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Highly Efficient Solvent Extraction of Water-Soluble Macrocyclic Metal Ligands, Hydroxycalix[*n*]arene-*p*-sulfonates ($n = 4, 6, 8$) with Trioctylmethylammonium Chloride

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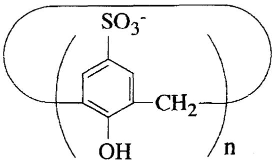
Water-soluble hydroxycalix[*n*]arene-*p*-sulfonates, $\mathbf{1}_n^{n-}$ ($n = 4$, 6, and 8), were quantitatively extracted from an aqueous solution into chloroform with trioctylmethylammonium ion (TMA^+) over a wide pH range. The extraction reaction of $\mathbf{1}_n^{n-}$ with TMA^+Cl^- and the extraction constants were determined from slope analyses of linearized extraction data and by the mole-ratio method. It was demonstrated that $\mathbf{1}_n^{n-}$, having *n* moles of sulfonato groups in an aqueous solution, could be extracted as $\mathbf{1}_n\ (TMA^+)_n$ by associating with *n* moles of TMA^+ at a pH lower than that at which protonic dissociation of hydroxyl groups takes place, and that $\mathbf{1}_n\ (TMA^+)_{(n+j)}$ was extracted at a pH higher than that for *j* moles of hydroxyl groups dissociate to form $\mathbf{1}_n^{(n+j)-}$. The extractability of $\mathbf{1}_n^{n-}$ increased in the order of *n* ($4 < 6 < 8$); also, the pH range where complete extraction took place became wider in the same order. As a possible application of the present extraction system, metal extraction with $\mathbf{1}_4^{4-}$ was also shown for the purpose of selective separation of some metal ions.

It has been shown that some of the hydroxyl groups in calix[*n*]arene-*p*-sulfonates, $\mathbf{1}_n^{n-}$, have relatively high acidity,[1—3] and that they can form coordination compounds with some metal ions, even in an acidic aqueous solution[4,5] in addition to an alkaline solution.[6,7] Sulfonato groups introduced to give water-solubility to calix[*n*]arenes, therefore, make them peculiar metal ligands having a macrocyclic structure. Their characteristic properties as metal ligands vary with the size of the macrocyclic ring, i.e., with the change in the value of *n*.[8]

Recently, we have reported on the complex formation reaction of $\mathbf{1}_n^{n-}$ with the alkylammonium ion, A^+.[9] During the process of this study we found that the molecular associates, $\mathbf{1}_n(A)_{n+1}$, precipitate, and that they are easily soluble in organic solvents.[9] These facts suggest that water-soluble calix[*n*]arenes, $\mathbf{1}_n^{n-}$, can be extractable into organic solvents containing the alkylammonium ion, A^+. If this is possible, $\mathbf{1}_n^{n-}$ complexed with a metal ion can also be extracted, and may be expected to construct a new separation system which can selectively extract some metal ions from an aqueous phase into an organic phase.

In the present study, we investigated the solvent extraction of $\mathbf{1}_n^{n-}$ in the aqueous phase using various alkylammonium chlorides, A^+Cl^- including trioctylmethylammonium chloride (TMA^+Cl^-) in various organic solvents, including chloroform (Scheme 1). The extraction results indicated that $\mathbf{1}_n^{n-}$ in the aqueous phase can be completely extracted into chloroform using TMA^+Cl^- over a wide pH range. The composition of the extracted species and the extraction constants (K_{ex}) were determined.



Scheme 1. Molecular structure for $\mathbf{1}_n^{n-}$.

Experimental

Reagents. $Na_n\mathbf{1}_n$ was obtained commercially from Sugai Kagaku Co. (Wakayama, Japan) and used after recrystallization from a mixture of water and methanol. Weighed amounts of them were dissolved in water to prepare 0.01 M ($1\ M = 1\ mol\,dm^{-3}$) stock solutions. Their concentrations were determined by the titration method using standard 0.1 M NaOH. These solutions were used for solvent extractions after appropriate dilution. TMA^+Cl^- was obtained from Dojindo Laboratories Co. (Kumamoto, Japan) and used without further purification. By dissolving weighed amounts of TMA^+Cl^- with chloroform, 0.01 M and 0.015 M solutions were prepared, and the concentrations were determined by the precipitation titration method using a standard sodium tetraphenylborate solution. Other ammonium salts, tetrabutylammonium perchlorate (Fluka Chemie AG) and benzyldimethyltetradecylammonium chloride (Dojindo Laboratories Co.), were also used.

Known amounts of metal chlorides or nitrates were dissolved with 0.1 M to 0.01 M of HCl to prepare 0.01 M metal-ion solutions. Most were standardized by the EDTA titration method.[10] After diluting to 0.001 M, they were used for the solvent-extraction experiment. Standard sodium chloride (99.99%, Matsunaga Kagakukogyo Co., Japan, for quantitative analysis) was used after heating at 600 °C for 1 h.

Apparatus. Absorbance and UV-vis absorption spectra were measured with a Shimadzu UV-180 and a UV-160 spectrophotometer using a 1 cm or a 0.5 cm light-pass length quartz cell. The pH was measured with a Horiba-F21 pH meter. The concentrations of metal ions were measured using a Seikodensi SPS-1200VR inductively coupled plasma-atomic emmision spectrophotometer (ICP-AES).

Solvent Extraction of $\mathrm{Na}_n\mathbf{1}_n$. Fifteen milliliters of aqueous $\mathrm{Na}_n\mathbf{1}_n$ and chloroform $\mathrm{TMA^+Cl^-}$ solutions were taken into a 50 mL centrifuge tube, respectively, and the tube was shaken for 10 min at 400 strokes/min using a Iwaki KM shaker. After centrifuging for 3 min at 2000 rpm, an aliquot of the aqueous phase was transferred into a 25 mL measuring flask containing 5 mL of 0.1 M NaOH and diluted with water to the mark in order to measure the absorbance due to $\mathbf{1}_n^{n-}$ at 264 nm for $\mathrm{Na_4}\mathbf{1_4}$ and $\mathrm{Na_6}\mathbf{1_6}$, and at 289 nm for $\mathrm{Na_8}\mathbf{1_8}$. The percent extraction of $\mathbf{1}_n^{n-}$, %*E*, was calculated from Eq. 1, where $[\mathbf{1}_n^{n-}]_{\mathrm{w,i}}$ and $[\mathbf{1}_n^{n-}]_{\mathrm{w,e}}$ mean preparative and equilibrium concentrations in the aqueous phase before and after extraction, respectively.

