Chromatographic Partitioning of Cesium by a Macroporous Silica-Calix[4]arene-crown Supramolecular Recognition Composite

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A macroporous silica-based 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) supramolecular recognition polymeric composite, (Calix[4]+Oct)/SiO_2-P, was synthesized. It was performed by impregnating and immobilizing Calix[4]arene-R14 and n*-octanol into the pores of the macroporous SiO_2-P particles support.* n*-Octanol was used to modify Calix[4]arene-R14 through hydrogen bonding. The effect of eight typical fission products contained in highly active liquid waste (HLW) on the adsorption of Cs(I), one of the heat generators, was investigated at 298 K by examining the effect of contact time and the HNO_3 concentration in a range of 0.3–7.0 M. (Calix[4]+Oct)/SiO_2-P showed excellent adsorption ability and high selectivity for Cs(I) at 4.0 M HNO_3 over the tested elements. The partitioning of Cs(I) from a simulated HLW was operated by (Calix[4]+Oct)/SiO_2-P packed column. Cs(I) was able to be effectively eluted by water and separated from the tested metals. It is demonstrated that (Calix[4]+Oct)/SiO_2-P is promising to apply in chromatographic separation of Cs(I) from HLW.* © 2010 American Institute of Chemical Engineers AIChE J, 56: 2632–2640, 2010

Keywords: chromatographic separation, macroporous silica-based support, supramolecular recognition composite, cesium, highly active liquid waste

Introduction

Radioactive nuclides Cs-137 with the half-life of 30 yr and Sr-90 with the half-life of 28 yr are two heat emitting nuclides. They are usually contained in highly active liquid waste (HLW) produced in reprocessing of nuclear spent fuel (NSF). It is known that both Cs-137 and Sr-90 are harmful to the safety of the vitrified HLW in final geological disposal. Another radioactive nuclide, Cs-135 with the half-life of 2×10^6 yr, has a long-term adverse impact on environment because of its mobility in final repository. On the other hand, the elimination of Cs-135 and Cs-137 is required for reducing significantly the need of cooling fission products containing solutions, and the time of vitrified waste storage before its disposal in geological formation. So, effective separation of the heat emitting nuclides from HLW is meaningful.

The most investigations concerning separation and recovery of Cs(I) from HLW carried out currently is focused on

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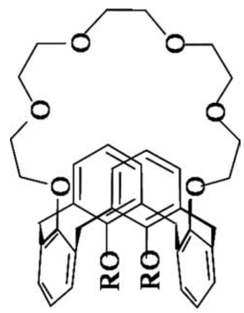

Figure 1. Molecular structure of supramolecular recognition agent calix[4]crown-crown.

liquid-liquid solvent extraction. A few partitioning techniques such as universal solvent extraction process,[1–3] fission product extraction,[4,5] and cesium separation by calix-crown extraction processes,[6] e.g., have been reported. Some supramolecular recognition agents such as highly lipophilic calix[4]arene-bis(*tert*-octyl benzo-crown-6) (BOB CalixC6) and aza-calix[4]arene-crown derivatives, e.g., show high selectivity for Cs(I) over Na(I), K(I), Rb(I), and the other metals.[7]

It is known that the calix[4]crown compounds as shown in Figure 1 are generally composed of a calixarene and a crown ether moiety bonded together by the phenolic oxygens of the calixarene and a polyether chain.[8,9] The macrocyclic ring in calix[4]arenes acts as a molecular backbone to ligate functional groups. There are many examples where the ring itself engages in binding such as with its p-basic phenolic cavities to alkali metals cations, with the phenolic oxygen atoms or to organic molecules by CH-p or p-*p*-stacking interactions. Although the crown ether complexes with metal ions, the calix[4]crown can assume various conformations, e.g., cone, partial cone, 1,2-alternate, and 1.3-alternate, and so on, that play a crucial role in the selectivity for different metal ions. Especially, some derivatives of 1.3-alternate calix[4]crown-6 ether synthesized have been shown to possess high selectivity for Cs(I) and to form a 1:1 type of the complex, rendering them suitable for the removal of Cs(I) from nuclear waste.[10,11] The Cs/Na and Cs/K selectivity ratios for some of these calixarenes exceeding 10^4 and 10^2 as measured by liquid-liquid solvent extraction. Some investigations carried out showed that calix[4]crown compound has excellent selectivity for alkali and alkaline-earth metal ions.

Extraction chromatography is one of the main separation technologies. The macroporous silica-based chelating agent impregnated polymeric composite, a new kind of extraction resin, has been developed recently. Compared to the conventional polymeric matrix resins, the macroporous silica-based type of extraction resin has rapid adsorption and elution kinetics, high-mechanical strength, and significantly low-pressure loss in a packed column.

Based on the macroporous silica-based composite and the MAREC (Minor Actinides Recovery from HLW by Extraction Chromatography) process developed previously,[12–14] an advanced chromatographic separation technology entitled SPEC (Strontium/Cesium Partitioning from HLW by Extraction Chromatography) process as shown in Figure 2 has been developed recently.[15,16] It was used specially to recover two heat emitting nuclides, Cs(I) and Sr(II), from an acidic HLW. Two supramolecular recognition compounds, 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) and $4,4',(5')$-di(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6), were used as the complexing agents. Cs(I) was separated in the first column packed with a macroporous silica-based impregnated supramolecular recognition composite, Calix[4]arene-R14/SiO_2-P.[17,18] After conditioning the HNO_3 concentration in effluent, Sr(II) was

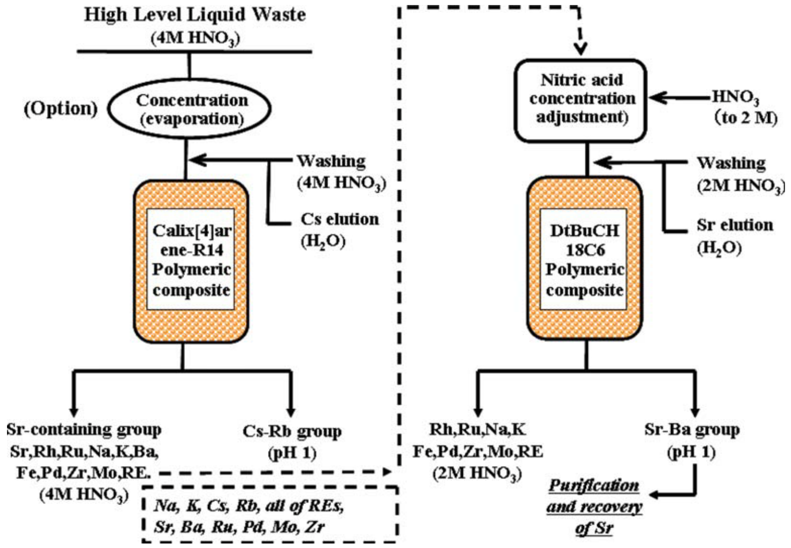

Figure 2. An advanced SPEC process for heat generator partitioning from an acidic HLW utilizing two novel macroporous silica-based composites by extraction chromatography.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

