Template Adsorbent Composed of Particles Impregnated with Pre-organized Ligand through Its Metal Complexes: Uranyl Ion-Selective Adsorbents

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The development of functional materials which react selectively with a target metal ion or molecule is an important theme in the field of separation chemistry. Water-soluble hydroxycalix[6]arene-*p*-sulfonate ion, $H_2L_6^{6-}$ (1_n , $n = 6$, H_2 means that the ligand is a di-protonic acid) and its *O*-carboxymethyl derivative were shown to be functional materials for UO_2^{2+} , that is, they are superuranophiles both in selective reactivity and high stability of the complex.^{1,2} In the present study, the UO_2^{2+} -selective adsorbent was composed of a non-polar organic resin, XAD-7, and silica-gel particles loaded with an ionic associate of another superuranophile,^{3,4} $H_4L_8^{8-}$ (1_n , $n = 8$, Fig. 1) and methyltriocetylammmonium ion, MTA^+ , (MTA^+)₁₁ (HL_8^{11-}). They were prepared by first impregnating the MTA^+ associate of a UO_2^{2+} - $H_4L_8^{8-}$ complex,⁵ then stripping UO_2^{2+} using 0.5 M (1 M = 1 mol L⁻¹) sulfuric acid. It was found that they have an evident template effect in the adsorption of UO_2^{2+} , in comparison with those loaded with a $H_4L_8^{8-}$ - MTA^+ associate prepared in the absence of UO_2^{2+} and in the presence of Ti^{4+} .

Forty milliliters of a mixture solution containing 1.0 mmol of $Na_8H_4L_8$ and 2.0 mmol of $UO_2(NO_3)_2$ were taken into a 100 mL separating funnel. Then, 40 mL of a chloroform solution containing 12 mmol of MTA^+Cl^- was added to the funnel. By shaking at 200 strokes/min for 10 min, the MTA^+ associate with a UO_2^{2+} - $H_4L_8^{8-}$ complex, (MTA^+)₁₁(UO_2)₂ ($H_3L_8^{15-}$), was extracted at pH 8.0.⁶ After separating the chloroform phase, 10 g of Amberlite XAD-7 (R) or 30 g of silica gel (S, Wako gel-C100) particles was added. Chloroform was then evaporated off by heating at 40°C. Another complex-type adsorbent, having particles loaded with an MTA^+ associate of Ti^{4+} - $H_4L_8^{8-}$ complex was also prepared by similar procedures in the presence of Ti^{4+} at pH 3.0, instead of UO_2^{2+} . The ligand-type adsorbents, in which an MTA^+ associate of $H_4L_8^{8-}$, (MTA^+)₁₁ (HL_8^{11-}),⁷ is loaded on the particles, (L)MTAL8-R and (L)MTAL8-S, were prepared using similar procedures in the absence of metal ions. The complex-type adsorbents were packed into a glass column of 1.5 cm i.d. and treated with 200

mL of 0.5 M (for UO_2^{2+}) or 2.5 M sulfuric acid (for Ti^{4+}) in order to remove metal ions. After washing the column with 100 mL of deionized water, the particles were air-dried, and used as complex-type adsorbents: (U)MTAL8-R, (U)MTAL8-S, (Ti)MTAL8-R and (Ti)MTAL8-S.

The extent of impregnation was measured by gravimetry after recovering the associate with chloroform and then evaporating. A part of the eluate was taken in a separation funnel and back extracted with 2 M hydrochloric acid. The amount of the ligand was measured by spectrophotometry at 289 nm in an aqueous solution of pH 13.0.⁶

The adsorption of UO_2^{2+} by the batch-wise method was carried out as follows. Into a 50 mL Erlenmeyer flask, 0.1 g (XAD-7) or 0.3 g (silica gel) of adsorbent was taken; then, 25 mL of the UO_2^{2+} solution containing sodium hydrogen carbonate of a desired pH was added. The reaction was performed for a given time under mild and occasional mixing; then, an aliquot of the aqueous phase was taken, and its UO_2^{2+} concentration, C , was determined by the Arsenazo-III method.⁸ The adsorption capacity, Q , was calculated according to $Q = (C_0 - C) \times 25/w$ mmol g⁻¹, where w and C_0 denote the weight of the adsorbent used and the initial concentration of UO_2^{2+} in the aqueous phase, respectively. The percent adsorption and the distribution ratio, D , were obtained from $(C_0 - C)/C_0 \times 100\%$ and from Q/C mL g⁻¹, respectively. The saturated adsorption capacity, Q_{∞} , was obtained from another adsorption experiment performed for 48 h in a solution containing an excess amount of UO_2^{2+} .

The results are summarized in Table 1. The amount of impregnated associate was 34.9–38.2% for XAD-7 and about 17% for each silica gel particle, indicating that the amount of associate impregnated differed with the kind of support, but not with the ligand- and complex-type. The appearances of each adsorbent such as color, size and rough feel of a particle, were similar to each other both before and after impregnation. Loading greater amounts than those given in Table 1, however, caused over-loading and sticky particles. Similar amounts of $H_4L_8^{8-}$, such as 0.107–0.0861 mmol g⁻¹ for XAD-7 and about 0.033 mmol g⁻¹ for silica-gel particles, were also found in accordance with the amount of ionic associate impregnated, irrespective of the ligand- and complex-type. These adsorbents were stable and no release of the ionic associates was observed in water.