$$\%E = \{\{[\mathbf{1}_n^{n-}]_{\mathrm{w,i}} - [\mathbf{1}_n^{n-}]_{\mathrm{w,e}}\}/[\mathbf{1}_n^{n-}]_{\mathrm{w,i}}\} \times 100. \qquad (1)$$

Extractions of $\mathrm{Na}_n\mathbf{1}_n$ with an excess amount of $\mathrm{TMA^+Cl^-}$ were carried out at $[\mathrm{Cl^-}] = 0.10$ M for $\mathbf{1}_4^{4-}$, $[\mathrm{Cl^-}] = 0.50$ M for $\mathbf{1}_6^{6-}$ and $\mathbf{1}_8^{8-}$ using 0.02—0.001 M $\mathrm{TMA^+Cl^-}$ chloroform solutions. After equilibrium was attained, the concentration, $[\mathbf{1}_n^{n-}]_{\mathrm{w,e}}$, was measured. Since an excess amount of $\mathrm{TMA^+Cl^-}$ was used, $[\mathrm{TMA^+Cl^-}]_{\mathrm{o,i}} = [\mathrm{TMA^+Cl^-}]_{\mathrm{o,e}}$ can approximately be held, where $[\mathrm{TMA^+Cl^-}]_{\mathrm{o,i}}$ and $[\mathrm{TMA^+Cl^-}]_{\mathrm{o,e}}$ are the initial and equilibrium concentrations in the organic phase. Extractions of $\mathrm{Na}_n\mathbf{1}_n$ from an aqueous solution containing an excess amount of sodium chloride were carried out using a 0.010 M $\mathrm{TMA^+Cl^-}$ chloroform solution in the concentration range of 2.0—0.20 M NaCl, so that we could approximate $[\mathrm{Cl^-}]_{\mathrm{w,e}} = [\mathrm{Cl^-}]_{\mathrm{w,i}}$.

The back extractions of $\mathbf{1}_n^{n-}$ in the organic phase were carried out by shaking with 3 M $\mathrm{H_2SO_4}$ for 60 min at 400 strokes/min. After centrifuging for 3 min at 2000 rpm, both phases were separated and the absorbance of the aqueous phase was measured to determine the concentration of $\mathbf{1}_n^{n-}$ in the organic phase.

Solvent Extraction of Metal Complexes with $\mathrm{Na}_n\mathbf{1}_n$. Into a 50 mL of centrifuge tube, 15 mL ($1\ \mathrm{mL} = 1\times10^{-3}\ \mathrm{dm^{-3}}$) of an aqueous mixture solution of 1×10^{-3} M $\mathrm{Na}_n\mathbf{1}_n$ and 2×10^{-4} M metal ion was taken. The pH of the aqueous solution was adjusted to a given value by the addition of NaOH in advance. Then, 15 mL of a chloroform $\mathrm{TMA^+Cl^-}$ solution was added, and the tube was shaken for 10 min at 400 strokes/min. Extraction studies of rare earth metal ions, $\mathrm{Ln^{3+}}$, were carried out similarly using a mixture solution of $\mathrm{Na}_n\mathbf{1}_n$ (2×10^{-3} M) and $\mathrm{Ln^{3+}}$ ions (total concentrations $= 4\times10^{-4}$ M). After centrifuging for 3 min at 2000 rpm, 10 mL of the chloroform phase was transferred into another 50 mL tube and shaken with 10 mL of 2 M HCl for 30 min at 400 strokes/min in order to back-extract a metal ion. The metal-ion concentration in the chloroform phase, $[\mathrm{M}]_{\mathrm{o,e}}$, was obtained by measuring those in the back-extracted aqueous phase. The percent extraction of a metal ion, %*E*, was obtained from the following equation, where $[\mathrm{M}]_{\mathrm{w,i}}$ means the preparative concentration of the metal ion in the aqueous phase:

$$\%E = \{[\mathrm{M}]_{\mathrm{o,e}}/[\mathrm{M}]_{\mathrm{w,i}}\} \times 100. \qquad (2)$$

The pH of the aqueous phase was measured after equilibrium was attained.

Results and Discussion

Solvent Extraction of $\mathrm{Na}_n\mathbf{1}_n$ with Trioctylmethylammonium Chloride (Capriquat, $\mathrm{TMA^+Cl^-}$). Table 1 gives the results of the solvent extractions of $\mathbf{1}_n^{n-}$ by means of percent extraction (%*E*) for $\mathbf{1}_n^{n-}$ together with those for some related compounds at two pHs. These results indicate that $\mathbf{1}_n^{n-}$ can be quantitatively extracted from both weakly acidic and basic solutions into chloroform in the presence of $\mathrm{TMA^+Cl^-}$. However, since a slightly smaller %*E* was observed for $\mathbf{1}_8^{8-}$ at pH 9.15 compared to those for other extractions, it will be explained by a shortage of $\mathrm{TMA^+Cl^-}$, as described later. In fact, we could quantitatively extract $\mathbf{1}_8^{8-}$ using excess $\mathrm{TMA^+Cl^-}$ in a similar extraction.

Table 1. Percent Extraction, %*E* of $\mathbf{1}_n^{n-}$ and Some Related Organic Sulfonates by Solvent Extraction with Capriquat ($\mathrm{TMA^+Cl^-}$) in Chloroform[a)]

		Amount of $\mathbf{1}_n^{n-}$ in aqueous solution/μmol		
$\mathbf{1}_n^{n-}$	pH	Before extraction	After extraction	%*E*
$\mathbf{1}_4^{4-}$	4.67	15.9	0.029	99.8
	9.15		0.044	99.7
$\mathbf{1}_6^{6-}$	4.67	15.2	0.027	99.8
	9.15		0.012	99.9
$\mathbf{1}_8^{8-}$	4.67	15.9	0.0084	99.9
	9.15		0.879	94.5[e)]
PS[b)]	4.67	15.0	3.08	79.5
	9.15		2.18	85.5
NS[c)]	4.63	15.0	1.72	88.5
	9.20		1.17	92.2
CTCT[d)]	4.63	15.0	1.03	93.1
	9.20		0.638	95.7[e)]

a) $[\mathrm{TMA^+Cl^-}] = 0.01$ M, volume of chloroform = 15 ml, $[\mathrm{Na}_n\mathbf{1}_n]_{\mathrm{w,i}} = 1.0\times10^{-3}$ M, volume of $\mathrm{H_2O}$ = 15 ml, temperature = about 25 °C. b) PS = *p*- phenolsulfonate. c) NS = 2,7-naphthalenedisulfonate. d) CTCT = cyclotetrameric naphthalenophaneoctasulfonate, cf. Ref. 11. e) Smaller value of %*E* is explained by the shortage of $\mathrm{TMA^+Cl^-}$.

