Self-Coextraction of Sodium Ions with Calix[4]arene Tetracarboxylate

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Solvent extraction of sodium ions with *p*-t-octylcalix[4]arene tetracarboxylate from an aqueous solution containing sodium ions (0.1 mol dm^{-3}) into chloroform was investigated. It was found that two sodium ions are simultaneously extracted by a single molecule of the extractant and that extraction of the second sodium ion is facilitated by the complexation of the first with the calix[4]arene derivative. The extraction behavior of sodium ions strongly supports the coextraction mechanism of sodium and another metal ion with calix[4]arene tetracarboxylate.

Multidentate functionality is one of the most interesting properties of calixarenes. Coextraction of sodium and other metal ions with calix[4]arene tetracarboxylate, which was reported by Ludwig *et al.*[1,2] and the authors,[3,4] may be attributed to the tetradentate functionality and cone conformation of this extractant. However, neither the coextraction mechanism of sodium and other metal ions nor the role of sodium ions on the enhancement of the coextraction have been elucidated in detail to date. In order to elucidate the mechanism, in the present work, the extraction of sodium with *p*-t-octylcalix[4]arene tetracarboxylate was examined in detail and, in addition, the ^{1}H-NMR chemical shift of the extractant molecule was measured under the same extraction conditions. The competitive extraction of the four kinds of alkali ions was also investigated.

25,26,27,28-Tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene was synthesized in a similar manner to that described in the previous paper.[5] The extraction of sodium was carried out according to a conventional batchwise method. Aqueous solutions were prepared by dissolving sodium nitrate in 0.1 mol dm^{-3} HEPES buffer solutions so as to maintain the sodium concentration constant at 0.1 mol dm^{-3}. The pH was adjusted by adding a small amount of concentrated nitric acid. The organic solution was prepared by diluting the extractant with chloroform to 5 mmol dm^{-3}. Equal volumes (5 cm^3) of both phases were mixed in a test tube and shaken at 303 K for 2 h. After phase separation, the pH of the aqueous solution was measured. The loaded sodium in the organic solution was stripped with fresh 1.2 mol dm^{-3} hydrochloric acid and the concentration measured by atomic absorption spectrophotometry (AAS). The extraction of sodium was also examined by ^{1}H-NMR spectrometry. Experimental conditions were nearly the same as that of the batchwise extraction except for the use of deuterium solvent. After phase separation, the ^{1}H-NMR spectra of the extractant were recorded. The competitive extraction of alkali ions was similarly carried out by using aqueous solutions containing four different alkali metal ions.

Figure 1 shows the ^{1}H-NMR spectra of the aryl peak of the extractant at several pH values. Arduini *et al.*[6] and Arimura *et al.*[7] reported that the chemical shift changes of *p*-t-butylcalix[4]arene tetraester observed on complexation with sodium were due to the structural change caused by surrounding sodium with phenoxy oxygens and carbonyl groups. The aryl peak of the sodium-containing extractant now appears at 7.05 ppm compared with the original peak at 6.90 ppm. Although the extent of the shift increased with increasing pH, the second shift was not observed. Since the ratio of the integral ratios between the original and shifted peaks may be related to the sodium loading loading percentage of the extractant, the relationship between the loading percentage of sodium and the shifted percentage of the extractant was investigated.

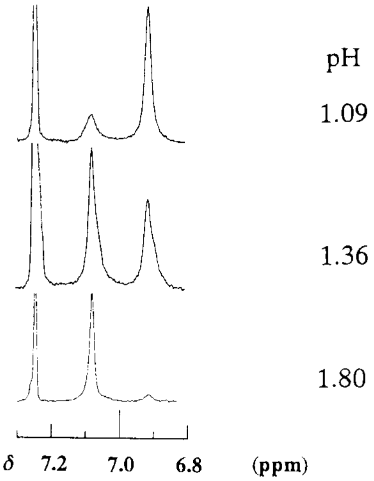

Figure 1. ^{1}H-NMR spectra of the aryl peak of the extractant at several pH values.

Figure 2 shows the effect of pH on percentage loading, % Loading, of sodium and on the chemically shifted percentage, % Shifted. The % Loading was calculated from the amount of the extracted sodium as measured by AAS. The shifted percentage of the extractant was evaluated in terms of the integral ratio of the peak shift of the aryl protons by using ^{1}H-NMR spectrometry. At around pH 2, % Loading of sodium becomes 200%, which means that the stoichiometry of the extractant and sodium ion is 1:2. Whereas, since the chemical shift change was observed only once, % Shifted becomes 100%. Furthermore, the shape of both plots are analogous and at the shoulder (pH 1 - 2) of both plots the % Loading is nearly twice that of % Shifted. If the plots of % Shifted completely coincide with those of % Loading over the first half of shoulder region, then complexation takes place, until the extractant is saturated with the first sodium inside the calix[4]arene cavity, where chemical shift change is observed. However, the values of the shifted percentage were nearly half those of % Loading over the whole pH range under the present condition, which suggests that both sodium ions are not complexed inside the cavity, but that the first sodium is complexed inside the cavity, thus causing the chemical shift change and the second one is complexed outside the cavity causing no chemical shift change. This consideration may be further strongly supported by the competitive extraction of alkali metal ions as discussed below.

