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Highly Selective Solvent Extraction of Uranyl Ion Using Super Uranophiles in the Presence of Methyltrioctylammonium Chloride

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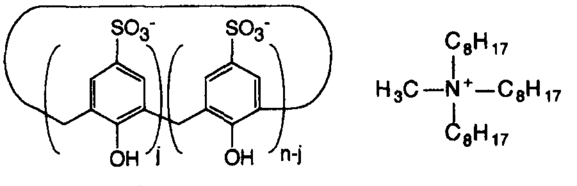
A highly selective solvent extraction of uranyl ion, UO_2^{2+}, was carried out by using superuranophiles, i.e., hydroxycalix[*n*]arene-*p*-sulfonates, $H_j\mathbf{1}_n^{n-}$ ($n = 6, j = 2$; $n = 8, j = 4$), in aqueous solution in the presence of methyltrioctylammonium chloride, MTA^+Cl^-, in chloroform. In the present extraction, UO_2^{2+} in the aqueous phase reacted first selectively and quantitatively with $H_j\mathbf{1}_n^{n-}$ to form a complex, $(UO_2\mathbf{1}_6H_{-3})^{9-}$ or $((UO_2)_2\mathbf{1}_8H_{-3})^{11-}$, respectively. Then, the resultant complexes combined with MTA^+ to form hydrophobic and electrically neutral ionic associates, $(MTA^+)_9\,(UO_2\mathbf{1}_6H_{-3})^{9-}$ or $(MTA^+)_{11}\,((UO_2)_2\mathbf{1}_8H_{-3})^{11-}$, and were extracted quantitatively into chloroform. No interference by the coexisting-metal ions was observed. The presence of a large amount of chloride and carbonate ions decreased the extractability of UO_2^{2+}. The extracted UO_2^{2+} was recovered by the stripping method using 2 M sulfuric acid, retaining $H_j\mathbf{1}_n^{n-}$ in the chloroform phase as a MTA^+ associates. The organic phase could be repeatedly used for subsequent extractions.

It was found by Shinkai et al.[1,2] that hydroxycalix[6]arene-*p*-sulfonate, $H_2\mathbf{1}_6^{6-}$ ($n = 6$; $j = 2$ in Scheme 1 which is shown in the form of *j*-th protonic acid), has a great selective reactivity along with a relatively high stability to UO_2^{2+} in the complex formation with various metal ions. Based on these findings, $H_2\mathbf{1}_6^{6-}$ was given the name "superuranophile", together with its *O*-methylcarboxylate and those of heptamer homologues.[2] The high selective reactivity of these ligands was considered to originate from their macrocyclic rigid structure, which is suitable for the binding with UO_2^{2+}. Since then, many hydrophobic calix[6]arene derivatives have been used for the solvent extraction of UO_2^{2+}. Shinkai et al. extracted UO_2^{2+} using *O*-carboxyl derivatives of *p*-*t*-butyl- or *p*-hexylcalix[6]arene into chloroform in the presence of Ni^{2+} and Zn^{2+}.[3] They also carried out the extraction of UO_2^{2+} into chloroform using the pyridylmethoxy-[4] and hydroxamate[5,6] derivatives. In order to increase the selective reactivity of an extractant for UO_2^{2+}, the alternative methoxy- and carboxylated derivatives of calix[6]arene were also synthesized and used for the extraction.[7,8] The solvent extraction of UO_2^{2+} by a hydroxamate derivative of calix[4]arene was also reported.[9]

Recently, we reported that octamer homologue, $H_4\mathbf{1}_8^{8-}$ is also a superuranophile with extremely high and selective reactivity to UO_2^{2+} over Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}.[10] Its selectivity factors for UO_2^{2+} over such metal ions were found to be about 10^5 to 10^{10} times larger than those of hexamer, $H_2\mathbf{1}_6^{6-}$.[11] In addition to the high selective reactivity to UO_2^{2+}, the stability of the complex was also much higher than that of hexamer.[10] These facts indicate that octamer is a superior superuranophile to hexamer.


$H_j\mathbf{1}_n^{n-}$ MTA^+

Scheme 1. Water-soluble hydroxycalix[*n*]arene-*p*-sulfonate ions expressed as a *j*-th protonic acid, $H_j\mathbf{1}_n^{n-}$ ($n = 4,8$; $j = n/2$, $n = 6; j = 2$) and methyltrioctylammonium ion, MTA^+.

On the other hand, we found that water-soluble hydrophilic $H_j\mathbf{1}_n^{n-}$ including a tetramer homologue, $H_2\mathbf{1}_4^{4-}$, can be extracted efficiently with MTA^+ over a wide pH range into chloroform by forming ammonium sulfonates, which are hydrophobic ionic associates.[12,13] These findings led us to apply $H_j\mathbf{1}_n^{n-}$ to the solvent extraction of metal ion as an extraction reagent in order to separate them from each other. We found that tetramer, $H_2\mathbf{1}_4^{4-}$ can selectively extract Mn^{2+} into chloroform in an aqueous solution under the presence of MTA^+Cl^-.[14]

From these experimental results, we anticipated that UO_2^{2+} in aqueous solution could also be quantitatively and selectively extracted using hexamer and octamer, due to their high affinity and selectivity for UO_2^{2+}. Thus we applied this extraction system to the solvent extraction of UO_2^{2+}. An outline of the plenary study was already reported in our brief report.[15] In the present paper, we report the details of the extraction study of UO_2^{2+} using superuranophiles including those by a tetramer ligand in the presence of MTA^+Cl^- in chloroform. As expected, UO_2^{2+} was extracted selectively and quantitatively as a $UO_2^{2+} : H_j\mathbf{1}_n^{n-} : MTA^+ = 1:1:9$ associate complex for hexamer ($n = 6$) and $2:1:11$ for octamer ($n = 8$), respectively. It was also found that the ligand-MTA^+ associate in chloroform could also extract UO_2^{2+} in aqueous solution with similar selectivity and efficiency to those in the extraction of the UO_2^{2+}-ligand complexes. Extracted UO_2^{2+}

could be recovered by stripping from chloroform with 2 M sulfuric acid. The water-soluble ligand was retained as a ligand-MTA$^+$ associate in chloroform through the process of the stripping and could be used for further repeated extraction of UO_2^{2+}. The effect of coexisting-metal ions and anions for this extraction was also studied.