Table 1 also indicates that linear monosulfonate, *p*-phenolsulfonate (PS) and planar disulfonate, 2,7-naphthalenedisulfonate (NS) and cyclotetrameric naphthalenophaneoctasulfonate, derived from 1,8-dihydroxy-3,6-naphthalenedisulfonate (original acronym, CTCT),[11)] were partly extractable by a similar method. These facts indicate that the high extractability of $\mathbf{1}_n^{n-}$ can be ascribed to the macrocyclic and flexible structure, which can form a rather spheric and hydrophobic associate with $\mathrm{TMA^+}$.

Extraction of $\mathbf{1}_4^{4-}$ with Several Other Ammonium Ions. Since it can be expected that other alkylammonium ions can also extract $\mathbf{1}_n^{n-}$, we investigated the solvent extraction of $\mathbf{1}_4^{4-}$ using tetrabutylammonium perchlorate ($\mathrm{TBA^+ClO_4^-}$) and benzyldimethyltetradecylammonium chloride (Zephiramine, $\mathrm{Zph^+Cl^-}$) in chloroform at pH 3.0. The results are given in Table 2. The values of %*E* for $\mathrm{TBA^+}$ and $\mathrm{Zph^+}$ are obviously smaller than that for $\mathrm{TMA^+}$. The hydrophobicity of $\mathrm{TBA^+}$ may be too small to extract $\mathbf{1}_4^{4-}$ efficiently. $\mathrm{Zph^+}$may be too bulky to associate with $\mathbf{1}_4^{4-}$, because $\mathrm{Zph^+}$ has two big benzyl and tetradecyl groups. We thus used $\mathrm{TMA^+Cl^-}$ as an ammonium ion for the present extraction study.

Effect of Organic Solvents. Table 3 gives the %*E* of

Table 2. Percent Extraction, %*E* of $\mathbf{1}_4^{4-}$ from the Aqueous Solution into Chloroform with Several Ammonium Salts[a)]

Ammonium salts	%*E*
Capriquat[b)]	99.7
Tetrabutylammonium perchlorate	7.05
Zephiramine[c)]	88.5

a) [ammonium salts] = 0.010 M, $[\mathrm{Na_4}\mathbf{1}_4]_{\mathrm{w,i}} = 1.06\times10^{-3}$ M, pH = 3.0. b) Trioctylmethylammonium chloride. c) Benzyldimethyltetradecylammonium chloride.

Table 3. Percent Extraction, %*E* of $\mathbf{1}_4^{4-}$ from the Aqueous Solution into Several Organic Solvents with $\mathrm{TMA^+Cl^-}$ [a)]

Organic solvent	%*E*
Chloroform	99.7
Kerosene	4.91
Toluene	16.6
Diisopropyl ether	26.2
1-Octanol	99.5

a) $[\mathrm{TMA^+Cl^-}]_{\mathrm{o,i}} = 0.010$ M, $[\mathrm{Na_4}\mathbf{1}_4]_{\mathrm{w,i}} = 1.06\times10^{-3}$ M, pH = 3.0.

$\mathbf{1}_4^{4-}$ for the extractions with $\mathrm{TMA^+Cl^-}$ in various organic solvents. The value of %*E* was larger in the order of chloroform $\geqq$ 1-octanol $\gg$ diisopropyl ether > toluene > kerosene, indicating that a polar solvent is effective for the extraction of $\mathbf{1}_4^{4-}$. The precipitate, which seems like an ionic associate of $\mathbf{1}_4^{4-}$ with $\mathrm{TMA^+}$, usually appeared at an interface of the nonpolar organic and aqueous phases. This fact may indicate the poor solubility and ineffectiveness of nonpolar organic solvents in the extraction of the $\mathbf{1}_4^{4-}$–$\mathrm{TMA^+}$ complex. Table 3 suggests that 1-octanol is also an effective solvent; however, since the solubility of $\mathrm{TMA^+Cl^-}$ for 1-octanol is considerably smaller than that for chloroform, we subsequently used chloroform as an organic solvent for the present extraction.

Effect of Extraction Time. Figure 1 shows %*E* for the extraction of $\mathbf{1}_4^{4-}$ at pH 1.0 (△) and 11.0 (○) as a function of the shaking time. The %*E* reaches a maximum value in at least 10 min; this value is constant for more than 5 h, indicating that the extraction reaches to equilibrium in at least 10 min, and that the time is independent of the pH of the aqueous phase. Thus, we subsequently shook the solutions for 10 min for $\mathrm{Na}_n\mathbf{1}_n$ extractions.

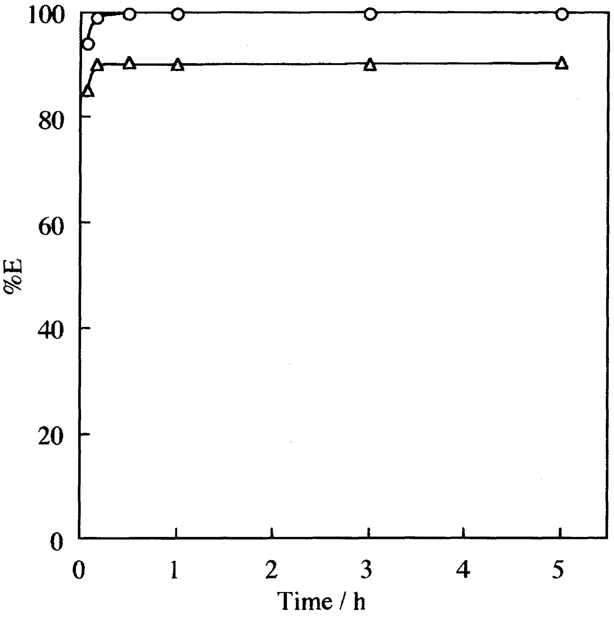


Fig. 1. Effect of shaking time on the extraction of $\mathbf{1}_4^{4-}$. $[\mathrm{Na_4}\mathbf{1}_4]_{\mathrm{w,i}} = 9.94\times10^{-4}$ M, $[\mathrm{TMA^+Cl^-}]_{\mathrm{o,i}} = 9.98\times10^{-3}$ M, △: pH = 1.0, ○: pH = 11.0.