then partitioned in the second one packed with the macroporous silica-based composite, DtBuCH18C6/SiO_2-P.[19,20] Calix[4]arene-R14/SiO_2-P showed excellent selectivity and high-recognition ability for Cs(I) over Na(I), K(I), Sr(II), and Ba(II) with the exception of Rb(I).[21] However, the effect of some typical fission products such as REs(III), Mo(VI), Zr(IV), Pd(II), and Ru(III), etc., on the Cs(I) adsorption onto the Calix[4]arene-R14/SiO_2-P materials has not been understood yet. In addition, calix[*n*]arene-crown is a kind of the compound having high lipophilicity. The impregnation of Calix[4]arene-R14 into the pores of the macroporous SiO_2-P particles support was unsatisfactory. It made the use of the Calix[4]arene-R14/SiO_2-P composite material in the SPEC process be restricted. Tri-*n*-butyl phosphate (TBP), a hydrophilic agent having $-P{=}O$ functional group, was used to modify the Calix[4]arene-R14 molecule, but the modification effect was insignificant.[18]

To find a method to partition Cs(I), an improved macroporous silica-based supramolecular recognition material, (Calix[4]+Oct)/SiO_2-P, was synthesized. It was prepared by impregnating and immobilizing both Calix[4]arene-R14 and *n*-octanol into the pores of the macroporous SiO_2-P particles. *n*-Octanol molecule having $-OH$ group was used to modify Calix[4]arene-R14 through hydrogen bonding. The effects of some typical coexistent fission products such as Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), and Zr(IV) on the adsorption of Cs(I) onto (Calix[4]+Oct)/SiO_2-P was studied at 298 K. It was conducted by investigating the effects of contact time and the HNO_3 concentration in the range of 0.3–7.0 M. The chromatographic partitioning of Cs(I) from a 4.0 M HNO_3 solution containing 5.0×10^{-3} M of the tested metals was performed by (Calix[4]+Oct)/SiO_2-P packed column utilizing 4.0 M HNO_3 and water as eluants. The possibility and feasibility of the Cs(I) separation from a simulated acidic HLW were demonstrated.

Experimental

Reagents

Chemical reagents $RE(NO_3)_3{\cdot}6H_2O$ (RE = La and Y), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $ZrO(NO_3)_2{\cdot}H_2O$, and $CsNO_3$ used were of analytical grade. Both ruthenium nitrosyl nitrate solution with 1.5 wt % of Ru(III), and rhodium nitrosyl nitrate solution with 1.6 wt % of Rh(III) were provided by Strem Chemicals, USA. Palladium nitrate solution with 4.5 wt % of Pd(II) was provided by the Tanaka Noble Metal Co., Inc., Japan. La(III) and Y(III) were used to understand the adsorption behavior of all trivalent rare earths and minor actinides. The concentrations of all of the tested elements used were 5.0×10^{-3} M (M = mol/dm^3). The HNO_3 solutions of different concentrations employed were prepared temporarily.

A new supramolecular recognition compound, 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) with a purity greater than 97%, was provided by the Innovation and Chimie Fine, France. A long-chain organic compound containing -OH functional group, *n*-octanol with a purity more than 99.5%, was an available commercial product. It was used to modify the macrocyclic Calix[4]arene-R14 molecular through intermolecular interaction force.

Dichloromethane, methanol, and the other reagents used were of analytical grade and were used without further treatment.

The novel macroporous silica-based supramolecular recognition composite, (Calix[4]+Oct)/SiO_2-P, was synthesized. The macroporous SiO_2-P particles support employed was prepared as described previously.[22] A symbol P in SiO_2-P shows styrene-divinylbenzene copolymer, which was prepared by means of a polymerization reaction taking place inside the macroporous SiO_2 substrate. The mean pore size, pore fraction, and bead diameter of the macroporous SiO_2-P particles support were 0.6 μm, 0.69, and in the range of 40–60 μm, respectively.

Synthesis of the macroporous silica-based supramolecular recognition composite

The macroporous SiO_2-P particles were treated actively at least three times by acetone and methanol prior to synthesis of (Calix[4]+Oct)/SiO_2-P. The purpose was to increase significantly the affinity of copolymer inside the macroporous SiO_2-P particles support for Calix[4]arene-R14. *n*-Octanol was used as a molecular modifier of Calix[4]arene-R14. The pre-experiment showed that in the presence of *n*-octanol, Calix[4]arene-R14 molecule was easily to impregnate and immobilize into the SiO_2-P particles support. The synthesis procedure of (Calix[4]+Oct)/SiO_2-P is described as follows.

The weighted quantity of Calix[4]arene-R14 and the calculated amount of *n*-octanol were dissolved completely with 100 cm^3 of dichloromethane in a 300 cm^3 of glass flask at room-temperature. The given quantity of the SiO_2-P particles activated was then added under shaking. Following the mixture was stirred mechanically for 90 min, it was then moved into a silicon-oil bath and stirred for 12 h at 323 K to impregnate both the Calix[4]arene-R14 and *n*-octanol molecules into the pores of the macroporous SiO_2-P particles by physical evaporation. After drying in a vacuum drying oven around 323 K for an overnight, a macroporous colorless silica-based supramolecular recognition composite, (Calix[4]+Oct)/SiO_2-P, was obtained. It was then characterized by TG-DSC and elemental analysis, respectively. The synthesis pathway of (Calix[4]+Oct)/SiO_2-P is shown in Figure 3.