Experimental

Reagent and Solution. Water-soluble hydroxycalix[n]-arene-*p*-sulfonates, $Na_nH_j\mathbf{1}_n$, were obtained from Sugai Kagaku Kogyo Co. (Wakayama Japan) and used after recrystallization from methanol–water solution. After dissolving in water to make a 0.01 M (1 M = 1 mol dm^{-3}) stock solution, the concentration was standardized by a pH titration method using standard 0.1 M NaOH.[16] MTA$^+$Cl$^-$ was obtained from Dojindo Laboratories Co. (Kumamoto, Japan), dissolved in chloroform and its concentration was determined by titration with a standard tetraphenylborate solution. The reagents used for metal ions were those of reagent grade obtained from Wako Junyaku Co. or Katayama Kagaku Co. (Osaka, Japan). These were standardized by the EDTA titration method[17] after dissolving them to make 0.01 M solutions, then diluted one tenth and used for the extraction experiment. The stock solutions for Ti^{4+} and Zr^{4+} were prepared by diluting 1.00×10^3 ppm standard solutions for atomic absorption spectrometry (AAS). The primary standard reagents, sodium carbonate (Wako Junyaku Co.) and sodium chloride (Matsunaga Chemical Co.), were used to prepare solutions of known concentrations of carbonate and chloride ions.

Apparatus and Determination of Concentration. UO_2^{2+} in an aqueous solution was determined by the arsenazo-III absorption method.[18] The concentration of $H_j\mathbf{1}_n^{n-}$ was determined by the UV-absorption method in the acidic aqueous solution of pH 1.0 at 264 (n = 6) and 274 nm (n = 8) in a 1cm light-pass length cell using a Shimadzu UV-180 spectrophotometer. Alkaline earth metal ion was determined by the AAS method by using a Hitachi 180-30 atomic-absorption photometer in the aqueous solution. The concentrations of other metal ions were measured by the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) method by using a Seiko-Densi SPS-1200VR emission spectrophotometer in the aqueous phase. pH was measured using a Horiba F-21 pH meter.

Procedure for Solvent Extraction, Determination of Percent Extraction, %*E*, and Distribution Ratio, *D*. In a 50 mL glass-stoppered tube, 15 mL of an aqueous mixture solution of $Na_nH_j\mathbf{1}_n$, metal ion (M^{m+}) and sodium carbonate was taken. After adding 15 mL of MTA$^+$Cl$^-$ chloroform solution, the tube was shaken for 10 min using a Iwaki V-S shaker at 400 strokes per min at room temperature (about 25 °C). The tube was then centrifuged for 3 min at 2000 rpm to separate both phases. An aliquot of the aqueous solution was taken to measure [M^{m+}]. M^{m+} in the chloroform phase was back-extracted with 2 M sulfuric acid and determined as above after diluting to the appropriate concentration. The percent extraction (%*E*) was calculated by

$$\%E = \{([M^{m+}]_{w,i} - [M^{m+}]_{w,e})/[M^{m+}]_{w,i}\} \times 100, \quad (1)$$

where $[M^{m+}]_{w,i}$ and $[M^{m+}]_{w,e}$ are the initial and equilibrium concentrations of M^{m+} in the aqueous phase. The distribution ratio, *D* was calculated by

$$D = \{([M^{m+}]_{w,i} - [M^{m+}]_{w,e})/[M^{m+}]_{w,e}\}. \quad (2)$$

Solvent Extraction by MTA$^+$–$H_j\mathbf{1}_n^{n-}$ Associate in Chloroform. Into 500 mL of 0.01 M $H_j\mathbf{1}n^{n-}$ aqueous solution, the pH was adjusted to 7.5; then, equivalent amount of MTA$^+$Cl$^-$ (0.35 mmol for hexamer, 0.50 mmol for octamer) in chloroform was added and shaken for about 10 min to extract $H_j\mathbf{1}n^{n-}$ as MTA$^+$ associates. After separating the aqueous phase, the chloroform solution was used for the metal ion extraction experiment.

Back-Extraction. Into a new 50 mL centrifuge tube containing 10 mL of hydrochloric acid or sulfuric acid, 10 mL of the chloroform phase was taken after completing the extraction procedure. After the tube was shaken for a given time, the metal ion concentration in the aqueous phase was determined. The recovery of metal ion, *R*, was calculated according to

$$R = \{[M^{m+}]_{R,e}/([M^{m+}]_{w,i} - [M^{m+}]_{w,e})\} \times 100. \quad (3)$$

Here, $[M^{m+}]_{R,e}$ is the equilibrium concentration of a metal ion in the acidic recovery solution.

Results and Discussion

Effect of Shaking Time. Figure 1 shows %*E* of UO_2^{2+} as a function of the shaking time at pH 7.5. The %*E* reaches 100% in 6 and 3 min by hexamer and octamer, respectively, and is almost constant by further shaking. Therefore, 10 min was employed as the shaking time in the present extraction studies. On the other hand, no extraction was observed at all by tetramer, even with longer shaking-times, such as 120 min. Thus, we concluded that tetramer cannot extract UO_2^{2+} from an aqueous solution at pH 7.5 because of its poor complexing ability to UO_2^{2+}.[11]

Effect of pH. The effect of the pH on the extraction of UO_2^{2+} is shown in Fig. 2 in the pH range of 2—12.5. $H_j\mathbf{1}_n^{n-}$ presents 5 times of UO_2^{2+} and MTA$^+$Cl$^-$ presents 50 times of UO_2^{2+} in the case of n = 4 and 6, and 75 times in the case of n = 8. Again, no extraction was observed for the tetramer in the range pH 2 to 12, even with 120 min shaking. On the other hand, the extraction by hexamer started at pH 5.5, and the value of %*E* increased quickly with increasing pH and reached 100% at pH 7.0. The extraction of UO_2^{2+} by

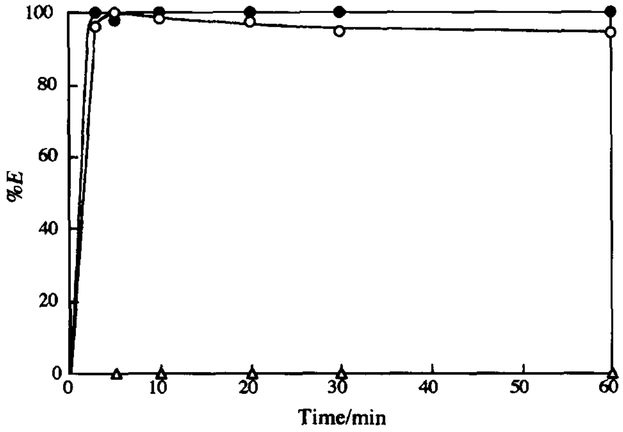


Fig. 1. Effect of shaking time on the extraction of UO_2^{2+} by $H_j\mathbf{1}_n^{n-}$ in the presence of MTA$^+$Cl$^-$ at about 25 °C. △: $H_2\mathbf{1}_4^{4-}$, ○: $H_2\mathbf{1}_6^{6-}$, ●: $H_4\mathbf{1}_8^{8-}$, $[H_j\mathbf{1}_n^{n-}]_{w,i} = 1.0\times10^{-3}$ M, $[UO_2^{2+}]_{w,i} = 2.0\times10^{-4}$ M, $[Na_2CO_3]_{w,i} = 2.0\times10^{-3}$ M, $[MTA^+Cl^-]_{o,i} = 0.010$ M (for $H_2\mathbf{1}_4^{4-}$ and $H_2\mathbf{1}_6^{6-}$), 0.015 M (for $H_4\mathbf{1}_8^{8-}$), volume of aqueous and organic phases = 15 mL, pH = 7.5±0.5.