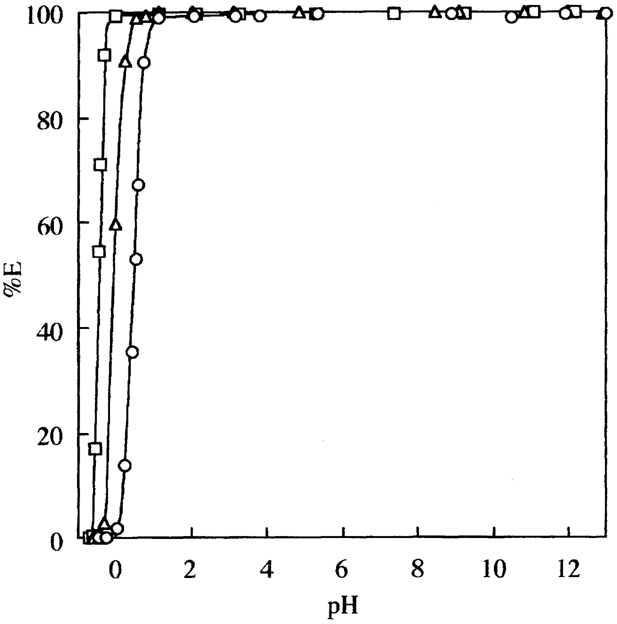


Fig. 2. Effect of pH on the extraction of $\mathbf{1}_n^{n-}$ with $\mathrm{TMA^+Cl^-}$ at about 25 °C. $[\mathrm{Na}_n\mathbf{1}_n]_{\mathrm{w,i}} = 1.0\times10^{-3}$ M, ○: $\mathbf{1}_4^{4-}$ with $[\mathrm{TMA^+Cl^-}]_{\mathrm{o,i}} = 0.010$ M, △: $\mathbf{1}_6^{6-}$ with $[\mathrm{TMA^+Cl^-}]_{\mathrm{o,i}} = 0.010$ M, □: $\mathbf{1}_8^{8-}$ with $[\mathrm{TMA^+Cl^-}]_{\mathrm{o,i}} = 0.015$ M.

Effect of pH. Figure 2 shows %*E* for the extraction of $\mathbf{1}_n^{n-}$ as a function of the pH, which was adjusted by the addition of HCl and NaOH. For HCl concentrations higher than 4 M, although $\mathbf{1}_n^{n-}$ could not be extracted, as the HCl concentration decreased they became extractable at pH = −0.30 ($[\mathrm{H^+}] = 2$ M) for $\mathbf{1}_4^{4-}$, pH = −0.47 ($[\mathrm{H^+}] = 3$ M) for $\mathbf{1}_6^{6-}$, pH = −0.60 ($[\mathrm{H^+}] = 4$ M) for $\mathbf{1}_8^{8-}$. When the pH became higher than those values, the %*E* increased quickly with pH and reached almost complete extraction at pH = 0.80 for $\mathbf{1}_4^{4-}$ at pH = 0.50 for $\mathbf{1}_6^{6-}$, and at pH = 0.0 for $\mathbf{1}_8^{8-}$. Such pH dependencies for the extractions of $\mathbf{1}_n^{n-}$ may indicate that sulfonic acid, $\mathrm{H}_n\mathbf{1}_n$, in the aqueous phase associates with $\mathrm{TMA^+}$ by releasing protons and forming the $\mathbf{1}_n^{n-}$–$\mathrm{TMA^+}$ complex, and that the complex moves into chloroform while retaining HCl in the aqueous phase, as follows:

$$\mathrm{L(SO_3H)}_{n(\mathrm{w})} + n\mathrm{TMA^+Cl^-_{(o)}} \rightleftharpoons \mathrm{L(SO_3^-TMA^+)}_{n(\mathrm{o})} + n\mathrm{HCl_{(w)}}. \quad (3)$$

Here, $\mathrm{L(SO_3H)}_n$ is sulfonic acid, $\mathrm{H}_n\mathbf{1}_n$, and (w) and (o) indicate the aqueous and organic phases, respectively.

Recovery of $\mathbf{1}_n^{n-}$ from Chloroform. The recovery of $\mathbf{1}_n^{n-}$ from the chloroform phase was studied using HCl of various concentrations. The results are summarized in Table 4. By shaking for 30 min with 2 and 3 M HCl, $\mathbf{1}_4^{4-}$ and $\mathbf{1}_6^{6-}$ were completely recoverable. The recovery of $\mathbf{1}_8^{8-}$ was attained by using a slightly higher concentration, 4 M HCl, and a slightly longer shaking time, 60 min.

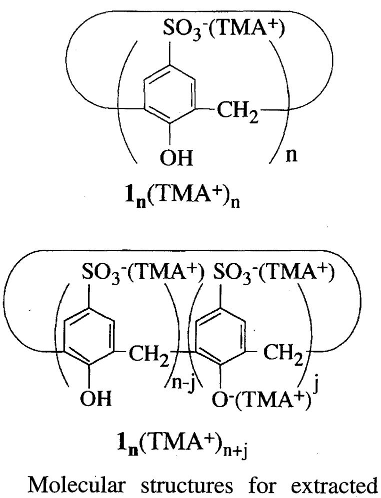
Binding Ratio of TMA$^+$ to $\mathbf{1}_n^{n-}$ in the $\mathbf{1}_n^{n-}$–TMA$^+$ Complexes. The binding ratio of the extracted complexes from the acidic aqueous phase into chloroform can be expected to be $\mathbf{1}_n^{n-}$: TMA$^+$ = 1 : *n*, as shown in Eq. 3 and Scheme 2. This estimation and that for species extracted from an alkaline solution were confirmed by the mole-ratio method; the results are shown in Fig. 3. Clear abrupt changes of the slope can be seen on each extraction line for %*E* vs. initial concentration ratio, $[\mathrm{TMA^+Cl^-}]_{\mathrm{o,i}}/[\mathbf{1}_n^{n-}]_{\mathrm{w,i}}$, in the organic and aqueous phases. The presence of such a clear point as the intersection of two straight lines of different slopes indicates not only the precise binding ratio of the complex, but also the formation of a reasonably stable complex. The binding ratio obtained from the clear abrupt points is summarized in Table 5.

