# Solvent Extraction of Water-Soluble Calixarenes and Their Metal Complexes with Trioctylmethylammonium Chloride

Masashi Nishida, Miwako Sonoda, Daido Ishii, and Isao Yoshida*
*Department of Industrial Chemistry, Kumamoto Institute of Technology, Ikeda-4, Kumamoto 860*

(Received December 17, 1997; CL-970951)

Water-soluble hydroxycalix[n]arene-p-sulfonates, $\mathbf{1}_n^{n-}$ (n=4,6 and 8) in an aqueous solution were extracted efficiently with trioctylmethylammonium chloride(capriquat), $TMA^+Cl^-$, into chloroform in the presence and absence of $Mn^{2+}$. The extracted species for $\mathbf{1}_4^{4-}$ was estimated to be the ionic associates, such as $\mathbf{1}_4(TMA)_4$ at pH 4.6 and $\mathbf{1}_4(TMA)_5$ at pH 9.1. By the present $\mathbf{1}_4^{4-}$ - $TMA^+$ extraction system, $Mn^{2+}$ was separated from $Mg^{2+}$, $Al^{3+}$, $Ca^{2+}$, $Sc^{3+}$, $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Zr^{4+}$, $Ln^{3+}$(except $Ce^{3+}$), $Hf^{4+}$ and $UO_2^{2+}$ at pH 8.0.

---

By introducing sulfonic acid groups to the p-position of the hydroxyl groups in hydroxycalix[n]arenes, Shinkai et al. first synthesized some water-soluble calix[n]arenes such as sodiumhydroxycalix[n]arene-p-sulfonates($Na_n\mathbf{1}_n$ ; n=4, 6, and 8) in 1986.[1-3] At the same time they,[3] and later we[4] and other researchers[5,6] studied the acid dissociation properties of $\mathbf{1}_n^{n-}$ and found that the presence of sulfonate groups markedly increases the acidity of the hydroxyl groups in $\mathbf{1}_n^{n-}$ to cause acid dissociation to take place even in an acidic solution. We also found that the increase in the acidity of hydroxyl groups leads $\mathbf{1}_n^{n-}$ to a specific metal ligand having a peculiar macrocyclic structure where phenolate groups can coordinate to a metal ion even in the acidic solution.[7] Recently, it was also found that $\mathbf{1}_n^{n-}$ can form a variety of host-guest type complexes with various organic guests in water.[1,8,9] During a study on the host-guest type complexes concerning $\mathbf{1}_n^{n-}$ with alkylammonium ions, we observed the fact that $\mathbf{1}_n^{n-}$ forms precipitates with alkylammonium ions and the precipitates are soluble in organic solvents.[10]

Since it can be expected that the associate of $\mathbf{1}_n^{n-}$ at its sulfonate groups with alkylammonium ion in chloroform is able to coordinate to some specific metal ion as a peculiar metal ligand using their hydroxyl groups, $\mathbf{1}_n^{n-}$ in the organic phase must be a specific extraction reagent when the appropriate alkylammonium ion is present. In the present study, thus, we carried out the extractions of $\mathbf{1}_n^{n-}$ and $Mn^{2+}$-$\mathbf{1}_4^{4-}$ complex in the presence of capriquat($TMA^+Cl^-$) in order to construct a new extraction system for the determination and separation of metal ions.

$Na_n\mathbf{1}_n$ was obtained from Sugai Kagaku Co.(Wakayama Japan) and used after recrystallization from a methanol-water mixture. After dissolving it in water to make a 0.01 M ( M=mol $dm^{-3}$) stock solution, the concentration was standardized by the pH titration method using a standard 0.1 M NaOH. Capriquat was obtained from Dojindo Laboratories Co.(Kumamoto Japan), dissolved in chloroform, and its concentration was determined by the titration method with a standard sodium tetraphenylborate solution.