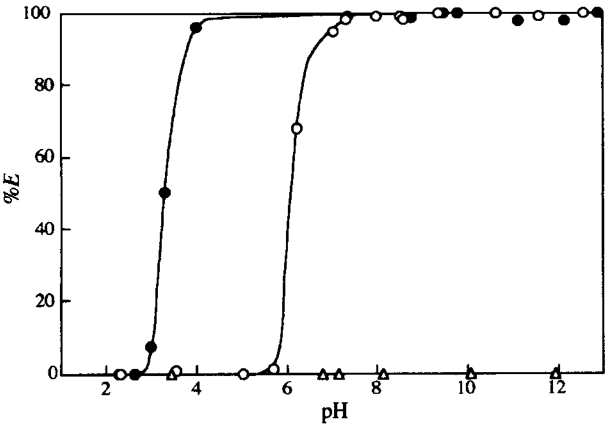


Fig. 2. Effect of pH on the extraction of UO_2^{2+} with $H_j\mathbf{1}_n^{n-}$ in the presence of MTA^+Cl^- at about 25 °C. △: $H_2\mathbf{1}_4^{4-}$, ○: $H_2\mathbf{1}_6^{6-}$, ●: $H_4\mathbf{1}_8^{8-}$, $[UO_2^{2+}]_{w,i} = 2.01\times10^{-4}$ M, $[H_j\mathbf{1}_n^{n-}]_{w,i} = 1.09\times10^{-3}$ M, $[Na_2CO_3]_{w,i} = 2.0\times10^{-3}$ M, $[MTA^+Cl^-]_{o,i} = 1.0\times10^{-2}$ M (for $H_2\mathbf{1}_4^{4-}$ and $H_2\mathbf{1}_6^{6-}$), 0.015 M (for $H_4\mathbf{1}_8^{8-}$), volume of aqueous and organic phases = 15 mL. pH was adjusted by adding appropriate amounts of 0.1—0.01 M of HCl and NaOH into the reaction mixture.

octamer began at pH 3 and reached 100% at pH 4, showing a steeper pH dependency than that for hexamer. Such shapes in the extraction curve indicate that UO_2^{2+} is extracted following the complex formation with $H_2\mathbf{1}_6^{6-}$ or $H_4\mathbf{1}_8^{8-}$, and then associates with MTA^+ in the form of complexes. Thus, the extraction of UO_2^{2+} by octamer, which is a more powerful uranophile than hexamer, is possible in a more acidic solution.

Effect of the Concentration of $H_j\mathbf{1}_n^{n-}$. The extraction percent of UO_2^{2+}, %*E*, was also measured in aqueous solutions of various $H_j\mathbf{1}_n^{n-}$ ($n = 6, 8$) concentrations; the results are shown in Fig. 3 as a function of $[H_j\mathbf{1}_n^{n-}]_{w,i}/[UO_2^{2+}]_{w,i}$. This figure clearly shows that (1) the extraction of UO_2^{2+} becomes possible in the presence of $H_j\mathbf{1}_n^{n-}$, (2) the value for %*E* increases with an increase in $H_j\mathbf{1}_n^{n-}$ and reaches 100% at about 1.0 for hexamer and at 0.50 for octamer, respectively, showing clear abrupt points. Based on these facts, it was estimated that UO_2^{2+} was extracted as $UO_2^{2+}:H_j\mathbf{1}_n^{n-} = 1:1$ ($n = 6$) or $2:1$ ($n = 8$) complexes. Such binding ratios agree well with those for UO_2^{2+}–$H_j\mathbf{1}_n^{n-}$ complexes in aqueous solution.[10,11] The presence of the 2:1 binding ratio was also reported for the complex with *p*-*t*-butylcalix[8]arene, in which two moles of UO_2^{2+} were combined with one mole of the ligand at its hydroxyl groups in the molecular cavity.[19]

Effect of the Concentration of MTA^+Cl^-. The extraction of UO_2^{2+} was carried out by changing $[MTA^+Cl^-]_{o,i}$ and the results are shown in Fig. 4 as a function of $[MTA^+Cl^-]_{o,i}/[H_j\mathbf{1}_n^{n-}]_{w,i}$, where suffix o indicates the organic phase. The vertical axis shows the amount of UO_2^{2+} extracted instead of %*E*, because an excess amount of UO_2^{2+} was used compared to $H_j\mathbf{1}_n^{n-}$ in this extraction system. The amount of UO_2^{2+} extracted increased in proportion to $[MTA^+Cl^-]_{o,i}/[H_j\mathbf{1}_n^{n-}]_{w,i}$ and clear abrupt changes can be observed on each curve at 9 and 11 for hexamer and octamer, respectively, indicating that these amounts of MTA^+ associate with the hexamer or octamer complex to produce hydrophobic and organic solvent-extractable associates.

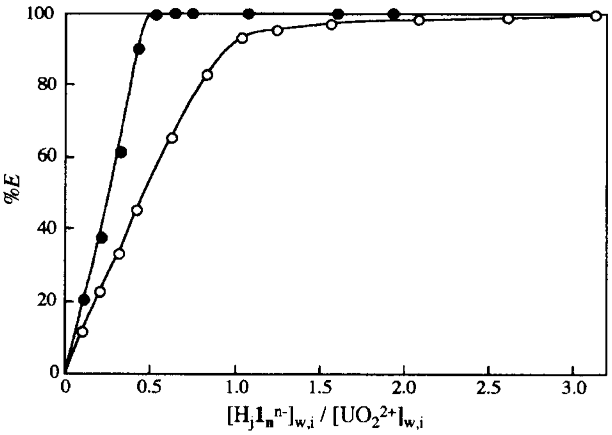


Fig. 3. Determination of the association ratio of MTA^+ with UO_2^{2+}–$H_j\mathbf{1}_n^{n-}$ complex by the extraction-molar ratio method. ○: $H_2\mathbf{1}_6^{6-}$, $[UO_2^{2+}]_{w,i} = 7.73\times10^{-4}$ M, $[H_2\mathbf{1}_6^{6-}]_{w,i} = 5.20\times10^{-4}$ M, pH = 9.4, ●: $H_4\mathbf{1}_8^{8-}$, $[UO_2^{2+}]_{w,i} = 1.27\times10^{-3}$ M, $[H_4\mathbf{1}_8^{8-}]_{w,i} = 5.72\times10^{-4}$ M, pH = 8.7, volume of aqueous and organic phases = 15 mL.