Table 5 indicates that $\mathbf{1}_4^{4-}$: TMA$^+$ = 1 : 4 at pH 2.0 and 1 : 5 at pH 9.1, $\mathbf{1}_6^{6-}$: TMA$^+$ = 1 : 6 at pH 2.0 and 1 : 8 at pH 9.1, $\mathbf{1}_8^{8-}$: TMA$^+$ = 1 : 8 at pH 2.0 and 1 : 10 at pH 10.4. At an intermediate pH between these, as shown in Table 5, the complexes having $\mathbf{1}_6^{6-}$: TMA$^+$ = 1 : 7 and $\mathbf{1}_8^{8-}$: TMA$^+$ = 1 : 9 are also extracted.

In order to explain the dependence of the binding ratio on the pH in the aqueous phase, we calculated the species-distribution curves of $\mathbf{1}_n^{n-}$ based on the acid dissociation constants[3,12,13] of the hydroxy groups using the computer program SPE.[14] The results are shown in Fig. 4 ($\mathbf{1}_4^{4-}$), Fig. 5 ($\mathbf{1}_6^{6-}$), and Fig. 6 ($\mathbf{1}_8^{8-}$). It has been demonstrated that $\mathbf{1}_n^{n-}$ is present as *n* valent sulfonato ions having *n* moles of hydroxy groups in a weakly acidic solution of pH < 2.

Table 4. Recovery of $\mathbf{1}_n^{n-}$ by Back Extraction with Dilute HCl

$\mathbf{1}_n^{n-}$	Concn of dilute HCl/M	Shaking time/min	Recovery/%
$\mathbf{1}_4^{4-}$	2	30	100.0
$\mathbf{1}_6^{6-}$	3	30	100.0
$\mathbf{1}_8^{8-}$	4	30	97.3
		60	99.0



Scheme 2. Molecular structures for extracted species, $\mathbf{1}_n(\mathrm{TMA^+})_n$ and $\mathbf{1}_n(\mathrm{TMA^+})_{n+j}$.

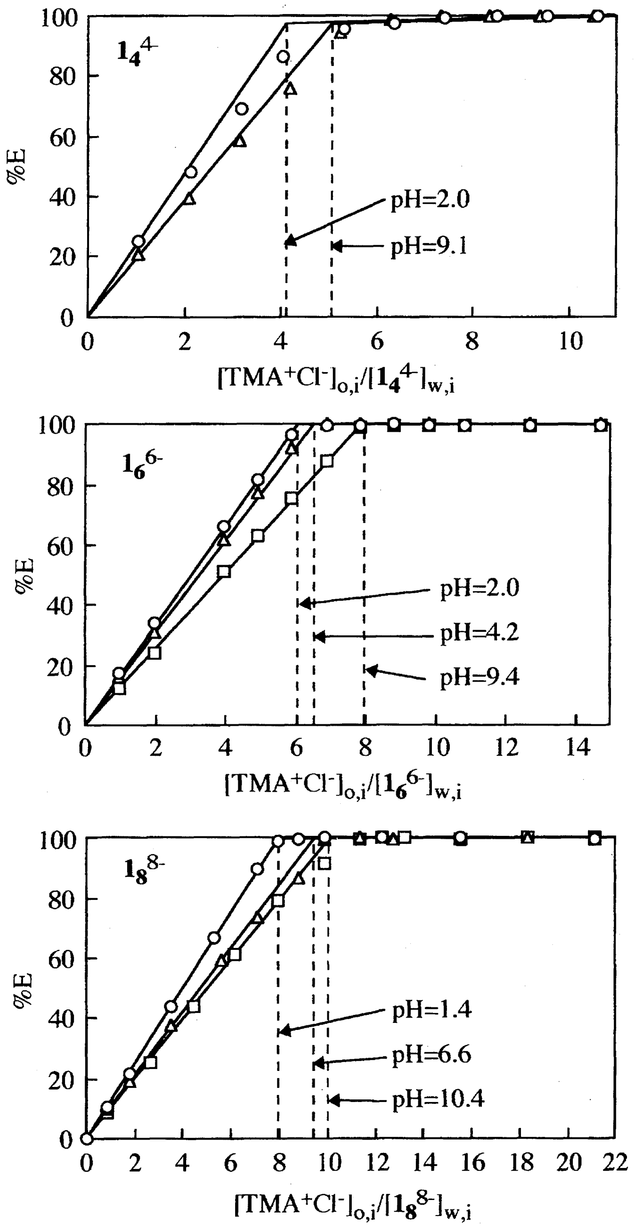


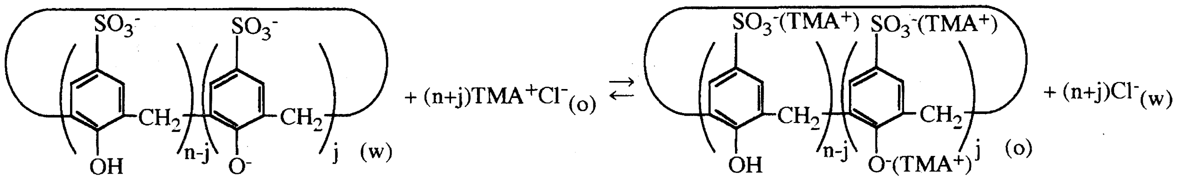
Fig. 3. Determination of binding ratio of $\mathbf{1}_n^{n-}$ with TMA$^+$ by the extraction-mole ratio method. $[\mathrm{Na_4}\mathbf{1}_4]_{\mathrm{w,i}} = 6.38\times10^{-4}$ M, ○: pH = 2.0, △: pH = 9.1. $[\mathrm{Na_6}\mathbf{1}_6]_{\mathrm{w,i}} = 6.98\times10^{-4}$ M, ○: pH = 2.0, △: pH = 4.2, □: pH = 9.4. $[\mathrm{Na_8}\mathbf{1}_8]_{\mathrm{w,i}} = 7.61\times10^{-4}$ M, ○: pH = 1.4, △: pH = 6.6, □: pH = 10.4.

