

Allosteric coextraction of sodium and metal ions with calix[4]arene derivatives 1

Role of the first-extracted sodium ion as an allosteric trigger for self-coextraction of sodium ions with calix[4]arene tetracarboxylic acid

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Abstract Solvent extraction of three alkali metal ions with *p*-*t*-octylcalix[6]arene hexacarboxylic acid, *p*-*t*-octylcalix[4]arene tetracarboxylic acid, corresponding linear trimeric and monomeric analogs was investigated. Cyclic tetramer selectively extracts sodium ion among alkali ions at extremely low pH, while the corresponding cyclic hexamer, the trimer, and the monomer exhibited only poor extraction ability for all alkali metals examined. The detailed extractive investigation of sodium ions with the cyclic tetramer was carried out. It was found that two sodium ions are simultaneously extracted by a single molecule of calix[4]arene derivative and that the second sodium extraction is facilitated by the uptake of the first sodium. The self-coextraction mechanism of sodium ions proposed in the present paper also strongly supports allosteric coextraction of sodium and other metal ions. In the competitive extraction of four alkali metal ions, potassium ion was slightly extracted as the second ion at low pH region, whereas it was hardly extracted in the individual extraction system. The result also supports the coextraction mechanism and role of the first-extracted sodium ion as an allosteric trigger. The extraction equilibrium constants of the cyclic tetramer and two sodium ions, K_{ex1} and K_{ex2} , were estimated.

Keywords Self-coextraction mechanism · Calix[4]arene tetraacetic acid · Allosteric trigger · Sodium selectivity · Peak shift

Introduction

Calixarenes and their derivatives have been attracting much attention as novel types of interesting host compounds [1, 2]. Their ability to recognize and discriminate metal ions is one of their remarkable features as specific receptors, on which some review articles about these interesting ionophores have been published [3–8]. A number of studies have been also conducted on the solvent extraction of various metal ions with calixarenes, especially alkali metal ions with neutral calixarene derivative. These results have supported the “size fitting effect” [9–17].

In our previous works, we reported that *p*-*t*-octylcalix[4]arene carboxylic acid selectively forms a complex with sodium ions over lithium and potassium ions [18, 19]. The extraction of trivalent rare earths [19] and copper ion [20] with this calix[4]arene derivative in the presence of sodium ion, was found to be drastically enhanced. These results were expected due to coextraction of sodium and other metal ions. The coextraction of sodium and lanthanide ions was firstly proposed by Ludwig et al. [21] during his presentation. The studies on coextraction of sodium and other metal ions with calix[4]arene derivatives have been independently investigated by Ludwig et al. [22–25], our group [18–20, 26, 27], Kakoi et al. [28–30], Uezu et al. [31]. Neither the coextraction mechanism of sodium and other metal ions nor the role of sodium on the enhanced metal extraction, however, have been elucidated in detail.

In the present work, the solvent extraction of three alkali metal ions with hexameric and tetrameric calixarene

The present paper is dedicated to Prof. Jack Harrowfield and Dr. Jacques Vicens on the celebration of their 65th birthday.

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derivatives together with the corresponding linear trimeric and monomeric analogs has been compared. In order to elucidate the extraction mechanism, the extraction of sodium ions with *p*-t-octylcalix[4]arene tetracarboxylic acid has been mainly examined in detail. The study on $^1\text{H-NMR}$ peak shift of the extractant molecule during sodium extraction has been also evaluated. The competitive extraction of four alkali metal ions has been also investigated. From the present data on sodium self-coextraction, coextraction mechanism of sodium and other metal ions has been strongly supported and successfully explained.

Experimental

Reagents

37,38,39,40,41,42-Hexakis(carboxymethoxy)-5,11,17,23,29,35-hexakis(1,1,3,3-tetramethyl-butyl)calix[4]arene (**1**), 25,26,27,28-Tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene in cone conformation (**2**), *p*-(1,1,3,3-tetramethylbutyl)phenoxy acetic acid (**3**), and linear trimer, 2,6-bis[2-carboxymethoxy-5-(1,1,3,3-tetramethylbutyl)benzyl]-4-(1,1,3,3-tetramethylbutyl)phenoxy-acetic acid (**4**) were synthesized in a similar manner to that described in the previous paper [32]. The chemical structures of the extractants are shown in Fig. 1.

Distribution study

The individual extraction of three alkali ions, lithium, sodium, and potassium ions, was carried out by a conventional batchwise method. Aqueous solution was prepared by dissolving alkali nitrate in 0.1 mol dm^{-3} HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]ethane sulfonic acid) buffer solution so as to maintain the alkali concentration constant at 0.1 mol dm^{-3} . The pH was adjusted by adding a small amount of nitric acid. Organic solution was prepared by diluting the extractant in chloroform to 5 mmol dm^{-3} . Equal volumes (5 cm^3) of both phases were added to a test tube and the mixture was shaken at 303 K for 2 h. The pH value of the aqueous solution was measured after the extraction. The equilibrated organic solution

was diluted with 1,4-dioxane to directly measure the extracted alkali concentration by atomic absorption spectrophotometer (abbreviated as AAS, Seiko Instruments SAS-7500). Furthermore, the equilibrated organic solution (1 cm^3) was mixed again with fresh 1.2 mol dm^{-3} hydrochloric acid (5 cm^3) in a teflon-coated bottle. The mixture was shaken at 303 K for 2 h to completely strip the extracted sodium ion. After phase separation, the concentration of sodium ion stripped into the aqueous phase was measured by AAS.