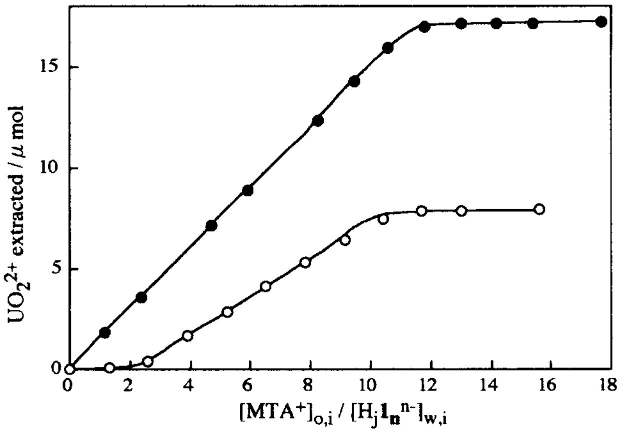
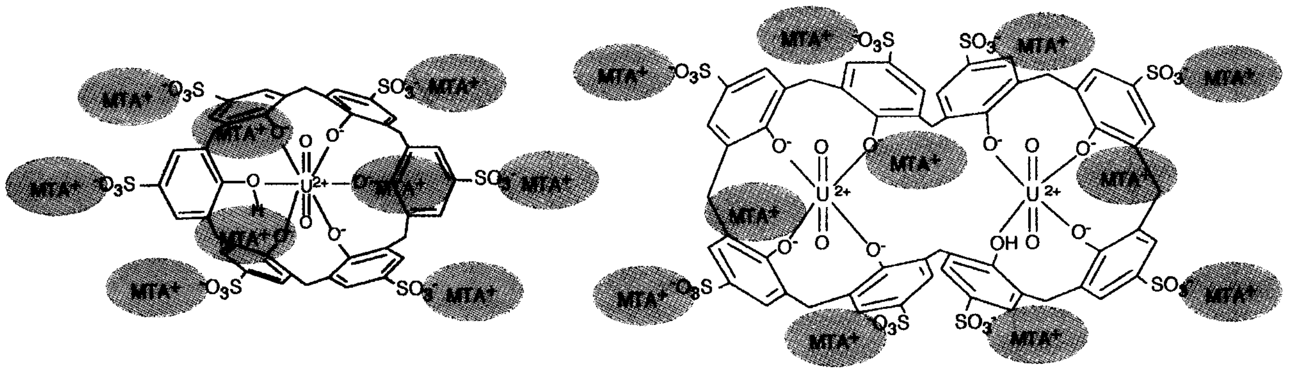


Fig. 4. Determination of the binding ratio of MTA^+ with UO_2^{2+}–$H_j\mathbf{1}_n^{n-}$ complex by the extraction-molar ratio method. ○: $H_2\mathbf{1}_6^{6-}$, $[UO_2^{2+}]_{w,i} = 7.73\times10^{-4}$ M, $[H_2\mathbf{1}_6^{6-}]_{w,i} = 5.20\times10^{-4}$ M, pH = 9.4, ●: $H_4\mathbf{1}_8^{8-}$, $[UO_2^{2+}]_{w,i} = 1.27\times10^{-3}$ M, $[H_4\mathbf{1}_8^{8-}]_{w,i} = 5.72\times10^{-4}$ M, pH = 8.7, volume of aqueous and organic phases = 15 mL.

From these facts, we can conclude that the species extracted are the ionic associates of 9 moles of MTA^+ with one mole of 1:1 UO_2^{2+}–hexamer complex,[11] $(TMA^+)_9\,[(UO_2^{2+})(\mathbf{1}_6^{8-})H_{-3}]$, and 11 moles of MTA^+ with one mole of 2:1 UO_2^{2+}-octamer complex,[10] $(TMA^+)_{11}\,[(UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3}]$. The estimated structures for the species extracted in chloroform are shown in Scheme 2 for hexamer **1** and octamer **2**. In the extraction by hexamer, no extraction was observed when $[MTA^+]_{o,i}$ was small. This is thought to be because MTA^+ associates with a complex only at a favorite position at an initial stage of the association reaction, and does not form an electrically neutral, extractable associate.

Absorption Spectra of UO_2^{2+} in the Organic and Aque-



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Scheme 2. Proposed structures for the ionic associates of UO_2^{2+}-complexes extracted in chloroform for hexamer **1** and octamer **2**.

ous Phases. Figure 5(a) shows the absorption spectra of the aqueous mixture solutions of UO_2^{2+} and $H_2\mathbf{1}_6^{6-}$ and that for extracted species by MTA^+Cl^- in the chloroform solution; here, $[UO_2^{2+}]_{o,e}$ is calculated according to $[UO_2^{2+}]_{w,i} - [UO_2^{2+}]_{w,e}$. Figure 4(b) shows those for octamer in the aqueous and organic solutions. These absorption spectra resemble each other and consist of a strong absorption band with an extinction coefficient in the range of 1.5×10^3 dm^3 mol^{-1} cm^{-1} at about 450 nm, which indicates that these absorption are attributable to charge-transfer absorption of the metal complexes and that UO_2^{2+} in the aqueous and organic phases have identical coordinating ligands, both on a series of $n = 6$ and 8.

