Super Uranophiles: Application to Highly Effective Solvent Extraction of Uranyl Ion in the Presence of Methyltrioctylammonium Chloride

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By using hydroxycalix[n]arene-*p*-sulfonates, $H_j\mathbf{1}_n^{n-}$(n=6 and 8) known as super uranophiles, uranyl ion, UO_2^{2+}, in aqueous solution was efficiently extracted by chloroform in the presence of methyltrioctylammonium chloride, MTA^+Cl^-. The extracted species were found to be the ionic associates, $[(UO_2^{2+})(\mathbf{1}_6^{8-})(H^+)_{-3}](MTA^+)_9$ and $[(UO_2^{2+})_2(\mathbf{1}_8^{12-})(H^+)_{-3}](MTA^+)_{11}$.

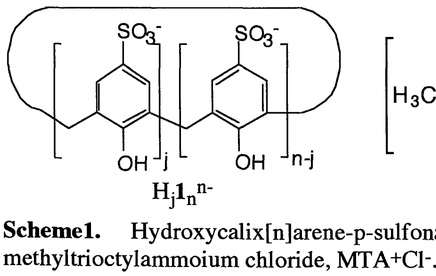
Of a series of hydroxycalix[n]arene-*p*-sulfonates, $H_j\mathbf{1}_n^{n-}$, hydroxycalix[6]arene-*p*-sulfonate ion, $H_2\mathbf{1}_6^{6-}$, has been reported to be a super uranophile,[1,2] i.e., a reagent with an extra high selective reactivity for uranyl ion, UO_2^{2+}. Recently we found that the octamer homologue, $H_4\mathbf{1}_8^{8-}$ is another uranophile,[3,4] having higher stability and selectivity for UO_2^{2+} than $H_2\mathbf{1}_6^{6-}$, and that $H_j\mathbf{1}_n^{n-}$(n=4,8; j=n/2, n=6; j=2) functions as a metal ligand because of its hydroxyl groups arranged on the lower rim of the macrocyclic molecule. It can be extracted with a lipophilic ammonium ion, such as MTA^+ by chloroform through formation of ionic associations with (n+i) moles of MTA^+ for n moles of sulfonate groups, and i moles of de-protonated hydroxyl groups, according to Eq.1. The value i varies with pH in the range of the value j.[5]

$$H_j\mathbf{1}_n{}^{n-}{}_w + (n+i)MTA^+Cl^-{}_o \rightleftarrows H_{j-i}\mathbf{1}_n(MTA)_{n+io} + n\,Cl^-{}_w + i\,HCl_w \quad (i\leqq j) \qquad (1)$$

In Eq.1, w and o denote aqueous and organic phases, respectively.

It is expected that the ionic associate in chloroform can still coordinate with a specific metal ion using its associating and remaining hydroxyl groups. To construct a new extraction system for the determination and separation of metal ions, we previously applied this system to the solvent extraction of Mn^{2+}, and found that $H_2\mathbf{1}_4^{4-}$ can extract Mn^{2+} selectively in the presence of foreign metal ions.[6,7] In the present study, we applied this system to the solvent extraction of UO_2^{2+} using super uranophiles.

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



Scheme1. Hydroxycalix[n]arene-p-sulfonate ions, $H_j\mathbf{1}_n^{n-}$ and methyltrioctylammoium chloride, MTA^+Cl^-.

In a 50 mL glass-stoppered tube, 15 mL of $Na_nH_j\mathbf{1}_n$, UO_2^{2+} and sodium carbonate aqueous mixture solution were mixed. After 15 mL of MTA^+Cl^- chloroform solution was added, the mixture was shaken for 10 min at 400 strokes per min at about 25 ℃. The extraction was not affected by 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 to measure UO_2^{2+} by the Arsenazo-III absorption method.[8] UO_2^{2+} in the chloroform phase was back extracted with 2M H_2SO_4 and determined as above. The percent extraction (%E) was calculated by the equation $\%E=\{([UO_2^{2+}]_{w,i}-[UO_2^{2+}]_{w,e})/[UO_2^{2+}]_{w,i}\}\times 100$, where $[UO_2^{2+}]_{w,i}$ and $[UO_2^{2+}]_{w,e}$ are the initial and equilibrium concentrations of UO_2^{2+} in the aqueous phase.