Into a 50 mL glass-stoppered tube, 15 mL of $Na_n\mathbf{1}_n$ aqueous and $TMA^+Cl^-$ chloroform solutions were taken, then the mixture was shaken for 10 min at 400 strokes per min at about 25 °C. The extractability was not affected by the further shaking, which indicates that equilibrium had been attained within 10 min. Then the tube was centrifuged for 3 min at 2000 rpm to separate both phases. An aliquot of the aqueous phase was taken, diluted and made up to pH 9.0 sample solution to measure the absorbance at 270 nm due to $\mathbf{1}_n^{n-}$ before($A_i$) and after($A_e$) extraction. The percent extraction, %E, was calculated according to $\%E=\{(A_i-A_e)/A_i\}x\ 100$.

The extraction of $Mn^{2+}$ from the aqueous $Na_4\mathbf{1}_4$ solution was carried out by the similar manner as above. $Mn^{2+}$ in the chloroform phase was back extracted with 2 M HCl. The back-extracted $Mn^{2+}$ was diluted, and the amount of $Mn^{2+}$ was determined by inductively coupled plasma atomic emission spectrophotometry(ICP-AES). The value of %E for $Mn^{2+}$ was calculated according to $\%E=(Mn_{(o)}/Mn_{(t)})x\ 100$, where $Mn_{(o)}$ is the amount of $Mn^{2+}$ in chloroform and $Mn_{(t)}$ is the amount of $Mn^{2+}$ added initially to the aqueous phase.

**Table 1.** Percent extraction (%E) of $\mathbf{1}_n^{n-}$ from the aqueous solution into chloroform with Capriquat ($TMA^+Cl^-$)[a]

| $\mathbf{1}_n^{n-}$ | pH | $\mathbf{1}_n^{n-}$ in aq. phase/ μ mol<br>before ext. | <br>after ext. | %E |
|---|---|---|---|---|
| $\mathbf{1}_4^{+}$ | 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[c] |
| PS[b] | 4.67 | 15.0 | 3.08 | 79.5 |
| | 9.15 | | 2.18 | 85.5 |

[a] $[TMA^+Cl^-]_{o,i}$=0.01 M, volume of chloroform=15 mL, $[Na_n\mathbf{1}_n]_i$=0.001 M, volume of $H_2O$=15 mL, temperture =about 25 ℃. [b] PS=p-phenolsulfonate ion. [c] Smaller value of %E is explained by the shortage of $TMA^+Cl^-$.

Table 1 shows the results of extraction of $\mathbf{1}_n^{n-}$. It was demonstrated that $\mathbf{1}_n^{n-}$(n=4,6,and 8) in the aqueous solution are extracted almost quantitatively both in the acidic and alkaline solutions. These results are in marked contrast to the fact that only a part of p-phenolsulfonic acid(PS) which is a monomer of $\mathbf{1}_n^{n-}$ could be extracted under the same conditions. This suggests that $\mathbf{1}_n^{n-}$ having a cyclic structure can form a spherical associate with $TMA^+$ resulting in an association complex with larger hydrophobicity than that for the monomeric linear complex, PS-$TMA^+$.

Figure 1 shows pH dependency of %E for $\mathbf{1}_4^{4-}$. No extraction of $\mathbf{1}_4^{4-}$ was observed at pH<-0.3(pH=-log[$H^+$] at pH<2). At pH=-0.2, the extraction became observable and the value of %E increased with increases in pH up to pH=1.5. At pH>1.5, the extraction of $\mathbf{1}_4^{4-}$ was complete. This pH dependency of the extraction of $\mathbf{1}_4^{4-}$ corroborates that $\mathbf{1}_4^{4-}$ in the aqueous solution forms an ionic associate with $TMA^+$ at