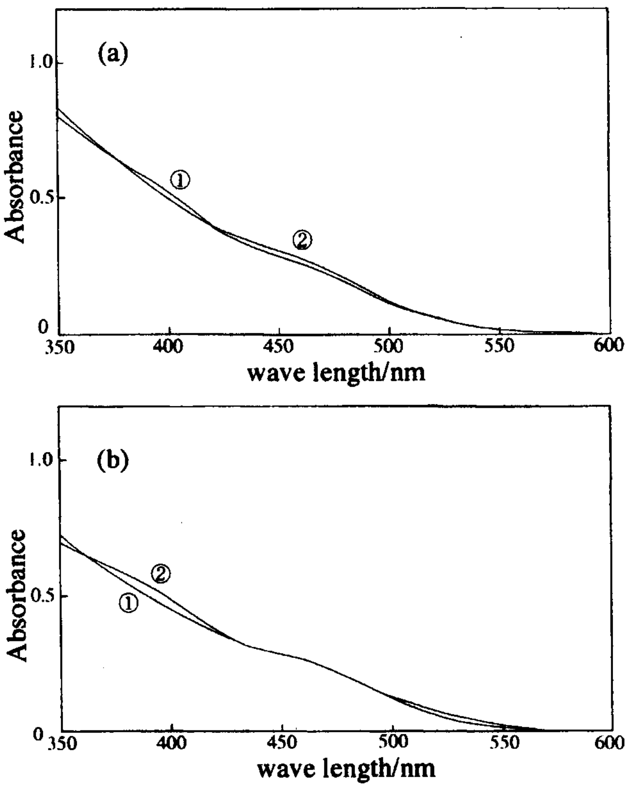

Fig. 5. Absorption spectra of UO_2^{2+}–$H_2\mathbf{1}_6^{6-}$ (a) and UO_2^{2+}–$H_4\mathbf{1}_8^{8-}$ (b) complexes in the aqueous ① and organic phases ②. (a): $[H_2\mathbf{1}_6^{6-}]_{w,i} = 1.0\times10^{-3}$ M, $[UO_2^{2+}]_{w,i} = 2.00\times10^{-4}$ M, $[MTA^+Cl^-]_{o,i} = 0.010$ M, $[UO_2^{2+}]_{o,e} = 1.99\times10^{-4}$ M, (b): $[H_4\mathbf{1}_8^{8-}]_{w,i} = 1.0\times10^{-3}$ M, $[UO_2^{2+}]_{w,i} = 2.00\times10^{-4}$ M, $[MTA^+Cl^-]_{o,i} = 0.015$ M, $[UO_2^{2+}]_{o,e} = 2.00\times10^{-4}$ M, light-path length = 1 cm, reference solution = reagent blank, volume of aqueous and organic phases = 15 mL.

Extraction Reaction. These facts suggests that UO_2^{2+} reacts with $H_j\mathbf{1}_n^{n-}$ to form complexes in the aqueous phase first; then, the resultant anion complexes combine with MTA^+ to form hydrophobic complex-associates and move into chloroform. The extraction of UO_2^{2+} by octamer occurs in the solution of pH > 3. In such a solution, it has been reported that octamer forms only a 2:1 complex-species, $((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})^{11-}$ with UO_2^{2+}.[10] Thus, the complex formation reaction will be given by Eq. 4, and its overall stability constant, β_{21-3}, is given by Eq. 5:[10,11]

$$2UO_2^{2+} + \mathbf{1}_8^{12-} = ((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})^{11-} + 3H^+, \tag{4}$$

$$\beta_{21\text{-}3} = [((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})^{11-})][H^+]^3/[UO_2^{2+}]^2[\mathbf{1}_8^{12-}]. \tag{5}$$

The extraction reaction of the complex-associate will be given by

$$((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})^{11-} + 11MTA^+Cl_o^- = (MTA^+)_{11}((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})_o^{11-} + 11Cl^- \tag{6}$$

because only an electrically neutral species can be extractable. The extraction constant, $K_{ex,8}$, is given by

$$K_{ex,8} = [(MTA^+)_{11}((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})^{11-}]_o[Cl^-]^{11} /[((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})^{11-}][MTA^+Cl^-]_o^{11}. \tag{7}$$

The distribution ratio, D, of UO_2^{2+} will be given by

$$D = [UO_2^{2+}]_o/[UO_2^{2+}] \fallingdotseq 2[(MTA^+)_{11}((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})^{11-}]_o /([UO_2^{2+}] + 2[((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})^{11-}]. \tag{8}$$

As shown in Figs. 1 and 2, the extractability of the complex-associate is very large, so the complex remaining in the aqueous phase must be small when $11[H_4\mathbf{1}_8^{8-}]_{w,i} < [MTA^+Cl^-]_{o,i}$. Thus,

$$D \fallingdotseq 2[(MTA^+)_{11}((UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3})^{11-}]_o/[UO_2^{2+}] = 2K_{ex,8}\cdot\beta_{21\text{-}3}[UO_2^{2+}][\mathbf{1}_8^{12-}][H^+]^{-3}[MTA^+Cl^-]_o^{11}[Cl^-]^{11-}. \tag{9}$$

We can derive the followimg equation by taking a logarithm and recombination of Eq. 9;

$$\log(D/[UO_2^{2+}][\mathbf{1}_8^{12-}]) = \log 2K_{ex,8} + \log\beta_{21\text{-}3} + 3pH + 11\log([MTA^+Cl^-]_o/[Cl^-]). \qquad (10)$$

Equation 10 shows that $\log(D/[UO_2^{2+}][\mathbf{1}_8^{12-}])$ increases linearly with an increase in pH, when $[MTA^+Cl^-]_o = [Cl^-]$. As the order of the last term in Eq. 10 is eleven, its effect on $\log D$ is so big that we cannot use Eq. 10 for the determination of the extraction constant. In fact, we calculated precisely the concentrations of $[MTA^+Cl^-]_o$ and $[Cl^-]$ in equilibrium by adjusting them based on $[UO_2^{2+}]_{o,e}$, and then obtained $\log(D/[UO_2^{2+}]][\mathbf{1}_8^{12-}]) - 11\log([MTA^+Cl^-]_o/[Cl^-])$, which was plotted against pH. The result is given in Fig. 6. A good linear line of slope 2.90 is obtained. This agrees well with the slope of Eq. 10. From the intercept of the line and vertical axis, $K_{ex,8} = 2.0\times10^{-13}$ was obtained using $\log\beta_{21\text{-}3} = 12.13$.[10] Here, $[\mathbf{1}_8^{8-}]_{w,e}$ was obtained by $[H_4\mathbf{1}_8^{8-}]_{w,e}$ and its side reaction coefficient, α_H, which was calculated based on pK_a values of $H_4\mathbf{1}_8^{8-}$. $[H_4\mathbf{1}_8^{8-}]_{w,e}$ was determined by the measurement of absorbance at 274 nm, after taking out an aliquot of equilibrium solution, diluting and adjusting its pH at 1.0.

It has been shown that hexamer reacts with UO_2^{2+} in a 1:1 ratio and forms four kinds of hydrogen complexes, $UO_2^{2+}(\mathbf{1}_6^{6-})H_h$ ($h = 0, -1, -2, -3$).[11] As previously shown, UO_2^{2+} is extractable at pH > 5.5. Thus, in the extraction by hexamer, three kinds of 1:1 complexes having $h = -1, -2$, and -3 will be present,[11] and all of them can be extractable with MTA^+ at the same time. Therefore, the extraction reaction by hexamer must be too complex to derive the equation for the extraction reaction despite of the basic reaction being similar to those for octamer.