The sodium extraction was also monitored by $^1\text{H-NMR}$ spectrophotometry. Experimental conditions were nearly the same as those mentioned above except for the use of deuterium solvent. After equilibrium, the peaks of the extractant molecule in the organic phase were recorded by proton nuclear magnetic resonance spectrometer (Jeol, JNM-GX270).

The competitive extraction of four alkali metal ions, lithium, sodium, potassium, and cesium ions with **2** was also investigated. Aqueous solution was prepared by dissolving together all alkali nitrates in 0.1 mol dm^{-3} HEPES solution so as that the concentration of each alkali ion was kept at 0.1 mol dm^{-3} . The rest procedures were similar manner according to the individual extraction.

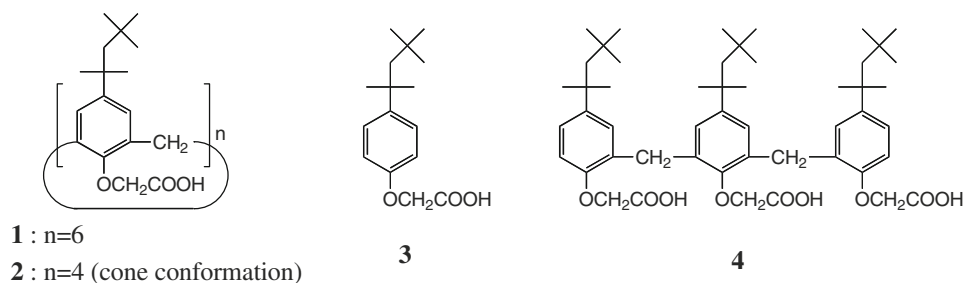
Results and discussion

Individual extraction of alkali metal ions with each extractant

Neutral calix[4]arene podands in cone conformation such as ester, ketone, and amide derivatives selectively form complexes with sodium ion among alkali metal ions [9–17]. In order to confirm that carboxylic acid derivative of calix[4]arene shows high sodium selectivity based on “size fitting effect”, the individual extraction of alkali metal ions with four types of the extractants was carried out.

The effects of pH on the loaded percentage of alkali metal ions on the extractants **1–4** are shown in Fig. 2a–d, respectively, where the loaded percentage, % Loaded, is defined as

Fig. 1 Chemical structures of the extractants



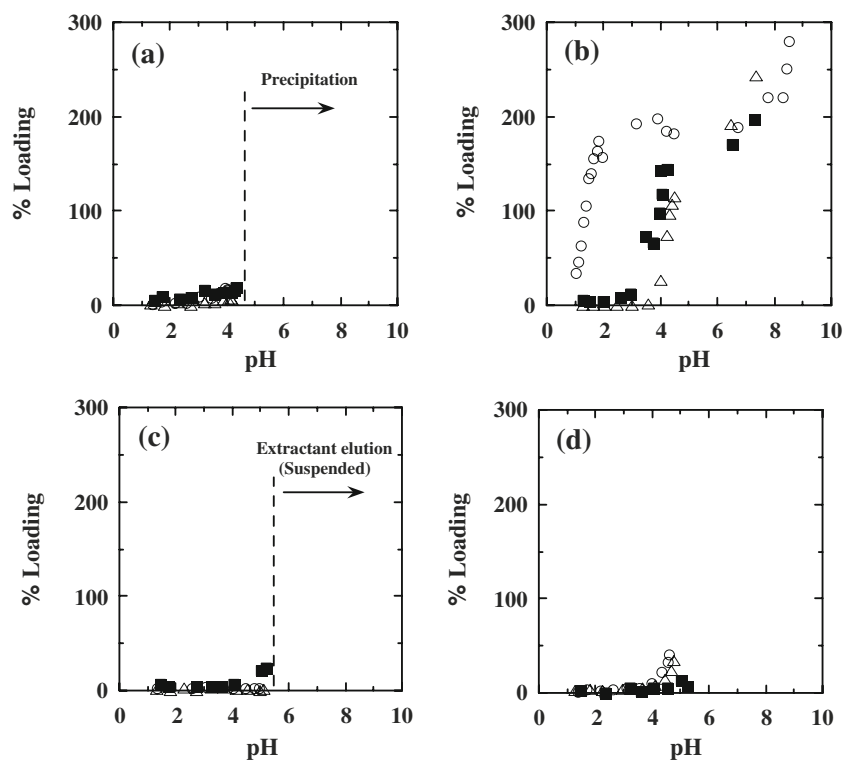


Fig. 2 Effect of pH on percentage loading of alkali metal ions on the extractants. (a) **1**, (b) **2**, (c) **3**, and (d) **4**. Open triangle: Li, open circle: Na, filled square: K, [Metal] = 0.1 mol dm⁻³, [1] = [2] = [4] = 5 mmol dm⁻³, [3] = 20 mmol dm⁻³

$$\% \text{ Loading} = \frac{\text{amount of sodium ion extracted}}{\text{total amount of the extractant}} \times 100. \quad (1)$$