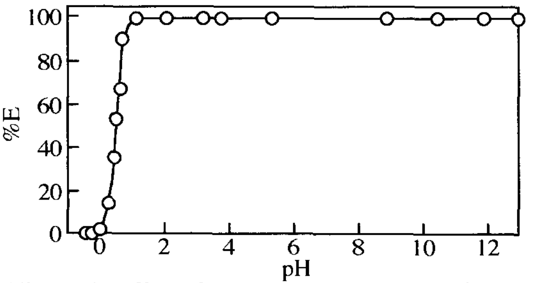


**Figure 1.** Effect of pH on the extraction of $\mathbf{1}_4^{4-}$ with Capriquat ($TMA^+Cl^-$) at about 25 ℃. $[Na_4\mathbf{1}_4]=1.05\times10^{-3}$ M, $[TMA^+Cl^-]=9.98\times10^{-3}$ M.

its sulfonate groups, then the associate transfers into chloroform as given in equation (1).

$$H(SO_3H)_4 + 4(TMA^+Cl^-)_o \rightleftharpoons H(SO_3TMA)_{4,o} + 4HCl \quad (1)$$

where H stands for $\mathbf{1}_4^{4-}$ other than its sulfonate groups and o denotes the species in the organic phase.

By back extraction using 2 M HCl, $\mathbf{1}_4^{4-}$ was recovered quantitatively into an aqueous phase from the chloroform phase.

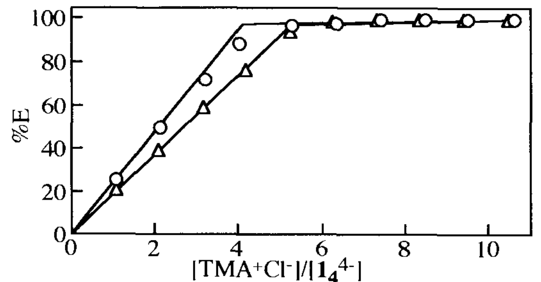
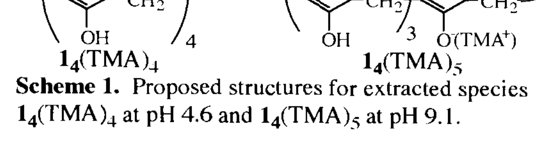


**Figure 2.** Determination of binding ratio of $\mathbf{1}_4^{4-}$ with $TMA^+$ by molar ratio method. $[Na_4\mathbf{1}_4]=6.38\times10^{-4}$ M, (○):pH=4.6, (△):pH=9.1.

Figure 2 indicates $TMA^+Cl^-$ concentration dependency of %E for $\mathbf{1}_4^{4-}$ at pH 4.6 (○). It is shown that %E increased up to 100 % with increases in the ratio of initial concentration, R, where R is $[TMA^+Cl^-]_{o,i}/[\mathbf{1}_4^{4-}]_i$ where i denotes the initial concentration. At R=4.0, the complete extraction was attained. This indicates that the association ratio of $\mathbf{1}_4^{4-}$ to $TMA^+$ is 1:4. In contrast, at pH 9.1, the value for %E increased with increases in R up to 5 and became 100 % as shown in Figure 2(△). This indicates that, at pH 9.1, the association ratio of $\mathbf{1}_4^{4-}$ to $TMA^+$ is 1:5. This is explained by the fact that the tetrasulfonate ion, $\mathbf{1}_4^{4-}$, in a weakly acidic solution such as pH 4.6, dissociates a hydroxyl proton and becomes tetrasulfonate + monophenolate ion, $\mathbf{1}_4^{5-}$ at pH 9.1,[2] then the resultant penta anion associates with $TMA^+$ to form penta alkylammonium salt, $\mathbf{1}_4(TMA)_5$. The proposed structures for these association complexes are shown in Scheme 1.



**Scheme 1.** Proposed structures for extracted species $\mathbf{1}_4(TMA)_4$ at pH 4.6 and $\mathbf{1}_4(TMA)_5$ at pH 9.1.