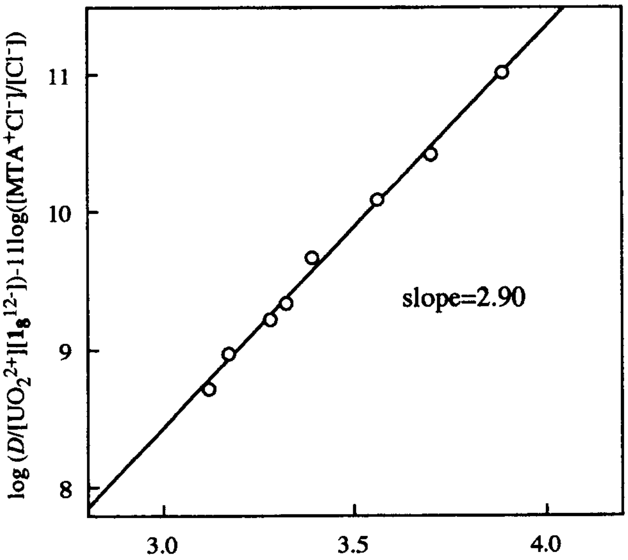

Fig. 6. Linear plot of $\log(D/[UO_2^{2+}][\mathbf{1}_8^{12-}]) - 11\log([MTA^+Cl^-]/[Cl^-])$ as a function of pH. $[H_4\mathbf{1}_8^{8-}]_{w,i} = 5.35\times10^{-4}$ M, $[UO_2^{2+}]_{w,i} = 5.02\times10^{-4}$ M, $[TMA^+Cl^-]_{o,i} = 0.0496$ M, $[NaHCO_3]_{w,i} = 2.5\times10^{-3}$ M, $[NaCl]_{w,i} = 0.0491$ M, volume of aqueous and organic phases = 20 mL.

Effect of Coexisting-Anion. It is well known that a carbonate ion forms a relatively stable complex with UO_2^{2+}. Therefore, the presence of a carbonate ion may interfere with the extraction of UO_2^{2+} and affects the value of %E. In the present study, however, the extractions of UO_2^{2+} were carried out in the carbonate solution to protect against the precipitation of metal ions. Equation 6 shows that the extraction of UO_2^{2+} occurs according to the ion exchange reaction of the complex anion in the aqueous phase with Cl^- of MTA^+Cl^- in chloroform by releasing Cl^- into the aqueous phase, the concentration of Cl^- in the aqueous phase will also affect the extraction reaction. Thus, we studied the effect of these anions on the extractions. The results are shown in Figs. 7 and 8 as a function of the relative concentration of the coexisting-

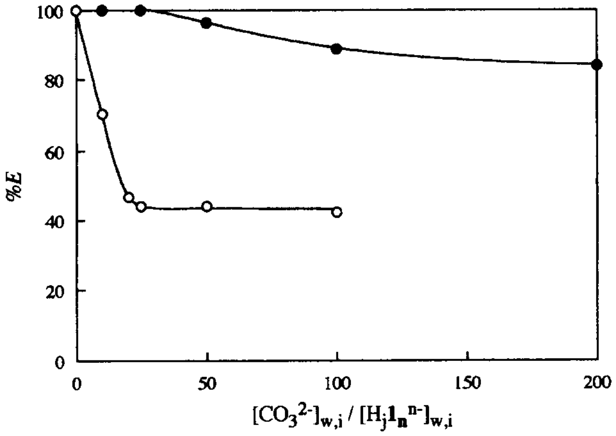

Fig. 7. Effect of CO_3^{2-} on the extraction of UO_2^{2+} by $H_j\mathbf{1}_n^{n-}$ in the presence of MTA^+Cl^- at about 25 °C. ○: $H_2\mathbf{1}_6^{6-}$, ●: $H_4\mathbf{1}_8^{8-}$, $[H_j\mathbf{1}_n^{n-}]_{w,i} = 1.0\times10^{-3}$ M, $[UO_2^{2+}]_{w,i} = 1.0\times10^{-4}$ M, $[TMA^+Cl^-]_{o,i} = 0.010$ M (for $H_2\mathbf{1}_6^{6-}$), 0.015 M (for $H_4\mathbf{1}_8^{8-}$), volume of aqueous and organic phases = 15 mL, pH = 7.3±0.2.

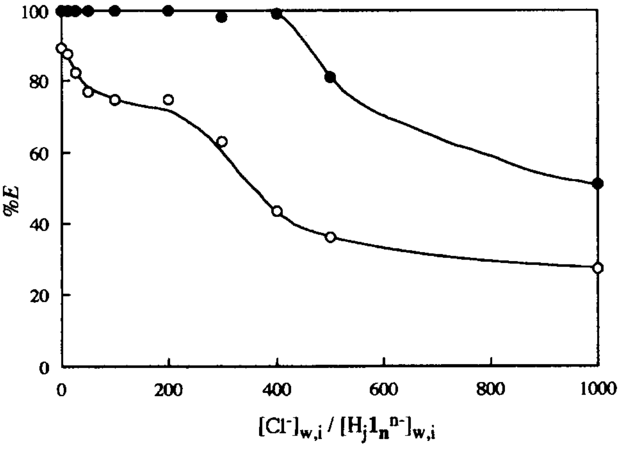

Fig. 8. Effect of Cl^- on the extraction of UO_2^{2+} by $H_j\mathbf{1}_n^{n-}$ in the presence of MTA^+Cl^- at about 25 °C. ○: $H_2\mathbf{1}_6^{6-}$, ●: $H_4\mathbf{1}_8^{8-}$, $[H_j\mathbf{1}_n^{n-}]_{w,i} = 1.0\times10^{-3}$ M, $[UO_2^{2+}]_{w,i} = 1.0\times10^{-4}$ M, $[TMA^+Cl^-]_{o,i} = 0.010$ M (for $H_2\mathbf{1}_6^{6-}$), 0.015 M (for $H_4\mathbf{1}_8^{8-}$), $[Na_2CO_3]_{w,i} = 2.0\times10^{-3}$ M, volume of aqueous and organic phases = 15 mL, pH = 7.3±0.2.

anions to $H_j\mathbf{1}_n{}^{n-}$.

In the extraction by hexamer, a decrease of *%E* with an increase in anions starts at the same and 20-times concentration for $CO_3{}^{2-}$ and Cl^-, respectively. On the other hand, there are no decreases in *%E* until 50-times for $CO_3{}^{2-}$ and 400-times for Cl^- in the extraction by octamer. These results indicate that the octamer is superior to the hexamer as an extraction reagent for $UO_2{}^{2+}$. Since it is clear that Cl^- does not interfere with the complex formation of $UO_2{}^{2+}$ with $H_j\mathbf{1}_n{}^{n-}$, the influence must originate in the extraction process of the complex by MTA^+Cl^-.