The extractant **1**, **3**, and **4** exhibit only poor extraction abilities for all alkali ions as shown in Fig. 2a, c, and d, respectively. They are not remarkable results, since the present extractants are ion-exchangeable type ones and picrate to enhance extraction efficiency was not used in the present extraction media. On the other hand, the extractant **2**, specifically extracts sodium ion at pH as low as 1 under the present experimental conditions. It significantly shows high sodium selectivity among alkali metal ions and another derivatives show only poor extractability to all alkali metal ions. The strong interaction of the calix[4]arene derivative with sodium ion is attributed to the “size fitting effect”. The fact that tetramer can extract not only sodium ion but also lithium and potassium ions nonetheless at relatively higher pH region suggests that the high extraction ability of the extractant **2** is attributed to the structural effect of cone conformation as well as size fitting effect, whereas they are hardly extracted with the other extractants. (The extractant **1** resulted in the precipitation at pH as high as 4.0.)

The fact that precipitation and emulsion were observed at pH around 4–5 for the extractant **1**, **3**, and **4**, while the experiment with the extractant **2** was carried out at pH region around 9 is notable. The amount of extracted

sodium ion with the extractant **2** increases with increasing pH at pH higher than 1 and approaches to a constant value of a plateau region, which is not equal to 100%, but 200%. It means that the amount of the extracted sodium ion is equivalent to just twice that of the extractant. Further extraction of sodium ion was observed at pH higher than 7. It is notable that the percentage loading of sodium ion with the extractant **2** increases beyond 100% of our expectation and steeply attained to 200% without a decline of the plot, because a sodium ion seemed to be sufficiently large to occupy the coordination site of calix[4]arene derivative and four pK_a values seemed to discretely appear.

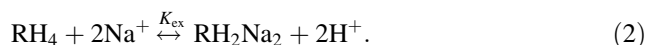
Detailed study of sodium extraction with calix[4]arene derivative

The extraction behavior that two sodium ions are loaded on a single molecule of calix[4]arene carboxylic acid is noteworthy, although incomprehensible. In order to elucidate such specific behavior, the detailed investigation is necessary. In advance of the reinvestigation for the loading of sodium ion, stripping of sodium ion loaded on the extractant **2** with acidic solution was carried out. The stripped percentages of sodium ion from the loaded extractant, **2** with dilute hydrochloric acid solution, 0.6 mol dm⁻³, 0.12 mol dm⁻³, pH = 1.10, 2.11, 3.00 are 100, 100, 100, 97, 77, respectively. The result shows that

dilute hydrochloric acid is effective to completely strip loaded sodium ion even at pH 2, while the forward extraction of sodium starts from pH around 1. Slight inconsistency of pH values between starting points of the extraction and the stripping is attributed to different sodium concentrations between forward (containing 0.1 mol dm^{-3}) and back (free) extractions. That is, aqueous solution for the extraction, while that for stripping is free from sodium ion.

Next, the loaded percentage of sodium ion on the extractant **2** was evaluated by measurement of sodium concentration in aqueous solution stripped from the sodium-loaded extractant. The effect of pH on the loaded percentage of sodium ion on the extractant **2**, evaluated by the stripping is shown in Fig. 3, together with the result from Fig. 2b as the forward extraction. Since both plots are in good agreement, the justification of the data that the loaded percentage of sodium ion reaches to 200% was confirmed.

In Fig. 3, plateau region of the loaded percentage at 100% was not observed under the present condition. It means that the extraction of sodium ion is not stepwise but continuous and simultaneous. The facts that the loaded percentage of sodium ion steeply reaches 200% as well as that the extraction of sodium ion not stepwise but continuously takes place suggest that a single molecule of the extractant molecule extracts two sodium ions at once as follows:



In order to confirm the stoichiometric relation in Eq. 1, the experiments were carried out wherein the sodium concentration was varied at pH 4–5. The Eqs. 3 and 4 are derived from the Eq. 1.