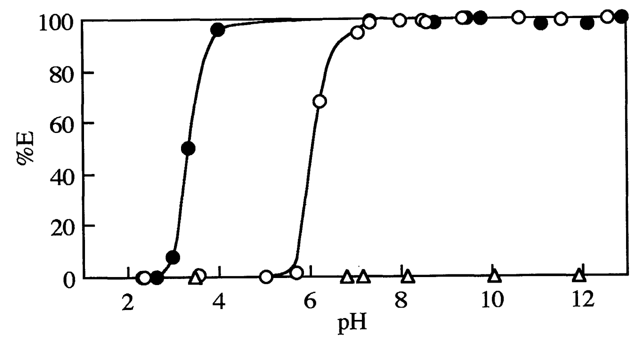


Figure 1. Effect of pH on the extraction of UO_2^{2+} with $H_j\mathbf{1}_n^{n-}$ at about 25 ℃. △:$H_2\mathbf{1}_4^{4-}$, ○:$H_2\mathbf{1}_6^{6-}$, ●:$H_4\mathbf{1}_8^{8-}$, $[UO_2^{2+}]_{w,i}$= 2.01×10^{-4} M, $[H_j\mathbf{1}_n^{n-}]_{w,i}$=1.09×$10^{-3}$ M, $[Na_2CO_3]_{w,i}$=2.0×10^{-3} M, $[MTA^+Cl^-]_{o,i}$=1.0×10^{-2} M(for $H_2\mathbf{1}_4^{4-}$ and $H_2\mathbf{1}_6^{6-}$ extractions), 1.5×10^{-2} M(for $H_4\mathbf{1}_8^{8-}$ extractions), volume of aqueous and organic phases = 15 mL each.

Figure 1 shows %E for the extractions with $H_j\mathbf{1}_n^{n-}$ as a function of pH. No extraction of UO_2^{2+} was observed with $H_2\mathbf{1}_4^{4-}$(△). This result should be due to the weak reactivity of $H_2\mathbf{1}_4^{4-}$ with UO_2^{2+}.[4] On the other hand, the extraction by $H_2\mathbf{1}_6^{6-}$(○) starts at pH 5.5 and the value of %E increases quickly with an increase in pH, to reach 100% at pH=7. This extraction curve seems to follow that for the complex formation of $H_2\mathbf{1}_6^{6-}$ with UO_2^{2+}.[4] The extraction of UO_2^{2+} by $H_4\mathbf{1}_8^{8-}$(●) starts at pH lower than 2.5 and reaches 100% at pH 4.0. The extraction curve also resembles that for the formation of UO_2^{2+} - $H_4\mathbf{1}_8^{8-}$ complexes.[3]

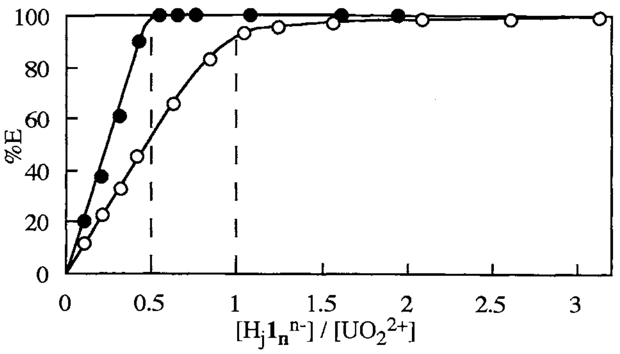


Figure 2. Effect of $H_j\mathbf{1}_n^{n-}$ concentration on the extraction of UO_2^{2+} at about 25 ℃. ○:$H_2\mathbf{1}_6^{6-}$, ●:$H_4\mathbf{1}_8^{8-}$, $[UO_2^{2+}]_{w,i}$= 2.51×10-4 M, $[MTA^+Cl^-]_{o,i}$=1.0×10-2 M and pH=9.4 for $H_2\mathbf{1}_6^{6-}$ extractions, $[MTA^+Cl^-]_{o,i}$=1.5×10-2 M and pH=8.8 for $H_4\mathbf{1}_8^{8-}$ extractions, volume of aqueous and organic phases = 15 mL each.