Effect of Coexisting-Metal Ion. The extractions of $UO_2{}^{2+}$ from the aqueous solutions containing 10 or 100 molar times metal ions were carried out to study the effect of coexisting-metal ions. The results are summarized in Table 1 for hexamer and in Table 2 for octamer. It has been shown that the presence of 100-times of alkali and alkaline earth metal ions slightly decreases *%E* in the extraction by hexamer. The presence of 100-times of Ca^{2+} decreased *%E* to 53.7 from 89.4%. These influences should be caused by Cl^- from metal chlorides, because the selective reactivity of hexamer to $UO_2{}^{2+}$ over metal ions including Ca^{2+} is large enough to extract $UO_2{}^{2+}$ from the aqueous solution containing excess foreign metal ions. Thus, no influence was observed at all in the presence of other di-, tri-, and tetravalent metal ions. Contrary, these seem to increase the values of *%E*. This may be due to the coexisting-metal ion assisting the molecular configuration of $H_2\mathbf{1}_6{}^{6-}$ to be more advantageous to make a complex with $UO_2{}^{2+}$. A similar effect due to the presence of Na^+ has been reported in the extraction of rare-earth metal ions by an alkylated calix[4]arene derivative.[20]

Table 1. Percent Extraction (*%E*) of $UO_2{}^{2+}$ and Foreign Metal Ions M^{m+} from Their Aqueous-Mixture Solution into Chloroform with $H_2\mathbf{1}_6{}^{6-}$ in the Presence of MTA^+Cl^-

M^{m+}			*%E*	
Metal ions	Added as	Amount/μmol	$UO_2{}^{2+}$	M^{m+}
None	—	—	89.4	—
Na^+	NaCl	160	89.1	0
K^+	KCl	147	85.1	0
		14.7	89.0	0
Mg^{2+}	$Mg(NO_3)_2$	139	86.4	1.38
		15.2	87.9	0.10
Ca^{2+}	$CaCl_2$	186	53.7	0.30
		18.4	83.4	0.08
Mn^{2+}	$MnSO_4$	15.6	94.3	0.74
Co^{2+}	$Co(NO_3)_3$	15.7	98.2	0
Ni^{2+}	$NiCl_2$	15.4	88.5	0
Cu^{2+}	$CuCl_2$	15.1	86.5	0
Zn^{2+}	$ZnCl_2$	15.1	93.2	0
Al^{3+}	$AlCl_3$	14.5	90.4	0.54
Cr^{3+}	$Cr(NO_3)_3$	14.9	96.2	0.30
Fe^{3+}	$Fe_2(SO_4)_3$	15.8	94.8	0
Ti^{4+}	$Ti(SO_4)_2$	15.7	100	25.5
Zr^{4+}	$ZrOCl_2$	14.8	90.6	4.03

$[H_2\mathbf{1}_6{}^{6-}]_{w,i} = 5.0\times10^{-4}$ M, $[UO_2{}^{2+}]_{w,i} = 1.0\times10^{-4}$ M, $[MTA^+Cl^-]_{o,i} = 0.010$ M, $[Na_2CO_3]_{w,i} = 1.0\times10^{-3}$ M, volume of aqueous and organic phases = 15 mL, pH = 7.5±0.5.

Table 2. Percent Extraction (*%E*) of $UO_2{}^{2+}$ and Foreign Metal Ions M^{m+} from Their Aqueous-Mixture Solution into Chloroform Phase with $H_4\mathbf{1}_8{}^{8-}$ in the Presence of MTA^+Cl^-

M^{m+}			*%E*	
Metal ions	Added as	Amount/μmol	$UO_2{}^{2+}$	M^{m+}
None	—	—	100	—
Na^+	NaCl	160	100	0.81
K^+	KCl	147	100	1.49
Mg^{2+}	$Mg(NO_3)_2$	139	100	0.23
		15.2	100	0.24
Ca^{2+}	$CaCl_2$	186	100	0.76
		18.4	100	0.30
Mn^{2+}	$MnSO_4$	15.6	100	0.25
Co^{2+}	$Co(NO_3)_2$	15.7	100	2.71
Ni^{2+}	$NiCl_2$	15.4	100	1.11
Cu^{2+}	$CuCl_2$	15.1	100	1.71
Zn^{2+}	$ZnCl_2$	15.1	100	2.26
Al^{3+}	$AlCl_3$	14.5	100	0
Cr^{3+}	$Cr(NO_3)_3$	14.9	100	0.18
Fe^{3+}	$Fe_2(SO_4)_3$	15.8	100	1.70
Ti^{4+}	$Ti(SO_4)_2$	15.7	100	10.9
Zr^{4+}	$ZrOCl_2$	14.8	100	2.51

$[H_4\mathbf{1}_8{}^{8-}]_{w,i} = 5.0\times10^{-4}$ M, $[UO_2{}^{2+}]_{w,i} = 1.0\times10^{-4}$ M, $[MTA^+Cl^-]_{o,i} = 0.010$ M, $[Na_2CO_3]_{w,i} = 1.0\times10^{-3}$ M, volume of aqueous and organic phases = 15 mL, pH = 8.0±0.5.

On the other hand, the values for *%E* by octamer were 100% for all metal ions. This would be due to the higher selective reactivity and stability to $UO_2{}^{2+}$. High-valence metal ions, such as Ti^{4+} and Zr^{4+}, also did not interfere with the extraction, while small amounts of them were co-extracted themselves. This may be due to the complex formation and extraction by excess $H_4\mathbf{1}_8{}^{8-}$ present in the extraction system.

Stripping of $\mathbf{UO_2{}^{2+}}$. $UO_2{}^{2+}$ in chloroform was stripped by dilute sulfuric acid and hydrochloric acid, and the results were shown in Tables 3 and 4. The recovery was 70—80%. The recovery by higher concentrations of these acids decreased, especially in the case of hydrochloric acid. This may be due to the extraction of $UO_2{}^{2+}$ as chlorocomplexes by MTA^+, because $H_j\mathbf{1}_n{}^{n-}$ moves into the aqueous phase in proportion to hydrochloric acid. It is very interesting to note that $UO_2{}^{2+}$ is recovered but $H_j\mathbf{1}_n{}^{n-}$ remains in organic phases by dilute sulfuric acid. This must be due to the sulfate of MTA^+ being so insoluble in organic phase that $H_j\mathbf{1}_n{}^{n-}$ can not be recovered into the aqueous phase, remaining as a counter ion of MTA^+ in the organic phase. This means that dilute sulfuric acid can recover only $UO_2{}^{2+}$ from a complex-associate, leaving a MTA^+–$H_j\mathbf{1}_n{}^{n-}$ associate in the organic phase.