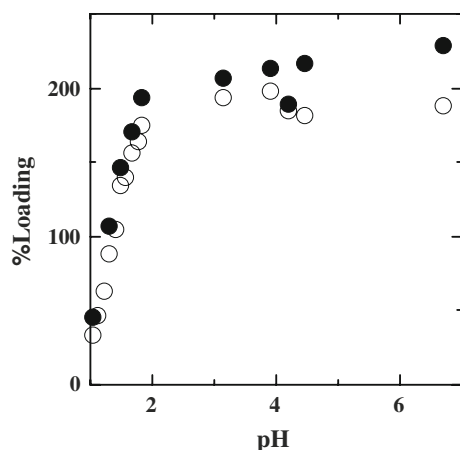


Fig. 3 Effect of pH on percentage loading of sodium ion on the extractant **2**. *Open circle*: data from forward extraction, *filled circle*: data from stripping

$$K_{\text{ex}} = \frac{[\text{RH}_2\text{Na}_2][\text{H}^+]^2}{[\text{RH}_4][\text{Na}^+]^2} \quad (3)$$

$$\log \frac{[\text{RH}_2\text{Na}_2]}{[\text{RH}_4]} - 2 \text{pH} = 2 \log[\text{Na}^+] + \log K_{\text{ex}} \quad (4)$$

The dependency of sodium concentration from Eq. 4 is shown in Fig. 4. As expected from Eq. 4, the plots lie on a straight line with a slope of 2. This result supports the concept that under the present extraction condition, two sodium ions are simultaneously extracted with a single molecule of the extractant as shown in Fig. 2b. The extraction equilibrium constant, K_{ex} , based from Eq. 2 is estimated to be 1.58×10^{-2} .

Now, how are two sodium ions extracted with a single molecule of the extractant? Although the coordination site of calix[4]arene compounds in cone conformation and the diameter of sodium ion are just fit, calix[4]arene compounds should not have sufficient space to simultaneously uptake two sodium ions in the coordination site made by phenoxy oxygens, carbonyl oxygens, and carboxyl groups. In order to clarify the extraction mechanism, the extraction of sodium ion was also examined in terms of the peak shift change of the extractant molecule by using $^1\text{H-NMR}$ spectrophotometry. The $^1\text{H-NMR}$ spectra for aryl peaks of the extractant **2** after the complexation with sodium ion are shown in Fig. 5. The original peak at 6.90 ppm becomes lower and a new peak appears at 7.05 ppm. The extent of the shift increased with the increase of pH. As described above, the complexation of both two sodium ions inside the site may be impossible. If two sodium ions are complexed inside the site, the second new peak shift should be observed as structural change of the extractant takes place. Although the extent of the shift increased with increasing pH, the second shift was not observed. Arduini et al. [33] and Arimura et al. [34] reported that the peak shift change

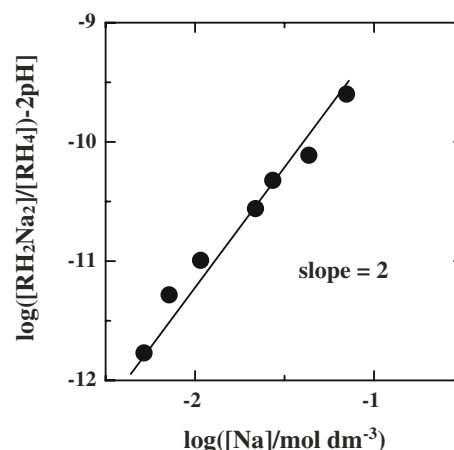


Fig. 4 Dependency of sodium ion concentration based from Eq. 4

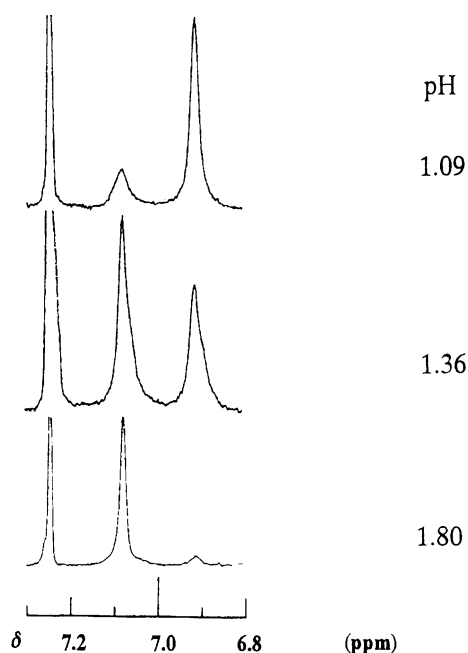


Fig. 5 Partial $^1\text{H-NMR}$ spectra of the extractant **2** in the complexation with sodium ion

of *p*-*t*-butylcalix[4]arene tetraester was observed in the complexation with sodium ion due to the structural change caused by surrounding the sodium ion by phenoxy oxygens and carbonyl groups. The present peak shift is quite similar to that reported by Arduini et al. and Arimura et al. It suggests that only single structural change of cyclic tetramer takes place during the extraction of two sodium ions.