Adsorption of the tested metals onto (Calix[4]+Oct)/SiO_2-P

All of the adsorption experiments were carried out at a constant temperature 298 K. It was performed by a TAITEC MM-10 Model thermostated water bath shaker. The aqueous phase was a HNO_3 solution containing 5.0×10^{-3} M of Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), Cs(I), and Zr(IV), while the solid phase was the amount of the (Calix[4]+Oct)/SiO_2-P composite. The experimental condition was phase ratio of 0.25 g to 5 cm^3 and the HNO_3 concentration range of 0.3 M to 7.0 M. As the two phases were mixed into a 50 cm^3 of ground glass-stopped flask, it was shaken mechanically at 120 rpm for a desired contact time. After the phase separation by a membrane filter with ~0.45 μm pore, the concentrations of the tested metals in aqueous phase were measured using a Varian 700-ES Model

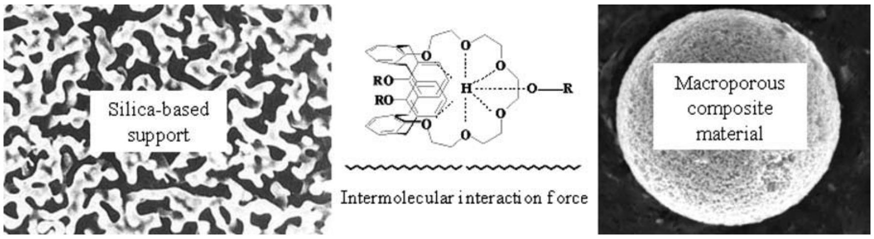

Figure 3. Synthesis pathway of the macroporous silica-based (Calix[4]+Oct)/SiO_2-P composite.

simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian, Inc., USA) with the exception of the content of Cs(I) that was analyzed using a Varian AA 240 FS Model atomic adsorption spectroscopy (Varian, Inc., USA). The distribution coefficients (K_d) of the tested elements onto the (Calix[4]+Oct)/SiO_2-P material were calculated as follows

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \quad (\mathrm{cm}^3/\mathrm{g}) \tag{1}$$

where C_o and C_e show the initial and equilibrium concentrations of the tested metals in aqueous phase, respectively. $W$and V represent the weight of the dry (Calix[4]+Oct)/SiO_2-P material and the volume of aqueous phase used in the experiments.

Chromatographic partitioning of the tested elements

Prior to the separation performance, the macroporous slica-based (Calix[4]+Oct)/SiO_2-P polymeric composite was packed into a Pyrex glass column with a dimension of 10 mm in inner-diameter, and 300 mm in length under 0.25–0.35 MPa of N_2 gas pressure. The density of the (Calix[4]+Oct)/SiO_2-P material in the column was 0.61 g/cm^3. It was then equilibrated by 4.0 M HNO_3 solution. The column operation temperature 298 K, used in the loading and elution cycle was controlled and maintained by the circulation of the thermostated water through an EYELA NTT-1200 Model water jacket (Tokyo Rikakikai Co., Ltd., Japan). The flow rate was controlled to 1.0 cm^3/min by combination of a NPG-50UL Model pressure gage (Nihon Seimitsu Kagaku Co., Ltd., Japan), with a 2GN15K Model pressure limiter (Oriental Motor Co., Ltd., Japan). The concentration of HNO_3 in feed solution was 4.0 M.

Following a 4.0 M HNO_3 solution containing 5.0×10^{-3} M of Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), Cs(I), and Zr(IV) as feed solution passed through the column packed with the (Calix[4]+Oct)/SiO_2-P polymeric composite, the given volumes of 4.0 M HNO_3 and distilled water as eluents were then pumped downflow through the adsorption column. 5 cm^3 aliquots of effluent fraction were collected using an EYELA DC-1500 Model auto-fractional collector (Tokyo Rikakikai Co., Ltd., Japan). The concentrations of various metals in effluent were analyzed by the ICP-OES, and/or the atomic adsorption spectroscopy as mentioned previously. The pH value in effluent was measured using a pHs 3C Model pH-meter (Shanghai Precision and Scientific Instrument Co., Ltd., China).

Results and Discussion

Dependence of the adsorption of (Calix[4]+Oct)/SiO_2-P on contact time

The calix[4]crown-crown molecule is composed of a crown ether and a calixarene. The function of the crown ether is to complex metal ions. The crucial role of the calixarene is to increase the selectivity of calix[4]crown-crown for different metal ions or organic compounds through intermolecular recognition.[23] The complexation of calix[4]crown-crown with metal ion is different from that of the conventional complexing agent with metals. It is considered to be the effective matching of size between the calixarene cavity and these metal ions, π-bonding interactions with the arene groups, and structural reorganization of the molecule.[24,25] The cavity of calixarene containing π-bonding interactions with the arene groups's upper-end-on view with foreground atoms deleted is shown in Figure 4. It was found that with the exception of Rb(I), a few alkali metals and alkaline earths such as Na(I), K(I), Sr(II), and Ba(II) had no adverse impact on the Cs(I) adsorption onto (Calix[4]+Oct)/SiO_2-P.[21] This is of great benefit to the effective elimination of Cs(I) by the use of the macroporous silica-based calix[4]arene-crown impregnated compiste. In fact, there is around 30 elements contained in HLW, the effect of the elements such as 16 species of rare

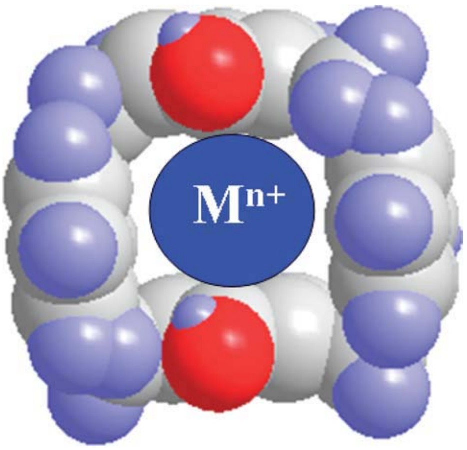

Figure 4. Cavity of calixarene containing π-bonding interactions with the arene groups's upper-end-on view with foreground atoms deleted.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

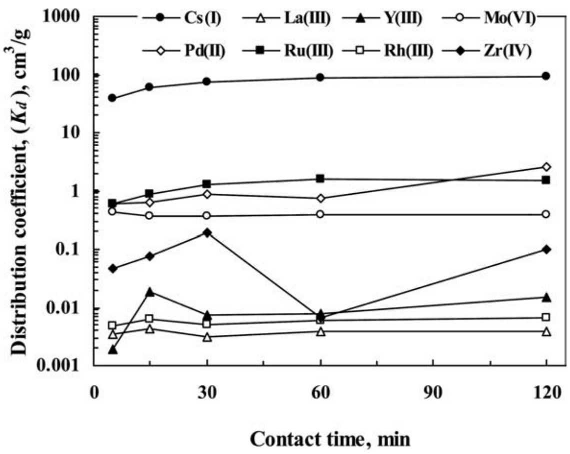

Figure 5. Dependence of the adsorption of the tested metals onto (Calix[4]+Oct)/SiO_2-P on contact time in 4.0 M HNO_3. [Metal]: 5mM, phase ratio: 0.25 g/5 cm^3, Shaking speed: 120 rpm.

earths Y(III) and La(III) to Lu(III), two minor actinides Am(III) and Cm(III), noble metals, and the other elements on the adsorption of Cs(I) has not been reported yet.

