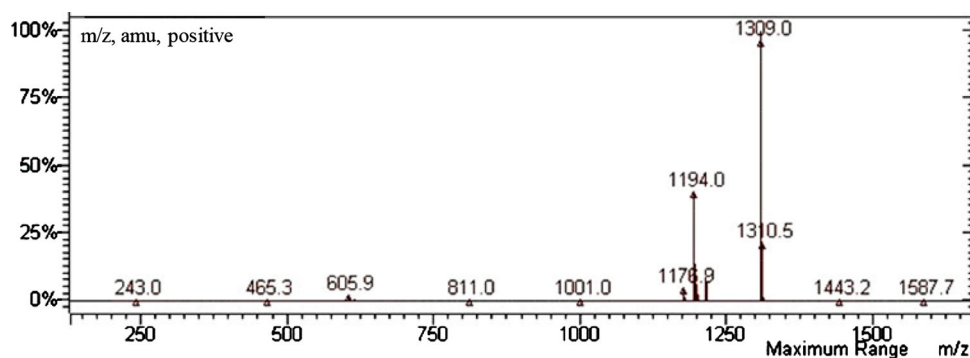**Fig. 6** ESI-MS spectrum of *Tert*ButylCalixC/*o*-nitroanisole system after extraction

Fig. 7 1:1 Type of mononuclear complex of *Tert*ButylCalixC and Cs(I)

could be concluded that the analogue of calix[4]biscrown tended to form 1:1 mononuclear complex with Cs(I) rather than 1:2 binuclear complex. The reason for this was that the occupation of one crown cycle in the *Tert*ButylCalixC molecule by one Cs(I) ion resulted in the loss of complex ability of the other crown cycle toward Cs(I). The possible complex is shown in Fig. 7.

Conclusions

Calixbiscrowns appear to be suitable extractants for the removal of cesium from HLW due to their recognition ability toward cesium. The optimum calixbiscrown for cesium separation is still unknown. With this in mind, a new calixbiscrown derivative named *Tert*ButylCalixC was successfully fabricated. The extraction of Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III) and Fe(III) ions from aqueous solution with *Tert*ButylCalixC/*o*-nitroanisole was conducted. *Tert*ButylCalixC/*o*-nitroanisole could selectively extract Cs(I). The extraction of Cs(I) with *Tert*ButylCalixC/*o*-nitroanisole depended on the HNO$_3$ concentration. The extraction process reached equilibrium within 30 min. Increasing temperature was adverse to the extraction and the suitable temperature was 298 K. ESI–MS preliminarily determined a 1:1 mononuclear complex was formed. The extraction properties and mechanism of the tested metals were discussed. The thermodynamic data for the solvent extraction Cs(I) and Rb(I) were obtained. *Tert*ButylCalixC/*o*-nitroanisole was proved to be effective for the separation of Cs(I).

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