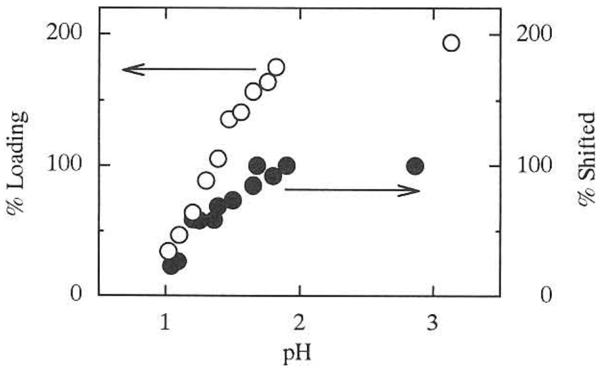

Figure 2. Effect of pH on % Loading of sodium ion and on % Shifted of the extractant. ○: % Loading of sodium ion, ●: % Shifted of the extractant, $[\mathrm{Na^+}]$ = 0.1 mmol dm^{-3}, [Extractant] = 5 mmol dm^{3}.

Figure 3 shows the effect of pH on % Loading of alkali metal ions in a competitive extraction system containing all of four different alkali metal ions. According to the experimental result for the individual extraction of three alkali metal ions, lithium, sodium, and potassium reported previously,[8] sodium was specifically and selectively extracted at a pH value around 1.0, while lithium and potassium were extracted from pH 3.5 and 3.0. However, in competitive extraction, potassium was found to be extracted even at a pH value as low as 1.4, though its extraction is low. This result may suggest that even potassium is extracted by the extractant complexed with sodium. That is, the extraction ability of the extractant while selective 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 result suggests that in competitive extraction the first sodium ion is specifically extracted and the second is extracted in competition with the other alkali metal ions, though sodium is still selectively extracted over the other three alkali metal ions. This extraction behavior as well may be attributed to the different coordination sites for the first and the second sodium ions. Therefore, the inference that the first sodium is complexed inside of the cavity giving rise to the chemical shift change and the second is complexed outside the cavity giving rise to no chemical shift change is considered to be reasonable. Since after complexation with the first sodium ion, another ion was preferentially extracted from other alkali metal ions, the extractant complexed with the first is preorganized providing a high ionic recognition property, though it is a little poorer than that of the original extractant.

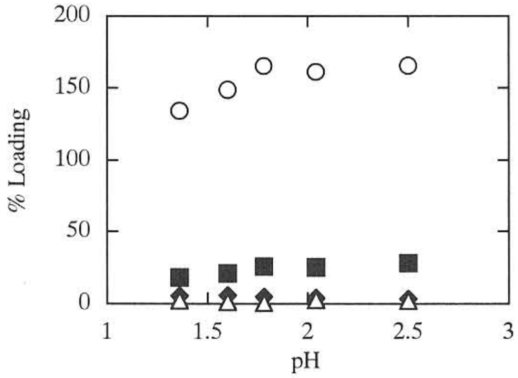

Figure 3. Effect of pH on % Loading in the competitive extraction of alkali metal ions. △: Li, ○: Na, ■: K, ◆: Cs, [Metal] = 0.1 mol dm^{-3}, [Extractant] = 5 mmol dm^{-3}.

Figure 4 shows the model of the simultaneous extraction of two sodium ions with the extractant under the present conditions. 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 preorganized by the first sodium ion, thus causing simultaneous extraction of two sodium ions. The enhancement of the extraction of the second sodium ion induced by that of the first is attributable not only to the enhancement of the dissociation of the second carboxyl group but also to the breakdown of intramolecular hydrogen bonding. As mentioned above, *p*-t-octylcalix[4]arene tetracarboxylate complexed with sodium co-extracts not only other metal ions such as lanthanides and copper but also the sodium ion itself. This result strongly supports the co-extraction behavior of various metals with sodium-loaded *p*-t-octylcalix[4]arene tetracarboxylate. Since the interaction between the extractant and the second sodium is not so strong as it occures by a simple ion-exchange mechanism, it is preferably substituted by other metals with higher affinities than sodium with carboxyl groups.

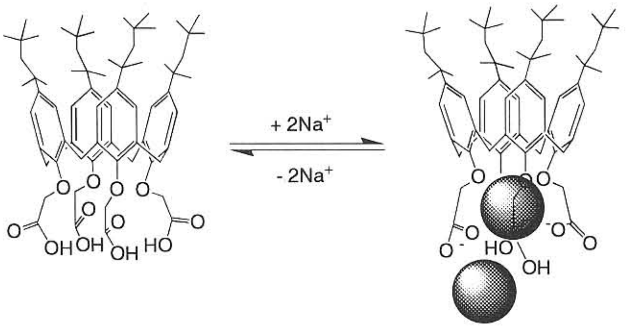

Figure 4. Model of the similtaneous extraction of two sodium ions with the extractant under the present conditions.

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