The ratio of the integral ratios between the original and the shifted peaks would be related to the loaded percentage of sodium ion on the extractant. The ratio was expressed as shifted percentage for aryl protons in the extractant, where the shifted percentage is defined by Eq. 5:

$$\% \text{ Shifted} = \frac{\text{shifted integral ratio of aryl protons}}{\text{total integral ratio of aryl protons}} \times 100. \quad (5)$$

The shifted percentage of aryl proton is correlated with the loaded percentage of sodium ion on the extractant. The effects of pH on the shifted percentage and the loaded percentage are shown in Fig. 6. The data of the loaded percentage were obtained from Fig. 2b. As described above, the loaded percentage increases monotonously with increasing pH at low pH without any inflection points and reaches 200% at pH around 2. It means that the stoichiometry of the extractant and sodium ion is 1:2. On the contrary, the peak shift change was observed only once (from 6.90 to 7.05 ppm) and consequently the shifted percentage reaches up to only 100%. It is also notable that the shapes of both plots are analogous. Giving careful consideration to them brings another interesting fact that

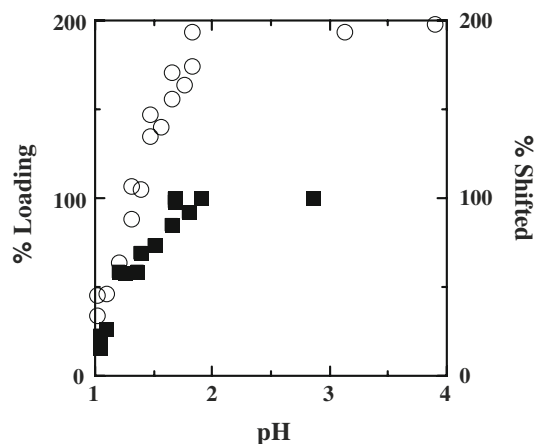


Fig. 6 Effect of pH on percentage loading of sodium ion and chemically shifted percentage for aryl protons of the extractant **2**. *Open circle*: percentage loading of sodium ion measured by AAS, *filled square*: shifted percentage of the extractant measured by $^1\text{H-NMR}$

the loaded percentage is nearly twice as much as the shifted percentage at whole pH region including the shoulders (pH 1–2) of both plots. Here, there are two conceivable mechanisms that two sodium ions are extracted with a single molecule of the extractant as shown in Fig. 7.

If the plots of the shifted percentage completely corresponds to that of the loaded percentage over the first half of shoulder region, that is, if both percentages agree very closely with each other up to 100% shown in Fig. 7a, sodium extraction would be a stepwise process as shown in Fig. 8a. That is, the second sodium extraction would take place after the extractant is saturated with the first sodium inside the calix[4]arene cavity, where the peak shift change is observed. The shifted percentage, however, is nearly half the value of the loaded percentage over the whole pH range under the present condition as shown in Fig. 7b. It suggests that the first and the second sodium ions are simultaneously extracted with a single molecule of the extractant as shown in Fig. 8b. Therefore, the coordination site and the extraction mode for each sodium ion are different. That is, for the coordination site, the first sodium ion is complexed inside cavity with the peak shift change, while the second is extracted outside cavity without the shift change. For the extraction mode, the first sodium is extracted by surrounding with four phenoxy oxygens, three carbonyl oxygens, and a carboxyl oxygen so as to the sodium ion dehydrated as eightfold coordination ion. (Strictly, four carboxyl groups equivalently release one proton, because only a single peak of aryl proton, but not three kinds peaks was observed. It makes the extractant more stable.) On the contrary, the second is just ion-exchanged with only a single proton from one of the rest carboxyl group without dehydrations.

Fig. 7 Schematic profiles of relation between the loaded and the shifted percentages.
a Stepwise extraction mechanism, **b** simultaneous extraction mechanism