In such solutions, $\mathbf{1}_n^{n-}$ will associate with *n* moles of TMA$^+$ at their sulfonato sites and form $\mathbf{1}_n(\mathrm{TMA^+})_n$. On the other hand, at higher pH values, where *j* moles of oxide groups are present in addition to n moles of sulfonato groups by protonic dissociation of hydroxy groups, $\mathbf{1}_n^{(n+j)-}$ will associate with (*n*+*j*) moles of TMA$^+$ and a complex, $\mathbf{1}_n(\mathrm{TMA^+})_{n+j}$, will be formed and extracted as shown in Scheme 3 and the following equation, respectively:

Table 5. Binding Ratio and Extraction Constants, K_{ex} a)

		Binding ratio				$\log K_{ex}$		
$\mathbf{1}_n^{n-}$	pH	Mole ratio	$n+j$ b)	$-(n+j)$ c)	Mean	From Eq. 9	From Eq. 10	Mean
$\mathbf{1}_4^{4-}$	2.0	4.1	3.89	3.72	3.81	7.12	7.16	7.14
	9.4	5.1	4.70	5.15	4.93	6.35	6.43	6.39
$\mathbf{1}_6^{6-}$	1.9	6.0	5.86	6.09	5.98	13.0	13.1	13.1
	9.4	8.0	8.23	7.85	8.04	12.8	12.6	12.7
$\mathbf{1}_8^{8-}$	1.4	8.0	7.70	8.09	7.90	20.8	20.1	20.5
	10.4	10.0	9.70	9.80	9.75	19.6	19.9	19.8

a) $K_{ex}=[\mathbf{1}_n(TMA^+)_{n+j}]_o\cdot[Cl^-]_w^{n+j}/[\mathbf{1}_n^{(n+j)-}]_w\cdot[TMA^+Cl^-]_o^{n+j}$. b) obtained from $\log D$ vs. $\log[TMA^+Cl^-]$ plots. c) obtained from $\log D$ vs. $\log[Cl^-]$ plots.



Scheme 3. Proposed extraction reaction of $\mathbf{1}_n^{(n+j)-}$ from an aqueous solution into chloroform with TMA^+Cl^-.

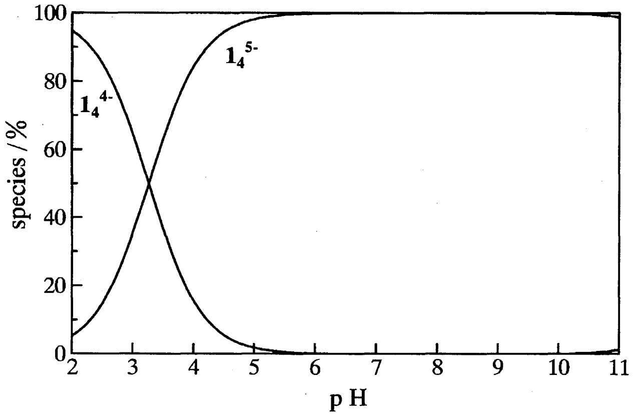


Fig. 4. Species concentration relative to total hydroxycalix[4]arene-*p*-sulfonate ion, $\mathbf{1}_4^{4-}$ as a function of pH. $\mu=0.1$, $t=25$ °C.

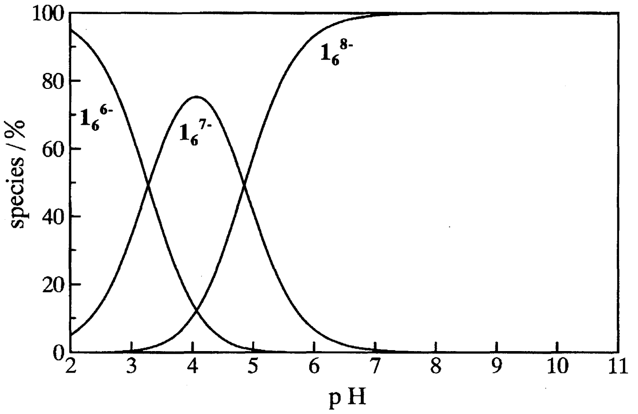


Fig. 5. Species concentration relative to total hydroxycalix[6]arene-*p*-sulfonate ion, $\mathbf{1}_6^{6-}$ as a function of pH. $\mu=0.1$, $t=25$ °C.

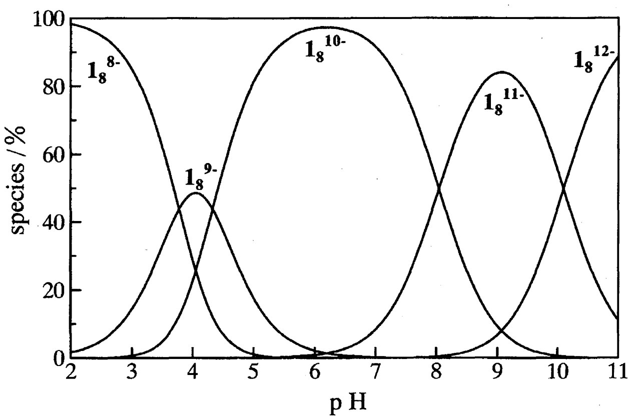


Fig. 6. Species concentration relative to total hydroxycalix[8]arene-*p*-sulfonate ion, $\mathbf{1}_8^{8-}$ as a function of pH. $\mu=0.1$, $t=25$ °C.

$$(\mathbf{1}_n^{(n+j)-})_w+(n+j)(TMA^+Cl^-)_o \rightleftharpoons \mathbf{1}_n(TMA^+)_{n+j,o}+(n+j)Cl^-_w. \quad (4)$$