The log D values and % adsorption given in Table 1 are distinctly larger in the order (U)MTAL8-R $\geq$ (Ti)MTAL8-R > (L)MTAL8-R and (U)MTAL8-S > (Ti)MTAL8-S > (L)MTAL8-S, respectively, for the XAD-7 and silica gel-adsorbents. These facts clearly indicate that the complex-type adsorbents are stronger than the ligand-type, and that in the

Fig. 1 Chemical structure of water-soluble hydroxycalix[*n*]arene-*p*-sulfonate ion.

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Table 1 Concentrations of ionic associate and $\text{H}_4\text{L}_8^{8-}$ of each adsorbent, and their % adsorption, log distribution ratio, log D , adsorption capacity, Q_∞ , and $Q_\infty/[\text{H}_4\text{L}_8^{8-}]$ for UO_2^{2+} at pH 7.5 ± 0.2 and about 25°C

Adsorbent	MTA ⁺ -H ₄ L ₈ ⁸⁻ , %	H ₄ L ₈ ⁸⁻ /mmol g ⁻¹	% adsorption ^b	log D^b	Q_∞ /mmol g ⁻¹	$Q_\infty/[\text{H}_4\text{L}_8^{8-}]$
(U)MTAL8-R	38.2	0.107	99.5	4.70(64.6)	0.218	2.04
(Ti)MTAL8-R	35.4	0.0957	93.7	3.57(4.79)	0.171	1.79
(L)MTAL8-R	34.9	0.0861	75.5	2.89(1.00)	0.151	1.75
(U)MTAL8-S	17.0	0.0332	99.0	4.39(20.9)	0.0704	2.12
(Ti)MTAL8-S	16.9	0.0329	97.4	3.97(7.94)	0.0670	2.04
(L)MTAL8-S	16.6	0.0330	82.4	3.07(1.00)	0.0399	1.21

a. Reaction time = 48 h. b. % adsorption and log D obtained using 0.1 g of XAD-7 (R) and 0.3 g of silica gel (S) adsorbents in 25 mL aqueous solution containing 2.5×10^{-3} mmol of UO_2^{2+} . The values in parenthesis are relative D values based on ligand type adsorbent for each matrix.

Fig. 2 Effect of the reaction time on the % adsorption of UO_2^{2+} by silica-gel adsorbents, ((U)MTAL8-S(○), (Ti)MTAL8-S(●) and (L)MTAL8-S(△) at room temperature (about 25°C)). Adsorbent = 0.20 g, H_2O = 50 mL, $[\text{UO}_2^{2+}]_0 = 1.00 \times 10^{-4}$ M, $[\text{NaHCO}_3] = 5.00 \times 10^{-4}$ M, pH = 7.5 ± 0.2 .

complex types the UO_2^{2+} type is stronger than the Ti^{4+} type in adsorptivity for UO_2^{2+} . The values for Q_∞ of the complex-type adsorbents are also larger than those by the ligand-type. The value of the ratio $Q_\infty/[\text{H}_4\text{L}_8^{8-}]$, that is, the number of active sites of the ligand in the associate, was 2.00 ± 0.14 for four kinds of complex-type, and 1.75 and 1.21 for two ligand-type adsorbents. This may show that the chelating ability of $\text{H}_4\text{L}_8^{8-}$ is fully working for UO_2^{2+} , even in the solid phase of the complex-type adsorbents, as in the aqueous solution,³ but not in the ligand-type adsorbents.

In addition to the above facts, it was also found that the adsorption rates of these adsorbents for UO_2^{2+} , which were measured in terms of the change of % adsorption with the reaction time in the initial stage of adsorption, were in the order (U)MTAL8-R > (U)MTAL8-S > (Ti)MTAL8-R > (Ti)MTAL8-S >> (L)MTAL8-S. The results for silica-gel adsorbents are shown in Fig. 2. These facts suggest that much of the $\text{H}_4\text{L}_8^{8-}$ in the complex-type adsorbents is kept in a pre-organized “cone” structure (Fig. 3, A), which is more favorable to bind UO_2^{2+} . On the other hand, in the ligand-type adsorbent, much of the ligand must be kept in “alternate” (Fig. 3, B) or “double partial cone” structures, which are unfavorable for picking up UO_2^{2+} unless their conformations change to a “cone” structure. The presence of such structures is shown for the more rigid hexamer homologue, $\text{H}_2\text{L}_6^{6-}$, even in aqueous solution.⁹

It has been reported that there was no template effect in the ligand-impregnated adsorbents which were prepared by encapsulating metal complexes followed by stripping the metal

Fig. 3 “cone” (A) and an “alternate” (B) structures for the ionic associate of MTA^+ and $\text{H}_4\text{L}_8^{8-}$, $(\text{MTA}^+)_{11}(\text{HL}_8^{11-})$, in the complex and ligand-type adsorbents.

ion.^{10,11} Thus, it can be concluded that the ligand-impregnated adsorbent, having the best conformation for binding UO_2^{2+} , is the first prepared template adsorbent for the adsorption of UO_2^{2+} .

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