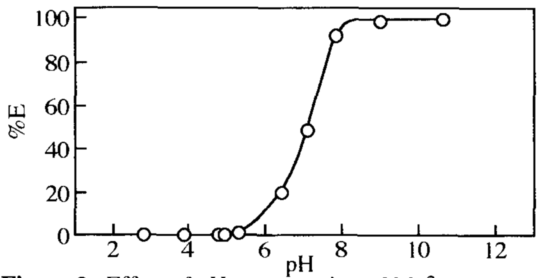


**Figure 3.** Effect of pH on extraction of $Mn^{2+}$ at about 25 ℃ $[Mn^{2+}]=2.06\times10^{-4}$ M, $[Na_4\mathbf{1}_4]=1.05\times10^{-3}$ M, $[TMA^+Cl^-]=9.98\times10^{-3}$ M.

Then, $Mn^{2+}$ in the aqueous solution containing $Na_4\mathbf{1}_4$ was extracted selectively from other metal ions into the $TMA^+Cl^-$ chloroform solution. The effect of pH upon extraction of $Mn^{2+}$ is given in Figure 3. The extraction of $Mn^{2+}$ starts at pH 5.5. At pH>5.5, the value of %E increases with an increase in pH up to pH 8.0 and then becomes 100%. The absorption spectrum of chloroform phase, which is reddish purple, was very similar to that[11] of the aqueous phase. This means that the $Mn^{2+}$-$\mathbf{1}_4^{4-}$ complex in the aqueous phase moves into chloroform keeping its structure in the aqueous phase. Almost no other metal ions could be extracted under similar conditions. Only two metal ions, $Ce^{3+}$ and $Ti^{4+}$ were partly extracted at pH 8.0 in the 27 kinds metal ions investigated. At pH 10, $Ln^{3+}$ and $Sc^{3+}$ were also partly extracted. The equilibrium extraction of $Mn^{2+}$ was attained in 10 min. These facts suggest that water-soluble calix[n]arenes which can work as very peculiar metal ligands as shown in our previous papers[7,11,12,13] are applicable to the selective solvent extraction of certain metal ions using an appropriate alkylammonium salt, such as capriquat, for highly efficient separation and analytical determination of metal ions.

## References

1 S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki, and O. Manabe, *J. Am. Chem. Soc.*, **108**, 2409(1986).

2 S. Shinkai, S. Mori, T. Tsubaki, T. Sone, and O. Manabe, *Tetrahedron Lett.*, **25**, 5315(1984).

3 S. Shinkai, K. Araki, H. Koreishi, T. Tsubaki, and O. Manabe, *Chem Lett.*, **1986**, 1351.

4 I. Yoshdia, N. Yamamoto, F. Sagara, D. Ishii, K. Ueno, and S. Shinkai, *Bull. Chem. Soc. Jpn.*, **65**, 1012(1992).

5 J.P.Scharff, M. Mahjoubi, and R. Perrin, *New J. Chem.*, **15**, 883(1991).

6 G. Arena, R. Cali, G. Giuseppelombardo, E. Rizzarelli, D. Sciotto, R. Ungaro, and A. Casnati, *Supramolecular Chem.*, **1**, 19(1992).

7 I. Yoshida, N. Yamamoto, F. Sagara, K. Ueno, D. Ishii, and S. Shinkai, *Chem. Lett.*, **1991**, 2105.

8 S. Shinkai, K. Araki, and O. Manabe, *J. Am. Chem. Soc.*, **110**, 7214 (1988).

9 S. Shinkai, K. Araki, M. Kubota, T. Arimura, and T. Matuda, *J. Org. Chem.*, **56**, 295(1991).

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

11 N. Yamamoto, M. Nishida, I. Yoshida, F. Sagara, K. Ueno, D. Ishii, and S. Shinkai, *Bunseki Kagaku*, **43**, 45 (1994).

12 I. Yoshida, K. Koyabu, M. Nishida, F. Sagara, D. Ishii, and S. Shinkai, *Anal. Sci.*, **10**, 353(1994).

13 M. Nishida, I. Yoshida, F. Sagara, D. Ishii, and S. Shinkai, *Bunseki Kagaku*, **43**, 295(1994).