The extraction constant for Eq. 4 is defined by

$$K_{ex}=[\mathbf{1}_n(TMA^+)_{n+j}]_o\cdot[Cl^-]_w^{n+j}/[\mathbf{1}_n^{(n+j)-}]_w\cdot[TMA^+Cl^-]_o^{n+j}. \quad (5)$$

The distribution ratio, D, of $\mathbf{1}_n^{n-}$ is given by

$$D=[\mathbf{1}_n(TMA^+)_{n+j}]_o/\alpha_{1n}[\mathbf{1}_n^{(n+j)-}]_w, \quad (6)$$

where α_{1n} is the side-reaction coefficient of $\mathbf{1}_n^{(n+j)-}$; the concentration ratio of the total ligand to $\mathbf{1}_n^{(n+j)-}$ in an aqueous solution and can be obtained from pK_a of $\mathbf{1}_n^{n-}$ and the pH of the solution. From Eqs. 5 and 6, we obtain

$$K_{ex}=D\cdot\alpha_{1n}[Cl^-]_w^{n+j}/[TMA^+Cl^-]_o^{n+j}. \quad (7)$$

Equation 7 can be written as

$$\log K_{ex}=\log D+\log\alpha_{1n}+(n+j)\log[Cl^-]_w$$
$$-(n+j)\log[TMA^+Cl^-]_o. \quad (8)$$

When pH and $[\mathrm{Cl}^-]_\mathrm{w}$ are constant, we obtain

$$\log D = (n+j)\log[\mathrm{TMA}^+\mathrm{Cl}^-]_\mathrm{o} + K_1, \tag{9}$$

where $K_1 = \log K_\mathrm{ex} - \log \alpha_{1n} - (n+j)\log[\mathrm{Cl}^-]_\mathrm{w}$ = constant. When pH and $[\mathrm{TMA}^+\mathrm{Cl}^-]_\mathrm{o}$ are constant, we obtain

$$\log D = -(n+j)\log[\mathrm{Cl}^-]_\mathrm{w} + K_2, \tag{10}$$

where $K_2 = \log K_\mathrm{ex} - \log \alpha_{1n} + (n+j)\log[\mathrm{TMA}^+\mathrm{Cl}^-]_\mathrm{o}$ = constant. From the plot of $\log D$ vs. $\log[\mathrm{TMA}^+\mathrm{Cl}^-]$ and $\log D$ vs. $\log[\mathrm{Cl}^-]$ we obtain values for $n+j$ and $-(n+j)$, respectively, as the binding ratio of $\mathbf{1}_n^{n-}$ and TMA$^+$ in the complex. The extraction constant, K_ex, can also be obtained from the values of K_1 and K_2.

As shown in Fig. 7(a), good linear relationships are obtained for $\log D$ vs. $\log[\mathrm{TMA}^+\mathrm{Cl}^-]_\mathrm{o,i}$ for $\mathbf{1}_8^{8-}$. Figure 7(b) also show good linear relationships for $\log D$ vs. $\log[\mathrm{Cl}^-]_\mathrm{w,i}$ plotted against $\mathbf{1}_8^{8-}$. Such good linear relationships were also obtained for $\mathbf{1}_4^{4-}$ and $\mathbf{1}_6^{6-}$; the values of the slopes are summarized in Table 5. These values agree well with those obtained by the mole-ratio method. The binding ratio of the $\mathbf{1}_8^{8-}$–TMA$^+$ complex extracted from an alkaline solution of pH 10.4 cannot be explained by the species-distribution curve

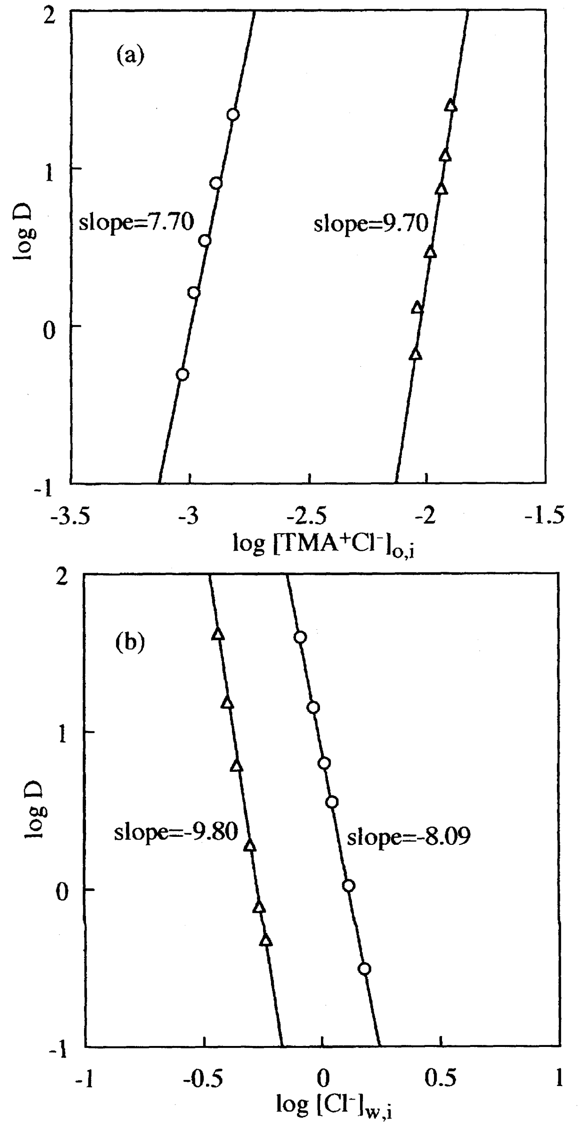


Fig. 7. Linear plots of $\log D$ as a function of $\log[\mathrm{TMA}^+\mathrm{Cl}^-]_\mathrm{o,i}$ (a) and $\log[\mathrm{Cl}^-]_\mathrm{w,i}$ (b) for $\mathbf{1}_8^{8-}$ extractions under $[\mathrm{Na}_8\mathbf{1}_8]_\mathrm{w,i} = 2.03\times10^{-4}$ M. (a) $[\mathrm{Cl}^-]_\mathrm{w,i} = 0.50$ M, ○: pH = 1.4, △: pH = 10.4, (b) $[\mathrm{TMA}^+\mathrm{Cl}^-]_\mathrm{o,i} = 4.01\times10^{-3}$ M, ○: pH = 1.4, $[\mathrm{TMA}^+\mathrm{Cl}^-]_\mathrm{o,i} = 0.0103$ M, △: pH = 9.4.