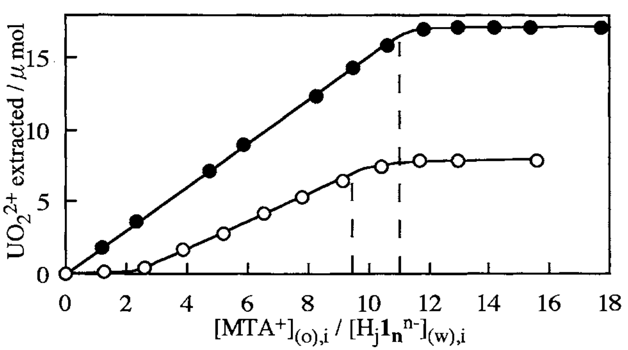


Figure 3. Effect of MTA^+ concentration on the extraction of UO_2^{2+} at about 25 ℃. ○:$H_2\mathbf{1}_6^{6-}$, ●:$H_4\mathbf{1}_8^{8-}$, $[UO_2^{2+}]_{w,i}$= 7.73×10-4 M, $[H_2\mathbf{1}_6^{6-}]_{W,i}$=5.20×10-4 M, pH=9.4 for $H_2\mathbf{1}_6^{6-}$ extractions, $[UO_2^{2+}]_{w,i}$=1.27×10-3 M, $[H_4\mathbf{1}_8^{8-},]_{W,i}$=5.72×10-4 M, pH=8.7 for $H_4\mathbf{1}_8^{8-}$ extractions, volume of aqueous and organic phases = 15 mL each.

To study the composition of the extracted species, the extractions of UO_2^{2+} were performed by changing the concentrations of $H_j\mathbf{1}_n^{n-}$ and MTA^+Cl^-. Figure 2 indicates changes in %E for the extraction by $H_2\mathbf{1}_6^{6-}$ (○) and by $H_4\mathbf{1}_8^{8-}$ (●) as a function of the initial concentration ratio, $[H_j\mathbf{1}_n^{n-}]_{w,i}/[UO_2^{2+}]_{w,i}$. There are clear abrupt changes at 1.0 in the extraction curve for $H_2\mathbf{1}_6^{6-}$ and at 0.50 for $H_4\mathbf{1}_8^{8-}$, respectively. It is obvious, thus, that UO_2^{2+} is extracted by chloroform through formation of 1:1 complex with $H_2\mathbf{1}_6^{6-}$, but 2:1 complex with $H_4\mathbf{1}_8^{8-}$. Figure 3 shows the amount of UO_2^{2+} extracted as a function of the initial concentration of TMA^+ in terms of $[TMA^+]_{o,i}/[H_j\mathbf{1}_n^{n-}]_{w,i}$. Clear abrupt changes in slope can also been seen at 9 for $H_2\mathbf{1}_6^{6-}$(○) and 11.0 for $H_4\mathbf{1}_8^{8-}$(●). These curves show that 9 and 11 moles of TMA^+ are used for the extraction of each complex.

We reported[3,4] that the compositions of the main uranyl complexes of super uranophiles are 1:1 for $H_2\mathbf{1}_6^{6-}$, $[(UO_2^{2+})(\mathbf{1}_6^{8-})(H^+)_{-3}]^{9-}$ and 2:1 for $H_4\mathbf{1}_8^{8-}$, $[(UO_2^{2+})_2(\mathbf{1}_8^{12-})(H^+)_{-3}]^{11-}$. From the compositions of the extracted species, it can also be concluded that UO_2^{2+} forms water-soluble 1:1 and 2:1 complex anions with the above super-uranophiles, respectively, then the resultant complexes associate with 9 and 11 moles of MTA^+ and are dissolved in chloroform as shown in Eqs.2 and 3.

$$UO_2^{2+}{}_w + H_2\mathbf{1}_6^{6-}{}_w + 9TMA^+Cl^-_o \rightleftarrows [(UO_2^{2+})(\mathbf{1}_6^{8-})(H^+)_{-3}](MTA^+)_{9,o} + 5HCl_w + 4Cl^-_w \tag{2}$$

$$2UO_2^{2+}{}_w + H_4\mathbf{1}_8^{8-}{}_w + 11TMA^+Cl^-_o \rightleftarrows [(UO_2^{2+})_2(\mathbf{1}_8^{12-})(H^+)_{-3}](MTA^+)_{11,o} + 7HCl_w + 4Cl^-_w \tag{3}$$

Since complex formation of UO_2^{2+} with super uranophiles is highly selective,[1,4] it is expected that the proposed extraction system can selectively extract UO_2^{2+}.

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