The adsorption of a few typical fission products Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), Cs(I), and Zr(IV) onto (Calix[4]+Oct)/SiO_2-P, with an increase in contact time in 4.0 M HNO_3 was investigated at 298 K. Two elements La(III) and Y(III) used in this work are the representative of all of the trivalent rare earths and minor actinides in order to reflect their adsorption onto (Calix[4]+Oct)/SiO_2-P. The related results are shown in Figure 5.

Figure 5 shows the effect of the representative metals Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), and Zr(IV) on the adsorption of Cs(I) onto the (Calix[4]+Oct)/SiO_2-P composite in 4.0 M HNO_3 at 298 K. All of the tested elements showed weak or almost no adsorption with an increase in contact time. Their distribution coefficients (K_d) onto (Calix[4]+Oct)/SiO_2-P were always below 2.5 cm^3/g. Such a low value in the distribution coefficient (K_d) was ascribed to the unmatching between the cavity of Calix[4] arene-R14 molecule and the size of the tested metal ion. It resulted in the weak complexation of the tested elements with (Calix[4]+Oct)/SiO_2-P.

La(III) and Y(III) had obvious no adsorption onto (Calix[4]+Oct)/SiO_2-P. It is predicted that in 4.0 M HNO_3, all of the RE(III) elements, Y(III) and La(III) to Lu(III), contained in HLW have no adsorption onto (Calix[4]+Oct)/SiO_2-P because of the lanthanide contraction. On the other hand, it is known that the ionic radii of the actinide elements decrease with an increase in atomic number, indicative of decreased shielding by f electrons of the outer valence electrons nuclear charge. It makes the actinide contraction and lanthanide contraction very similar. From this viewpoint, it is possible that the long-lived minor actinides Am(III) and Cm(III) show weak or almost no adsorption onto the (Calix[4]+Oct)/SiO_2-P composite. Therefore, 16 of rare earths and two of minor actinides contained in an acidic HLW show no adverse impact on the adsorption of Cs(I). It is meaningful and valuable for effective elimination of Cs(I) from these elements containing HLW.

Opposite to the elements mentioned previously, the adsorption of (Calix[4]+Oct)/SiO_2-P for Cs(I) was stronger. The distribution coefficient (K_d) of Cs(I) in 4.0 M HNO_3 increased obviously with an increase in contact time and basically kept constant following 60 min, showing the adsorption equilibrium. Its distribution coefficient (K_d) was 39.57 cm^3/g at 5 min, 72.43 cm^3/g at 30 min, 87.12 cm^3/g at 60 min, and 94.11 cm^3/g at 120 min, which was higher than that of 45.16 cm^3/g at 120 min in 4.0 M HNO_3 as the modification of Calix[4]arene-R14 with tri-*n*-butyl phosphate (TBP).[18] The high adsorption of Cs(I) onto (Calix[4]+Oct)/SiO_2-P is considered to the size matching between host and guest, i.e., the excellent match between the diameter of Cs(I) cation and the cavity of the Calix[4]-arene-R14 molecule comprising six oxygen atoms. The average distance between the Cs(I) and the oxygen atoms is in the region of 3.1 angstrom, equivalent to that separating the Cs from the water molecules of its first hydration later. In addition, an interaction has been revealed between Cs and the delocalized electrons (pi) of the benzenic units making up the calix[4]arene cavity. X-ray structures have shown that the calix[4]crown compounds are highly preorganized and enforce a cation-arene pi interaction in a well-defined cavity. To understand the matching relation of the metal cations and the cavity size of the Calix[4]arene-R14 molecule, ionic radius of some relevant elements are shown in Figure 6.

As can be seen, the ionic radius of all of REs(III) including Y(III) and La(III) to Lu(III), as well as the other FPs such as Mo(VI), Pd(II), Ru(III), Rh(III), Cs(I), and Zr(IV) are in the range of 0.0848–0.106 nm and 0.065 to 0.086 nm. The radius of cavity size of Calix[4]arene-R14 is reported to be about 0.162 nm, which is very close to that of Cs(I), 0.167 nm. So, the cavity size of Calix[4]arene-R14 well matched with that of Cs(I). It made the adsorption ability of Cs(I) ion onto (Calix[4]+Oct)/SiO_2-P high, while the other metals showed poor adsorption.

On the other hand, the ionic radius of Am(III) and Cm(III), 0.097 nm and 0.0982 nm, is very similar to those of REs(III). As a result, it is unmatched with that of the cavity size of (Calix[4]+Oct)/SiO_2-P. It is predicted that in the experimental conditions, the trivalent minor actinides have also no adsorption onto the (Calix[4]+Oct)/SiO_2-P composite.

It is known that there is a hydrophilic functional group —OH, contained in octanol molecule. Calix[4]arene-R14 is composed of a lipophilic calixarene and a hydrophilic crown ether having six oxygen atoms, which has high affinity for hydrogen. This makes it possible that -OH can associate with oxygen atom in crown ether inside Calix[4]arene-R14 through hydrogen bonding, and form to a stable associated species in the form of O—H---O.

In comparison with octanol, the limited modification of Calix[4]arene-R14 with TBP was found.[18] Because the functional group inside TBP is —P = O, but not —OH, an effective association between TBP and Calix[4]arene-R14 cannot be formed through hydrogen bonding. Therefore, octanol showed better modification for Calix[4]arene-R14 than that of TBP.

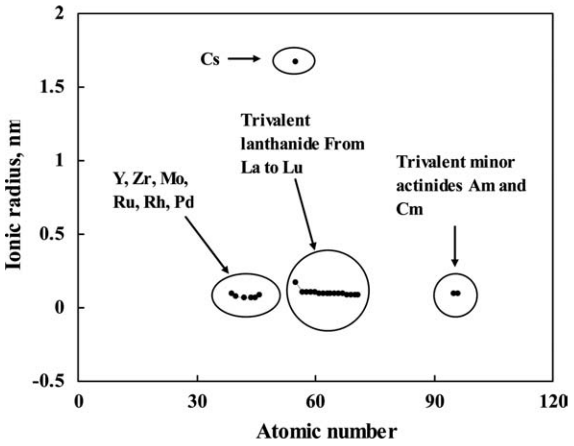

Figure 6. Ionic radius of the relevant metal.