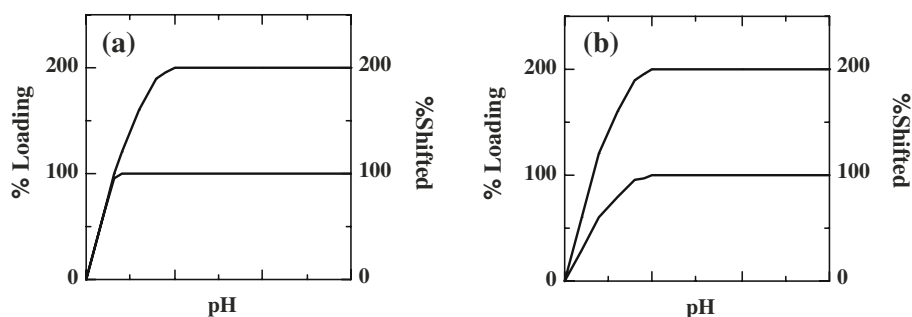
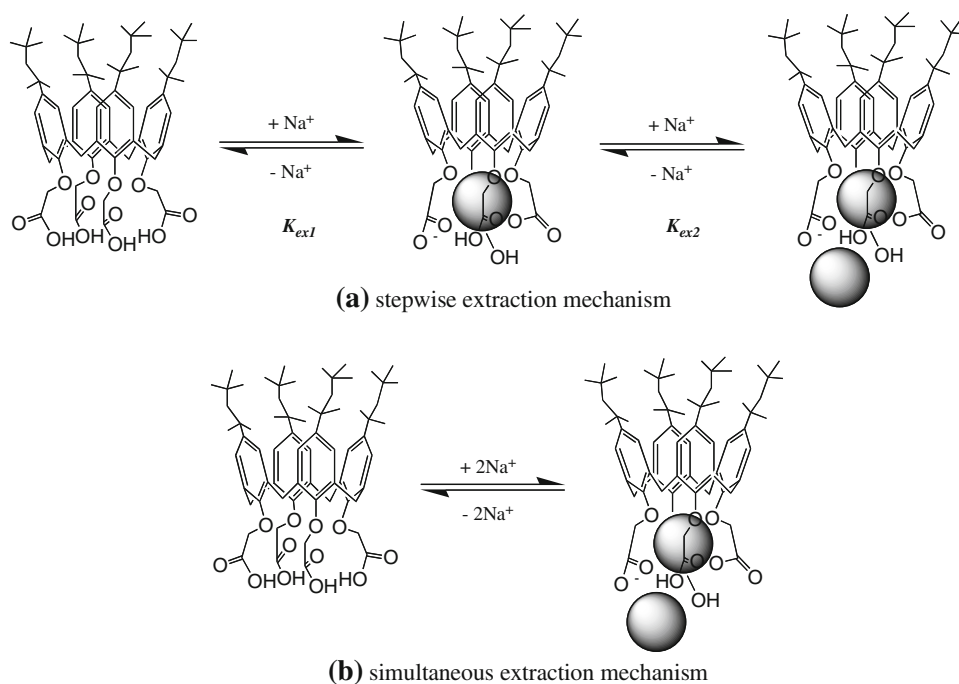


Fig. 8 Model of the simultaneous and stepwise extraction mechanisms of two sodium ions with the extractant under the present conditions



The first sodium is specifically extracted with calix[4]-arene derivative due to the size effect and the complete dehydration. We confidently propose the model, however, why does the uptake of the first sodium ion facilitate that of the second in spite of the steric repulsion between two sodium ions? We have adduced four reasons as follows:

1. Facilitation of acid dissociation attributed to the electron outflow from the rest carbonyl oxygens (not one carboxyl group for ion-exchange) during uptake of the first sodium.
2. Deformation of the strong intra- or intermolecular hydrogen bondings caused by the uptake of the first sodium ion.
3. Aggregation effect of functional groups and preorganization of coordination site.
4. Chelate effect caused by the decrease for the number of membered ring in the complexation reported in the previous paper [20].

Although a charge of the first sodium should be neutralized by a carboxyl group, the rest of carbonyl groups also coordinate it and electron densities of the carbonyl oxygens should decrease, consequently next pK_a value would decrease. The first reason seems to be reasonable. From the result of the extraction of lithium and potassium ions with **2**, both ions are also continuously extracted to 200%. The diameters of both ions are not fit for the coordination site of calix[4]arene and the extractive pH regions of both ions are not unusually low. The uptake of these ions has not taken place by surrounding with phenoxy oxygens and carbonyl oxygens, but by ion-exchange with carboxyl groups [19]. Thus, the second reason is also supportable. Since calix[4]arene is a kind of metacyclophane and is connected by methylene groups, so it is still flexible, although it is thought to be rigid. During uptake of the first sodium, phenoxy oxygens and carbonyl oxygens and a carboxyl group are tightly bound and the consequent

coordination site for the second ion would be more rigid and preorganized as described in the third reason. Free extractant gives rise to a sodium complex with a 14-membered ring, while sodium-complexed extractant do that with an eight-membered ring [20]. For the chelate effect, the complex with five- or six-membered ring is well-known to be stable, although the ligand forming the complex with eight-membered ring seems to be less effective, chelate effect offered by four-eight-membered rings could possibly enhance complementarily. The aggregation of weak affinities by the single molecule of the extractant preorganized in cone conformation, however, possibly affect the enhancement of the uptake. The fourth reason is also not improbable.

The extraction of the second sodium ion with carboxylic acid derivative of calix[4]arene loading the first sodium ion is regarded as “self-coextraction of sodium ions with the extractant”. The “self-coextraction of sodium ions” strongly and successfully supports “coextraction behavior of sodium and various other metal ions with the extractant” reported in our previous works and the works by Ludwig et al., Kakoi et al. and Uezu et al. [19–30]. The extraction of other ions is enhanced by coexistence of sodium ion compared with that in sodium-free system. The coextraction of sodium and other ions was supported. As described above, the interaction between the extractant and the first sodium is specific and strong and serves as an allosteric trigger causing coextraction with the second ion, while that between the extractant and the second caused by simple ion-exchange is not specific. Nevertheless, the second sodium ion is extracted at unusually low pH with the extractant loading the first sodium ion under the present condition. The second sodium must be easily substituted by other multivalent metal ions having higher affinity to the rest carboxyl groups as shown in Fig. 9.