Table 6. Percent Extraction, %*E* of Several Metal Ions from the Aqueous Solutions into Chloroform with $\mathbf{1}_4^{4-}$ and TMA$^+$Cl$^-$ a)

	%*E*			
Metal ions	pH 5.0	pH 7.0	pH9.0	pH 11.0
Mg^{2+}	0	0	0	0
Al^{3+}	0	0	0	0
Ca^{2+}	0	0	0	0
Sc^{3+}	0	0	17.2	53.5
Ti^{4+}	36.2	38.5	45.5	47.3
Cr^{3+}	0	0	0	0
Mn^{2+}	0	45.0	98.2	99.5
Fe^{3+}	0	0	0	0
Co^{2+}	0	0	12.0	9.5
Ni^{2+}	0	0	0	0
Cu^{2+}	0	0	1.5	3.3
Zn^{2+}	0	0	0	0
Zr^{4+}	0	0	0	0
Ce^{3+}	0	6.0	66.2	93.5
Hf^{4+}	0	0	0	0
$\mathrm{UO_2}^{2+}$	0	0	0	0

a) $[\mathrm{TMA}^+\mathrm{Cl}^-] = 0.01$ M, volume of chloroform = 15 ml, $[\text{metal ion}]_\mathrm{w,i} = 2.0\times10^{-4}$ M, $[\mathrm{Na}_4\mathbf{1}_4]_\mathrm{w,i} = 1.0\times10^{-3}$ M, volume of $\mathrm{H_2O}$ = 15 ml.

Table 7. Percent Extraction, %*E* of Ln^{3+} from the Aqueous Mixture Solution into Chloroform with $\mathbf{1}_4^{4-}$ and TMA$^+$Cl$^-$ a)

	%*E*		
Ln^{3+}	pH 5.5	pH 9.2	pH 11.7
Y^{3+}	0	2.73	53.5
La^{3+}	0	0	36.2
Ce^{3+}	1.40	46.3	83.6
Pr^{3+}	0	0.99	41.5
Nd^{3+}	0	0.37	43.1
Sm^{3+}	0	0.94	48.0
Eu^{3+}	0	0.25	49.1
Gd^{3+}	0	0.11	48.5
Tb^{3+}	0	0	46.1
Dy^{3+}	0	1.37	53.0
Ho^{3+}	0	1.94	53.1
Er^{3+}	0	2.37	53.4
Tm^{3+}	0	3.04	53.8
Yb^{3+}	0	2.00	51.8
Lu^{3+}	0	1.68	51.2

a) $[\mathrm{TMA}^+\mathrm{Cl}^-] = 0.02$ M, volume of chloroform = 15 ml, $[\mathrm{Ln}^{3+}_\mathrm{total}]_\mathrm{w,i} = 4.0\times10^{-4}$ M, $[\mathrm{Na}_4\mathbf{1}_4]_\mathrm{w,i} = 2.0\times10^{-3}$ M, volume of $\mathrm{H_2O}$ = 15 ml.

for $\mathbf{1}_8^{8-}$ shown in Fig. 6. In this case, the sodium ion may be extracted, covering the deficiency of TMA$^+$. The values for the extraction constant, K_{ex}, are also given in Table 5.

Extraction of Metal Ions by the $\mathbf{1}_4$–TMA$^+$ System. As shown above, the extraction of $Na_n\mathbf{1}_n$ with TMA$^+$Cl$^-$ was caused by the formation of the ionic associate, mainly at its sulfonato groups of $\mathbf{1}_n^{n-}$ with TMA$^+$, and the species extracted retained their hydroxyl groups, –OH, which can combine with metal ions. This suggests that metal chelates of $\mathbf{1}_n^{n-}$ can also be extractable with TMA$^+$ into chloroform.[15] We thus examined the solvent extraction of metal ions from an aqueous phase at various pH values using $Na_4\mathbf{1}_4$ and TMA$^+$Cl$^-$ dissolved in chloroform.

The extraction results are summarized in Tables 6 and 7. Table 6 indicates that metal ions, such as Mn^{2+}, Ce^{3+}, Sc^{3+}, Ti^{4+}, Co^{2+}, Cu^{2+}, are extractable and that the values of %E increase with a rise in pH. The order of %E is $Mn^{2+} > Ce^{3+} > Sc^{3+} > Ti^{4+} \gg Co^{2+} > Cu^{2+}$ at pH 11. The extractability of Mn^{2+} was the largest of these metal ions, and was quantitatively extracted at pH$>$8. No extraction occurred to Mg^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Zr^{4+}, Hf^{4+} or UO_2^{2+}.

Table 7 shows that the values of %E for rare earth metal ions, Ln^{3+}, are also small in acidic solution; however, they increases with rising pH in an alkaline solution and every Ln^{3+} is partly extractable at pH 11.7. Although, Ce^{3+} was extracted at an exceptionally low pH of 5.5 and a half of it was extracted at about pH 9.0, the value of %E seems to be increased in the order of the atomic number, except Y^{3+} and Ce^{3+}, i.e., in the order of the overall stability constants of $\mathbf{1}_4^{4-}$–Ln^{3+} complexes.[6] It is well known that the magnitude of the stabilities of Y^{3+} complexes is usually positioned between those for Ho^{3+} and Tm^{3+} complexes.[16] Both Mn^{2+} and Ce^{3+}, which were extractable at low pH with high %E, formed colored complexes with $\mathbf{1}_4^{4-}$.[6,17] This may be caused by the oxidation of metal ions in the complexes from lower to higher valency and the formation of more stable $\mathbf{1}_4^{4-}$-high-oxidation-number metal-ion complexes.

These facts suggest that $\mathbf{1}_4^{4-}$ is a peculiar extraction reagent for some metal ions. It has also been reported that $\mathbf{1}_6^{6-}$ is a super uranophile.[8] This indicates the possibility of $\mathbf{1}_6^{6-}$ taking place in a unique solvent extraction for some metal ions, including UO_2^{2+}. The present solvent-extraction system of $\mathbf{1}_n^{n-}$ with TMA$^+$, therefore, must be applicable to the concentration, separation and purification of metal ions by solvent extraction.

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