Dependence of the adsorption of (Calix[4]+Oct)/SiO_2-P on HNO_3 concentration

The structure of the calix[4]crown-crown molecule is composed of a highly lipophilic calixarene and a hydrophilic crown ether moiety bonded together via the phenolic oxygens of the calixarene and a polyether chain. Oxygen-atom usually has affinity for hydrogen through hydrogen bonding. It is known that in reprocessing of nuclear spent fuel, the concentration of HNO_3 in HLW is around 3.0 M. The change in the HNO_3 concentration in aqueous phase may have obvious effect on the complexation of calix[4]arene-crown for metal ions. The effective recognition of (Calix[4]+Oct)/SiO_2-P for the tested metals and the intermolecular association of (Calix[4]+Oct)/SiO_2-P with HNO_3 are probably two competitive reactions.

To know the effect of the HNO_3 concentration, the adsorption of a few typical FPs such as Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), Zr(IV), and Cs(I) onto (Calix[4]+Oct)/SiO_2-P was performed in a wide HNO_3 concentration range of 0.3 M to 7.0 M at phase ratio of 0.25 g/5 cm^3, shaking rate of 120 rpm, and contact time of 120 min at 298 K, while the effect of the tested FPs on the adsorption of Cs(I) was evaluated. The results are illustrated in Figure 7.

As can be seen, with an increase in the HNO_3 concentration, the distribution coefficient (K_d) of the typical fission products Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), and Zr(IV) onto (Calix[4]+Oct)/SiO_2-P was less than 4.0 cm^3/g, showing weak or no adsorption. It reflects the tested metals and their similar elements in chemical properties have no adverse impact on the adsorption and separation of Cs(I) from HLW. Especially, 15 of REs(III) including Y(III) and La(III) to Lu(III) have no adverse impact on the Cs(I) separation because of no adsorption of La(III) and Y(III), which results from the lanthanide contraction. According to the chemical similarity of the actinide contraction and lanthanide contraction, trivalent minor actinides MAs(III) also have no adverse impact on the Cs(I) adsorption and separation.

The average distance between the Cs and the oxygen atoms is in the region of 3.1 angstrom, equivalent to the one separating Cs from the water molecules of its first hydration later. In addition, an interaction has been revealed between Cs and the delocalized electrons (pi) of the benzenic units making up the calix[4]arene cavity. X-ray structures have shown that the calix[4]crown compounds are highly preorganized and enforce a cation-arene pi interaction in a well-defined cavity. This makes the Cs(I) adsorption onto (Calix[4]+Oct)/SiO_2-P stronger. It was found that the distribution coefficient (K_d) of Cs(I) onto (Calix[4]+Oct)/SiO_2-P increased from 0.3 M to 3.0 M HNO_3, slightly increased to 4.0 M HNO_3, and then decreased gradually to 7.0 M HNO_3. The concentration of HNO_3 in the maximum adsorption of the Cs(I) was determined to be 4.0 M. The corresponding distribution coefficient (K_d) of Cs(I) was 7.27 cm^3/g in 0.3 M HNO_3, 39.88 cm^3/g in 2.0 M HNO_3, and 94.08 cm^3/g in 4.0 HNO_3, and 35.60 cm^3/g in 7.0 HNO_3.

The difference in the distribution coefficients (K_d) of all of the tested metals reflected that in 4.0 M HNO_3 solution, Cs(I), one of the alkali metals which are comparatively difficult to form the complex usually, was capable of being recognized effectively and complexed strongly by a hard-atom O contained in Calix[4]arene-R14 molecule and probably formed a stable 1:1 type the complex as shown in Figure 8. The superior selectivity of Calix[4]arene-R14 for Cs(I) is due to the effective matching of size between the calixarene cavity and Cs(I) ion, as well as π-bonding interactions with the arene groups, and structural reorganization of the molecule.

Based on the adsorption of the tested metals, it was obvious that the adsorption of Cs(I) with (Calix[4]+Oct)/SiO_2-P and the intermolecular association of (Calix[4]+Oct)/SiO_2-P with HNO_3 molecule were two competitive reactions. The increasing distribution coefficient (K_d) of Cs(I) in 0.324–4.0 M HNO_3 reflected that the effective complexation of Calix[4]arene-R14 with Cs(I) was dominating. The decreasing distribution coefficient (K_d) of Cs(I) in the HNO_3 concentration range of 4.0–7.0 M revealed that the association reaction of Calix[4]arene-R14 with HNO_3 was dominative. In this case, the intermolecular association between Calix[4]

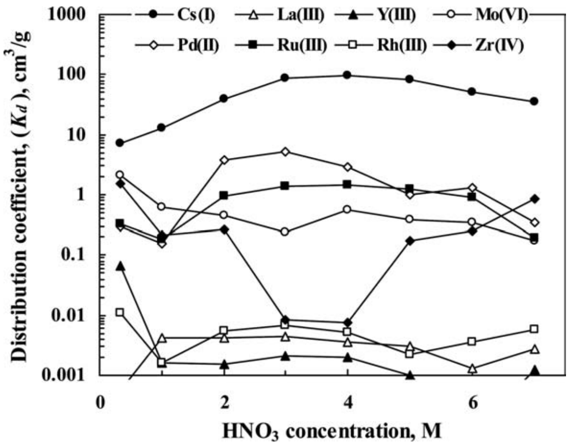

Figure 7. Dependence of adsorption of the tested metals onto (Calix[4]+Oct)/SiO_2-P on the HNO_3 concentration.

[Metal]: 5mM, phase ratio: 0.25 g/5 cm^3, Shaking speed: 120 rpm, Contact time: 120 min.

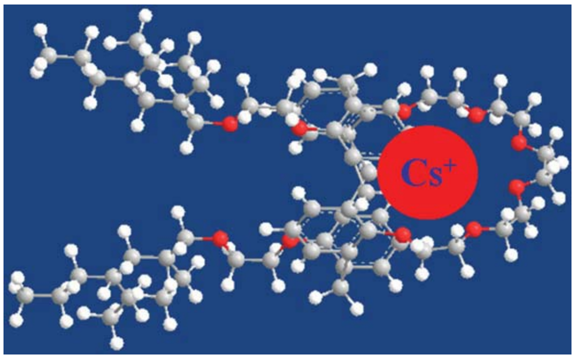

Figure 8. Complexing formation of Cs(I) with Calix[4]arene-R14.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

arene-R14 and HNO_3 through hydrogen bonding could significant decrease the available concentration of Calix[4] arene-R14 inside (Calix[4]+Oct)/SiO_2-P being capable of complexing Cs(I). So, the adsorption mechanism of Cs(I) was proposed as follows:

1 In a range of 0.3–4.0 M HNO_3, the complexation of (Calix[4]+Oct)/SiO_2-P with Cs(I) was dominative. The composition of the formed complex is [Cs(Calix[4]+Oct)/SiO_2-P]NO_3.