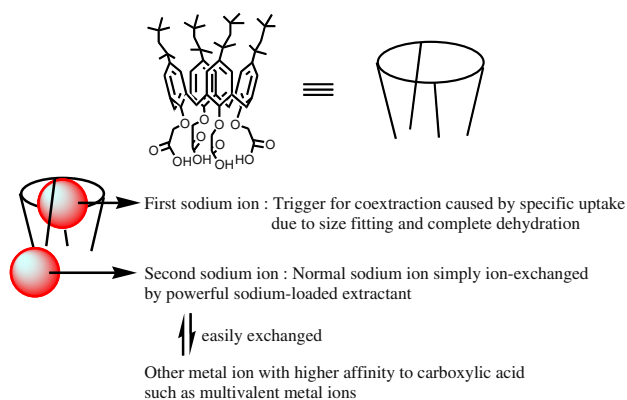


Fig. 9 Role of the first sodium ions as a trigger for enhanced extraction and ion-exchange of the second sodium ion with other metal ions

Competitive extraction of four kinds of alkali ions with calix[4]arene derivative

Explanation of two sodium ions extracted was given. There is an interesting result to support the above interpretation. The individual extraction of alkali metal ions with the extractant, **2**, exhibits high selectivity to sodium among three alkali ions. In the competitive system consisting four alkali ions, Li, Na, K, and Cs, it is expected that sodium ion is still preferably extracted and that it should be extracted up to 100% as the first ion inside the coordination site. Now, why is the second ion extracted outside it? The effect of pH on the loaded percentage of four alkali ions in competitive system is shown in Fig. 10. Sodium ion was extracted up to the percentage higher than 100% as expected, which is owing to further extraction of sodium ion as the second ion, while only small amount of potassium was also extracted. In the individual extraction, potassium was extracted from pH 3.0. In the competitive extraction, however, potassium was extracted even at a pH value as low as 1.4, although its loaded percentage is still low. The rest, lithium and cesium ions were hardly extracted. In general, for the competitive extraction system of the extractant, all ions are extracted as a mixture. In the present work, since the extraction of the second ion with the extractant loading the first sodium is facilitated, the selectivity is expected to be not specific but poor for the second extraction. Contrary to our expectation, the extractant loading the first sodium ion also selectively extracts sodium ion as the second ion, though small amount of potassium is also extracted. The result means that sodium-loaded calix[4]arene tetracarboxylic acid acts as a newly preorganized ionophore with high extraction ability and with relatively high sodium selectivity. That is, the

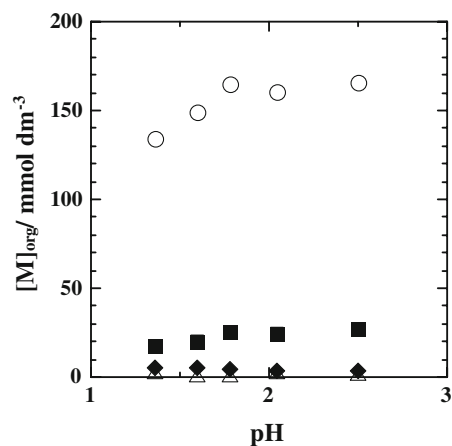
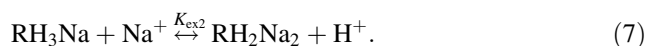
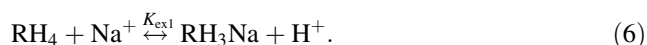


Fig. 10 Effect of pH on percentage loading in the competitive extraction of alkali metal ions with the extractant **2**. Open triangle: Li, open circle: Na, filled square: K, filled diamond: Cs, [Metal] = 0.1 mol dm⁻³, [Extractant] = 5 mmol dm⁻³

extraction ability of the extractant complexed with sodium is enhanced compared with the original sodium-free extractant, though the specific sodium selectivity observed in the individual extraction system is lowered to some extent in the competitive system. This extraction behavior as well would be attributed to the different coordination sites based on the extraction mechanism between the first and the second sodium ions. Therefore, the inference that the first sodium is complexed inside of the cavity as giving rise to the peak shift change and the second is formed complex outside the cavity as giving rise to no peak shift change is reasonable. Since complexation with the first sodium ion enhances the extraction ability of the extractant and the sodium concentration is kept as high as 0.1 mol dm^{-3} under the present conditions, the second sodium was easily complexed with the extractant pre-organized by the first sodium ion, consequently causing simultaneous extraction of two sodium ions as shown in Fig. 8b. Therefore, a mono-sodium complex as the intermediate shown in Fig. 8a would not exist at all under the present condition where sodium concentration is 0.1 mol dm^{-3} . It was found that *p*-*t*-octylcalix[4]arene tetracarboxylic acid complexed with sodium ion coextracts not only other metal ions such as lanthanides and copper but also even sodium ion itself and that the first-extracted sodium ion act as a very important allosteric trigger for the coextraction with the second metal ions.