Solvent Extraction of Metal Ion by $\mathbf{MTA^+}$–$\mathbf{H_j1_n{}^{n-}}$ Associate in Organic Solution. The ionic associate, MTA^+–$H_j\mathbf{1}_n{}^{n-}$ remains in the form of $(TMA^+)_n$ $(H_j\mathbf{1}_n{}^{n-})$ in the organic phase after stripping of the metal ion by dilute sulfuric acid, and it seems to be possible to use it for further

Table 3. Recovery of UO_2^{2+} and $H_2\mathbf{1}_6^{6-}$ from the Chloroform Phase by the Stripping Method

Stripping			Recovery/%	
Acids/M		Time/h	UO_2^{2+}	$H_2\mathbf{1}_6^{6-}$
HCl	0.1	1	68.7	1.48
	1.0	1	71.7	32.2
	3.0	1	67.4	104
H_2SO_4	0.1	1	80.4	1.48
	1.0	1	80.4	1.03
		2	77.7	0.95
		3	74.2	0.95
	2.0	1	72.9	1.03
		2	71.6	0.95
		3	74.5	1.18
	3.0	1	64.2	1.77

Table 4. Recovery of UO_2^{2+} and $H_4\mathbf{1}_8^{8-}$ from the Chloroform Phase by the Stripping Method

Stripping			Recovery/%	
Acids/M		Time/h	UO_2^{2+}	$H_4\mathbf{1}_8^{8-}$
HCl	0.1	1	72.4	1.01
	1.0	1	71.0	1.43
	3.0	1	65.1	22.8
	4.0	1	15.7	103
H_2SO_4	0.1	1	70.0	0.79
	1.0	1	76.5	0.55
		2	75.2	0.54
		3	75.4	0.54
	2.0	1	79.1	0.55
		2	78.6	0.57
		3	81.5	0.63
	3.0	1	66.3	0.95

solvent extraction of metal ions. Thus, we tried repeated solvent extraction using the used organic phase, and obtained almost identical results, such as shown in Tables 1 and 2. We also confirmed that such a repeated extraction could also be performed similarly by the newly prepared organic solution for MTA^+–$H_j\mathbf{1}_n^{n-}$.

Conclusion. The solvent extraction of UO_2^{2+} is carried out by using water-soluble hydroxycalix[*n*]arene-*p*-sufonates, $H_j\mathbf{1}_n^{n-}$ in the presence of trioctylmethylammonium-chloride, MTA^+Cl^-. The extractability increased in the order of *n*, that is, in the order of $H_2\mathbf{1}_4^{4-} \ll H_2\mathbf{1}_6^{6-} < H_4\mathbf{1}_8^{8-}$. This is equal to the order of the stability of the complex in the aqueous solution. $H_2\mathbf{1}_4^{4-}$, which hardly forms a complex with UO_2^{2+}, could not extract UO_2^{2+} at all. $H_2\mathbf{1}_6^{6-}$ and $H_4\mathbf{1}_8^{8-}$, both of which form stable complexes with high selectivity, could extract quantitatively and the extraction was not influenced by the presence of metal ions. Especially, the extraction by the latter was not influenced at all, and could extract UO_2^{2+} quantitatively over a wide pH range. The high concentration of carbonate and chloride ions caused a decrease in the extraction, especially for the hexamer. The stripping by dilute sulfuric acid could recover UO_2^{2+}, leaving ionic associates, MTA^+–$H_j\mathbf{1}_n^{n-}$, in chloroform, and the organic phase could be used for further extraction. The compositions of the extracted species were also studied and determined to be $(MTA^+)_9\ [(UO_2^{2+})(\mathbf{1}_6^{8-})H_{-3}]$ for the hexamer and $(MTA^+)_{11}\ [(UO_2^{2+})_2(\mathbf{1}_8^{12-})H_{-3}]$ for the octamer, and equations for the extraction were also proposed.

References

1 S. Shinkai, H. Koreishi, K. Ueda, and O. Manabe, *J. Chem. Soc., Chem. Commun.*, **1986**, 233.

2 S. Shinkai, H. Koreishi, K. Ueda, T. Arimura, and O. Manabe, *J. Am. Chem. Soc.*, **109**, 6371 (1987).

3 S. Shinkai, Y. Shiramama, H. Satoh, O. Manabe, T. Arimura, K. Fujimoto, and T. Matsuda, *J. Chem. Soc., Perkin Trans. 2*, **1989**, 1167.

4 S. Shinkai, T. Otsuka, K. Araki, and T. Matsuda, *Bull. Chem. Soc. Jpn.*, **62**, 4055 (1989).

5 T. Nagasaki, S. Shinkai, and T. Matsuda, *J. Chem. Soc., Perkin Trans. 1*, **1990**, 2617.

6 T. Nagasaki and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, **1991**, 1063.

7 K. Araki, N. Hashimoto, H. Otsuka, T. Nagasaki, and S. Shinkai, *Chem. Lett.*, **1993**, 829.

8 N. Baglan, C. Dinse, C. Cossonnet, R. Abidi, Z. Asfari, M. Leroy, and J. Vicens, *J. Radioanal. Nucl. Chem.*, **226**, 2618 (1997).

9 Y. K. Agrawal and M. Sanyal, *J. Radioanal. Nucl. Chem.*, **198**, 349 (1995).

10 M. Sonoda, H. Hayashi, M. Nishida, D. Ishii, and I. Yoshida, *Anal. Sci.*, **14**, 493 (1998).

11 M. Sonoda, M. Nishida, D. Ishii, and I. Yoshida, *Anal. Sci.*, **15**, 1207 (1999).

12 M. Nishida, M. Sonoda, D. Ishii, and I. Yoshida, *Chem. Lett.*, **1998**, 289.

13 M. Nishida, M. Sonoda, D. Ishii, and I. Yoshida, *Bull. Chem. Soc. Jpn.*, **71**, 2845 (1998).

14 M. Nishida, M. Sonoda, D. Ishii, and I. Yoshida, *Bunseki Kagaku*, **47**, 853 (1998).

15 M. Nishida, M. Sonoda, D. Ishii, and I. Yoshida, *Chem. Lett.*, **1999**, 1275.

16 M. Nishida, D. Ishii, I. Yoshida, and S. Shinkai, *Bull. Chem. Soc. Jpn.*, **70**, 2131 (1997).

17 K. Ueno, "Kire-to tekitei," Nankodo, Tokyo (1989).

18 H. Onishi and Y. Toita, *Bunseki Kagaku*, **18**, 592 (1969).

19 P. Thuery, N. Keller, M. Lance, J.-D. Vigner, and M. Nierlich, *Acta Crystallogr., Sect. C*, **51C**, 1570 (1995).

20 T. Oshima, T. Kakoi, F. Kubota, K. Ohto, M. Goto, and F. Nakashio, *Sep. Sci. Technol.*, **33**, 1905 (1998).