2 In a range of 4.0–7.0 M HNO_3, the intermolecular association of (Calix[4]+Oct)/SiO_2-P with HNO_3 was believed to be dominative. The possible association reaction was described as follows

$$HNO_3 + (\text{Calix}[4] + \text{Oct})/SiO_2\text{-}P \overset{4.0\ \text{M HNO}_3}{\rightleftharpoons} HNO_3\cdot(\text{Calix}[4] + \text{Oct})/SiO_2\text{-}P \quad (2)$$

Combination of the adsorption results of Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), and Zr(IV) obtained in this work with the adsorption of (Calix[4]+Oct)/SiO_2-P for some typical alkali and alkaline-earth metals,[21] it is obvious that in HNO_3 solution, all of the tested elements contained in HLW showed weak or almost no adsorption onto (Calix[4]+Oct)/SiO_2-P. It made it possible that with the exception of Rb(I), the other metals contained in HLW had no adverse impact on the Cs(I) adsorption. This is valuable for selective partitioning of Cs(I) from HLW by the use of the novel macroporous silica-based adsorbent.

Chromatographic partitioning of Cs(I)

The chromatographic separation of Cs(I) from a 4.0 M HNO_3 solution containing the tested metals was performed utilizing (Calix[4]+Oct)/SiO_2-P polymeric composite packed column at 298 K. The column dimensions used were 10 mm in inner-diameter and 300 mm in length. Prior to partitioning, the macroporous silica-based materials employed was pre-equilibrated fully using 4.0 M HNO_3. An acidic simulated HLW was composed of ~5.0×10^{-3} M of the tested FPs such as Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), Cs(I), Zr(IV), and 4.0 M HNO_3. The flow rate was controlled to 1.0 cm^3/min. Following the sample was collected, the corresponding pH value in effluent was determined. The mass balance of the tested metals in the separation operation was calculated. The partitioning results utilizing 4.0 M HNO_3 and water as eluents are illustrated in Figure 9.

As can be seen, with the supplement of feed solution to the adsorption column, the tested metals Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), and Zr(IV) showed almost no adsorption onto (Calix[4]+Oct)/SiO_2-P and quickly leaked out the column along with 4.0 M HNO_3. No adsorption behavior of these tested metals in the column separation experiments is quite similar to that of in the batch experiments. It obviously resulted from the weak complexation of the supermolecular recognition compound Calix[4]arene-R14 with these metals. Meanwhile, Cs(I) was adsorbed by (Calix[4]+Oct)/SiO_2-P and did not appear in effluent.

In terms of no separation behavior of La(III) and Y(III), it is predicted that in 4.0 HNO_3 solution, all of trivalent REs(III) such as Y(III), and from La(III) to Lu(III) and MAs(III) such as Am(III), Cm(III), etc., contained in HLW have no adsorption onto (Calix[4]+Oct)/SiO_2-P, and can flow into effluent along with La(III), Y(III), and 4.0 M HNO_3.

As water was then supplied to the column, Cs(I) adsorbed onto (Calix[4]+Oct)/SiO_2-P was eluted efficiently. Its elution band appeared in elution curve of Cs(I) was narrow, sharp, and showed no elution tailing, which means that Cs(I) was desorbed completely from the loaded (Calix[4]+Oct)/SiO_2-P polymeric composite and quickly flowed into effluent along with the water. Such excellent elution effect of Cs(I) in the column operation reflected that the macroporous silica-based supermolecular recognition agent impregnated polymeric adsorption material had rapid elution kinetics for Cs(I). It was considered to be the quick decomposition of the complex of Cs(I) and (Calix[4]+Oct)/SiO_2-P with a rapid decrease in the NO_3^- concentration in the resin bed. The elution equation was probably described as follows

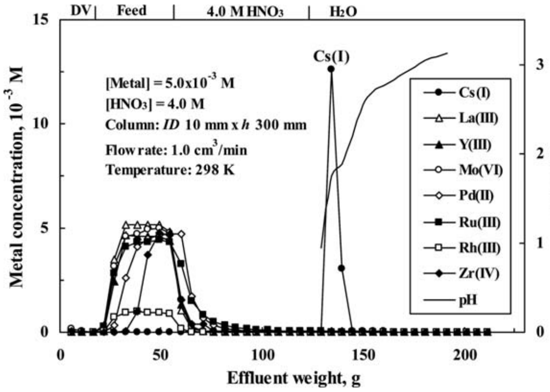

Figure 9. Chromatographic separation of Cs(I) from a simulated 4.0 M HNO_3 containing some typical fission products by (Calix[4]+Oct)/SiO_2-P packed column at 298 K.

Column: *ID* 10 mm × *h* 300 mm, Flow rate: 1.0 cm^3/min.

$$[\mathrm{Cs(Calix[4]+Oct)/SiO_2\text{-}P}]\mathrm{NO_3} \overset{\mathrm{H_2O}}{\rightleftharpoons} \mathrm{Cs^+} + \mathrm{NO_3^-} + \mathrm{(Calix[4]+Oct)/SiO_2\text{-}P} \quad (3)$$

According to the mass balance, the recovery percent of the tested metals was calculated to be 98.6% for Cs(I), and in the range of 98.1–102.7% for the others. A satisfactory partitioning and recovery of Cs(I) from the tested metals was achieved.