Determination of extraction equilibrium constants of sodium ions with calix[4]arene derivative

As described above, the intermediate complex should not exist under the condition of high sodium concentration. Strictly speaking, however, the extraction of the first and the second sodium ions should be independently evaluated. That is, stepwise extraction equilibrium constants for both sodium ions should be estimated. If the sodium concentration is low, the sodium extraction region would shift to higher pH one and the extraction would also change from pseudo-simultaneous to ordinary and original stepwise mechanism. The elementary extraction reactions of each sodium ion are represented as Eqs. 6 and 7:



From Eqs. 6 and 7, each stepwise extraction equilibrium constants are obtained as shown to be Eqs. 8 and 9:

$$K_{\text{ex}1} = \frac{[\text{RH}_3\text{Na}][\text{H}^+]}{[\text{RH}_4][\text{Na}^+]} \quad (8)$$

$$K_{\text{ex}2} = \frac{[\text{RH}_2\text{Na}_2][\text{H}^+]}{[\text{RH}_3\text{Na}][\text{Na}^+]} \quad (9)$$

Furthermore, total concentrations of the extractant, $[\text{H}_4\text{R}]_{\text{T}}$, and sodium ion, $[\text{Na}^+]_{\text{T}}$ are represented as Eqs. 10 and 11, respectively.

$$[\text{RH}_4]_{\text{T}} = [\text{RH}_4] + [\text{RH}_3\text{Na}] + [\text{RH}_2\text{Na}_2] \quad (10)$$

$$[\text{Na}^+]_{\text{T}} = [\text{Na}^+] + [\text{RH}_3\text{Na}] + 2[\text{RH}_2\text{Na}_2] \quad (11)$$

The theoretical plots calculated by the substitution of appropriate values to the stepwise extraction equilibrium constants, $K_{\text{ex}1}$ and $K_{\text{ex}2}$ is fitted from the experimental plots of the loaded percentage of sodium versus pH under the condition of sodium concentration to be 0.1, 0.04, and 0.01 mol dm^{-3} . The effect of pH on the loaded percentage of sodium ion with 2 from the solution containing various concentration of sodium ion together with the theoretical lines are shown in Fig. 11. The theoretical line deviated from the experimental plots to high pH region under the lower sodium concentration. It is attributed that the sodium concentration after the extraction decrease as it cannot be neglected. Even than, both appropriately correspond. The stepwise extraction equilibrium constants, $K_{\text{ex}1}$ and $K_{\text{ex}2}$ by fitting were estimated to be 0.316 and 0.791.

Conclusion

Solvent extraction of three alkali metal ions with *p*-*t*-octylcalix[6]arene hexacarboxylic acid, *p*-*t*-octylcalix[4]arene tetracarboxylic acid, corresponding linear trimeric and

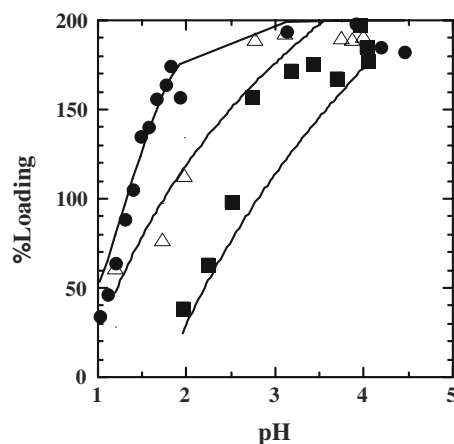


Fig. 11 Effect of pH on percentage loading of sodium ion with the extractant 2 from the solution containing various concentration of sodium ion together with the fitted lines. $[\text{Na}^+]$ filled circle: 0.1 mol dm^{-3} , open triangle: 0.04 mol dm^{-3} , filled square: 0.01 mol dm^{-3} , lines represent theoretical ones

monomeric analogs was investigated. Cyclic tetramer selectively extracts sodium ion among alkali ions at extremely low pH. The detailed extractive investigation of sodium ions with the cyclic tetramer, **2**, showed that two sodium ions are simultaneously extracted by a single molecule of calix[4]arene derivative and that the second sodium extraction is facilitated by the uptake of the first sodium. The self-coextraction mechanism of sodium ions proposed in the present paper also strongly supports allosteric coextraction of sodium and other metal ions. In the competitive extraction of four alkali metal ions, potassium ion was slightly extracted as the second ion at low pH region, whereas it was hardly extracted in the individual extraction system. The result also supports the coextraction mechanism and role of the first-extracted sodium ion as an allosteric trigger. The extraction equilibrium constants of the cyclic tetramer and two sodium ions, K_{ex1} and K_{ex2} , were estimated. The elucidation of self-coextraction mechanism of sodium ions leads to the elucidation of coextraction mechanism of sodium and other metal ions. Furthermore, extractability and separation efficiency would be controlled for the present medium by addition of sodium ion.

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