The pH value in effluent was measured. As the loaded (Calix[4]+Oct)/SiO_2-P composite material was eluted by water, the pH value was found to increase obviously from 0.8 to around 2.62 and then to 3.43. The acidity in effluent was always below pH 4.0. It revealed that in the column adsorption of Cs(I) and the tested typical FPs onto (Calix[4]+Oct)/SiO_2-P, a portion of HNO_3 molecule in feed solution composed of 4.0 M HNO_3 and 5.0×10^{-3} M of metal ions was simultaneously associated with the Calix[4]-arene-R14 molecule through hydrogen bonding and probably formed to a 1:1 type of the complex, HNO_3·(Calix[4]+Oct)/SiO_2-P. The elution of the loaded (Calix[4]+Oct)/SiO_2-P by water decreased the stability of HNO_3· (Calix[4]+Oct)/SiO_2-P, and then released the HNO_3 molecule from the associated complex. So, a comparatively low pH value less than 4.0 in effluent was observed. The association and disassociation of the complex of Calix[4]arene-R14 with HNO_3 were probably described as follows

$$\mathrm{HNO_3\cdot(Calix[4]+Oct)/SiO_2\text{-}P} \underset{\mathrm{4.0\ M\ HNO_3}}{\overset{\mathrm{H_2O}}{\rightleftharpoons}} \mathrm{HNO_3} + \mathrm{(Calix[4]+Oct)/SiO_2\text{-}P} \quad (4)$$

Calix[4]arene-R14 molecule is composed of a 18-crown-6 (18C6), and a calix[4]arene having a long carbon chain. It is known that almost all of the derivatives of the macrocyclic crown ethers such as dicyclohexano-18-crown-6 (DC18C6) and 4,4′,(5′)-di(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH 18C6), etc., are usually able to associate with HNO_3 through hydrogen bonding and form to 1:1 type of the complex.[26–29] However, the composition and structure of the associated complex of HNO_3 and Calix[4]arene-R14 have not been investigated yet.

In comparison with the adsorption results of the (Calix[4]+Oct)/SiO_2-P materials for some typical alkali and alkaline-earth metals,[21] it was found that in 4.0 M HNO_3, almost 27 of the typical fission and nonfission products such as Na(I), K(I), Sr(II), Ba(II), Y(III), from La(III) to Lu(III), Am(III), Cm(III), Mo(VI), Pd(II), Ru(III), Rh(III), and Zr(IV) showed no adsorption onto (Calix[4]+Oct)/SiO_2-P with the exception of Rb(I). Recently, the preliminary research was found that U(VI) and Np(V) also had no adsorption onto (Calix[4]+Oct)/SiO_2-P. It shows these metals have no adverse impact on the loading and elution of Cs(I) from HLW. As a result, application of the (Calix[4]+Oct)/SiO_2-P composite materials in effective partitioning of Cs(I), one of the main emitting heat nuclides, from HLW by extraction chromatography is promising.

The resistant behavior of the macroporous silica-based (Calix[4]+Oct)/SiO_2-P materials against γ-irradiation is being carried out at 298 K. The preliminary results showed that in 4.0 M HNO_3, (Calix[4]+Oct)/SiO_2-P had better resistance under the γ-radiation in the range of 0.5 MGy to 3.5 MGy.

On the other hand, Sr(II), another emitting heat nuclide, was demonstrated to be separated effectively from a 2.0 M HNO_3 effluent containing Cs(I) utilizing the macroporous silica-based *N,N,N′,N′*-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) or DtBuCH18C6 impregnated composite, DtBuCH18C6/SiO_2-P or TODGA/SiO_2-P.[30] However, compared to TODGA/SiO_2-P, DtBuCH18C6/SiO_2-P showed much better separation property for Sr(II). So, the use of two novel macroporous silica-based (Calix[4]+Oct)/SiO_2-P and DtBuCH18C6/SiO_2-P composites in the SPEC process in effective partitioning of Cs(I) and Sr(II) from an acidic HLW solution is feasible.

Concluding Remarks

Highly specific separation of Cs(I), one of the main emitting heat nuclides, from HLW,has always been one of the challenging works in the treatment of HLW, which is produced in reprocessing of nuclear spent fuel. Because Cs(I) is not easy to take place the complexation with conventional complexing agent, a satisfactory partitioning of Cs(I) from HLW has not been achieved. For this purpose, a macroporous silica-based supramolecular recognition composite, (Calix[4]+Oct)/SiO_2-P, was synthesized by molecular modification with *n*-octanol through hydrogen bonding.

The static-state adsorption of some typical FPs onto the (Calix[4]+Oct)/SiO_2-P composite was investigated at 298 K. The effect of 7 FPs on the Cs(I) adsorption was evaluated by checking the changes in the distribution coefficient (K_d) with the HNO_3 concentration in the range of 0.324–7.0 M and contact time. The Cs(I) adsorption increasing from 0.324 M to 4.0 M HNO_3, and decreasing to 7.0 M HNO_3. (Calix[4]+Oct)/SiO_2-P showed excellent adsorption ability and high recognition for Cs(I) over all of the tested elements. The chromatographic partitioning of Cs(I) from a simulated 4.0 M HNO_3 solution was performed by the (Calix[4]+Oct)/SiO_2-P materials packed column utilizing 4.0 M HNO_3 and water as elutens. The Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), and Zr(IV) tested had no adsorption and flowed into effluent along with 4.0 M HNO_3. Cs(I) adsorbed onto (Calix[4]+Oct)/SiO_2-P was eluted by water, and, thus, separated from the FPs.

The results are demonstrated that in 4.0 M HNO_3, the macroporous silica-based Calix[4]arene-R14/SiO_2-P composite is effective in chromatographic partitioning of Cs(I) from HLW. The relevant investigations using a genuine HLW will be carried out further.

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Literature Cited

1. Herbst RS, Law JD, Todd TA, Romanovskiy VN, Babain VA, Esimantovskiy VM, Smirnov IV, Zaitsev BN. Universal solvent extraction (UNEX) flow sheet testing for the removal of cesium, strontium, and actinides elements from radioactive, acidic dissolved waste. *Solvent Extr Ion Exch.* 2002;20:429–445.
2. Romanovskiy VN, Smirnov IV, Babain VA, Todd TA, Law JD, Herbst RS, Brewer KN. The universal solvent extraction (UNEX) process. I. Development of the UNEX process solvent for the separation of cesium, strontium, and the actinides from acidic radioactive waste. *Solvent Extr Ion Exch.* 2001;19:1–21.
3. Law JD, Herbst RS, Todd TA, Romanovskiy VN, Babain VA, Esimantovskiy VM, Smirnov IV, Zaitsev BN. The universal solvent extraction (UNEX) process. II. flowsheet development and demonstration of the UNEX process for the separation of cesium, strontium, and actinides from actual acidic radioactive waste. *Solvent Extr Ion Exch.* 2001;19:23–36.
4. Riddle CL, Baker JD, Law CA, McGrath DH, Meikrantz BJ, Mincher DR, Peterman TA. Fission product extraction (FPEX): Development of a novel solvent for the simultaneous separation of strontium and cesium from acidic solutions. *Solvent Extr Ion Exch.* 2005; 23:449–461.
5. Mincher BJ, Mezyk SP, Bauer WF, Elias G, Riddle C, Peterman DR. FPEX γ-radiolysis in the presence of nitric acid. *Solvent Extr Ion Exch.* 2005;25:593–601.
6. Simon N, Eymard S, Tournois B, Dozol JF. Cs selective extraction from high level liquid wastes with crown Calixarenes: Where are we today. The Atalante 2004 International Conference; June 21-24, 2004; France; 2004:1–57.
7. Bonnesen PV, Delmau LH, Haverlock TJ, Moyer BA. Alkaline-side extraction of cesium from Savannah River tank waste using a calixarene-crown ether extractant. Chemical and Analytical Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., Report ORNL/TM-13704, December; 1998:1–103.
8. Asfieri C, Dradi E, Pochina A, Ungaro R, Andreetti GD. Synthesis, X-ray crystal and molecular structure of a novel macro-bicyclic ligand: Crowned *p*-t-butyl-calix[4] arene. *J Chem Soc Chem Commun.* 1983;(19):1075–1077.
9. Asfari Z, Wenger S, Vicens J. Calixcrowns and related molecules. *J Inclusion Phenom Mol Recognit Chem.* 1994;19:137–148.
10. Ji H, Dabestani R, Brown GM, Hettich RL. Synthesis and sensing behavior of cyanoanthracene modified 1,3-alternate calyx[4]benzocrown-6: A new class of Cs^+ selective optical sensors. *J Chem Soc Perkin Trans.* 2001;2:585–591.
11. Sachleben RA, Urvoas A, Bryan JC, Haverlock TJ, Hay BP, Moyer BA. Dideoxygenated calix[4]arene crown-6 ethers enhanced selectivity for caesium over potassium and rubidium. *Chem Commun.* 1999; (17):1751–1752.
12. Wei YZ, Zhang A, Kumagai M, Watanabe M, Hayashi N. Development of the MAREC process for hllw partitioning using a novel silica-based cmpo extraction resin. 11th Internationl Conference on Nuclear Engineering; Shinjuku, Tokyo, Japan; April 20-23, 2003; No.03-209, CD-ROM- ICONE-11-36084.
13. Zhang A, Wei YZ, Kumagai M, Koma Y. A new partitioning process for high level liquid waste by extraction chromatography using impregnated adsorbents. 2003 ANS/ENS International Winter Meeting (Global 2003), New Orleans, LA; November 16-20, 2003.
14. Wei YZ, Zhang A, Kumagai M, Watanabe M, Hayashi N. Development of the MAREC process for HLLW partitioning using a novel silica-based CMPO extraction resin. *J Nucl Sci Technol.* 2004;41: 315–322.
15. Zhang A, Wei YZ, Hoshi H, Koma Y, Kamiya M. Chromatographic separation of cesium and strontium from high level liquid waste using silica-based calixarene-crown extraction resins. Proceedings of Global 2005, Tsukuba, Japan, Oct 9-13, 2005; Paper No. 056.
16. Zhang A, Hu Q, Chai Z. SPEC: A new process for strontium and cesium partitioning utilizing two macroporous silica-based supramolecular recognition agents impregnated polymeric composites. *Sep Sci Technol.* 2009;44:2146–2168.
17. Zhang A, Kuraoka E, Hoshi H, Kumagai M, Synthesis of two novel macroporous silica-based impregnated polymeric composites and their application in high level activity liquid waste partitioning by extraction chromatography. *J Chromatogr A* 2004;1061:175–182.
18. Zhang A, Wei YZ, Hoshi H, Koma Y, Kamiya M. Partitioning of cesium from a simulated high level liquid waste by extraction chromatography utilizing a macroporous silica-based supermolecular calix[4]arene-crown impregnated polymeric composite. *Solvent Extr Ion Exch.* 2007;25:389–405.
19. Zhang A, Chen C, Wang W, Wei YZ. Adsorption behavior of Sr(II) and some typical co-existent metals contained in high level liquid waste onto a modified macroporous silica-based polymeric DtBuCH18C6 composite. *Solvent Extr Ion Exch.* 2008;26:624–642.
20. Zhang A, Wang W, Chai Z, Kumagai M. Separation of strontium ions from a simulated highly active liquid waste using a composite of silica-crown ether in a polymer. *J Sep Sci.* 2008;31:3148–3155.
21. Zhang A, Xiao C, Xue W, Chai Z. Chromatographic separation of cesium by a macroporous silica-based supramolecular recognition agent impregnated material. *Sep Purif Technol.* 2009;66:541–548.
22. Wei YZ, Kumagai M, Takashima Y, Modolo G, Odoj R. Studies on the separation of minor actinide from high-level wastes by extraction chromatography using novel silica-based extraction resins. *Nucl Technol.* 2000;132:413–423.
23. Mandolini L, Ungaro R. *Calixarenes in Action: Calixarenes in Spherical Metal Ion Recognition*. London: Imperial College Press; 2000:62–84.
24. Reinhoudt DN, Engbersen JF, Brozozka Z, Van den Viekkert HH, Honig GWN, Holterman AJ, Verker UH. Development of durable K^+-selective chemically modified field effect transistors with functionalized polysiloxane membranes. *Anal Chem.* 1994;66:3618–3623.
25. Asfieri Z, Bohmer V, Harrowfield J, Vicens J, Saadioui M. *Calixarenes 2001: Molecular dynamics of cation complexation and extraction*. Dordrecht, The Netherlands: Kuuwer Academic Publishers; 2001:312–333.
26. Dietz ML, Bond AH, Clapper M, Finch JW. Isomer effects in the extraction of metal ions from acidic nitrate media by dicyclohexano-18-crown-6. *Radiochim. Acta.* 1999;85:119–126.
27. Kriz J, Dybal J, Makrlik E, Budka J. Interaction of hydronium ion with dibenzo-18- crown-6: NMR, IR, and theroretical study. *J Phys Chem A.* 2008;112:10236–10243.
28. Dybal J, Makrlik E, Vanura P, Budka J. Protonation of 25,27-bis(1-octyloxy)calix[4] arene-crown-6 in the 1,3-*alternate* conformation. *Monatsh Chem.* 2008;139:1175–1178.
29. Michael MN. The ionic hydrogen bond. 2. Intramolecular and partial bonds. Protonation of polyethers, crown ethers, and diketones. *J Am Chem Soc.* 1983;105:4906–4911.
30. Zhang A, Wei YZ, Hoshi H, Kumagai M. Chromatographic separation of strontium from a nitric acid solution containing some typically simulated elements by a novel silica- based TODGA impregnated polymeric composite in MAREC process. *Solvent Extr Ion Exch.* 2005;23:231–247.

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