Another Uranophile Sodium Hydroxycalix[8]arene-*p*-sulfonate: Its Acid Dissociation and Divalent Metal Ion Binding Properties

Miwako SONODA*, Kenji HAYASHI**, Masashi NISHIDA*, Daido ISHII* and Isao YOSHIDA*†

*Department of Industrial Chemistry, Kumamoto Institute of Technology,
Ikeda, Kumamoto 860-0082, Japan

**Tzurumisoda Co., Suehiro, Tzurumi, Yokohama 230-0045, Japan

Acid dissociation constants of the hydroxyl groups of sodium hydroxycalix[8]arene-*p*-sulfonate ($\mathbf{1}_8$ =Na₈H₄L) were measured by the pH titration method in an aqueous solution. The acid dissociation constants determined were as follows: $pK_{a1}=3.73\pm0.05$, $pK_{a2}=4.39\pm0.05$, $pK_{a3}=8.07\pm0.02$, $pK_{a4}=10.1\pm0.1$ under the conditions of $\mu=0.1$ with KNO₃ and 25°C. Furthermore, the complex formation reactions of $\mathbf{1}_8$ with some divalent metal ions such as Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, and UO₂²⁺ (M²⁺) were investigated by the pH titration method in aqueous solutions and the stability constants of the complexes were evaluated. No complex formation was observed for Cu²⁺. The slight formation of complexes having a 1:1 molar ratio (M²⁺: $\mathbf{1}_8$) was observed for all other divalent metal ions except for UO₂²⁺. In contrast, UO₂²⁺ formed a relatively stable 2:1 complex in addition to an unstable 1:1 complex. These results indicate that $\mathbf{1}_8$ is a highly selective metal ligand for UO₂²⁺ among the various divalent metal ions.

Keywords Water soluble calix[8]arene, acid dissociation constant, divalent metal complex, stability constant, high uranophile

The development of a peculiar ligand which can selectively extract UO₂²⁺ from seawater has attracted extensive attention from chemists for more than two decades because of its importance in relation to energy problems. As a possible unique solution for this problem, Shinkai *et al.*¹ synthesized a macrocyclic ligand with a nearly coplanar arrangement of either five or six donating groups which can serve as a specific donating group for UO₂²⁺ uptake. They examined the complexing ability of these groups with various divalent metal ions. They found that sodium hydroxycalix[5]arene-*p*-sulfonate, $\mathbf{1}_5$, sodium hydroxycalix[6]arene-*p*-sulfonate, $\mathbf{1}_6$, and their penta- or hexacarboxylated derivatives, $\mathbf{1}_5\text{CH}_2\text{COOH}$ and $\mathbf{1}_6\text{CH}_2\text{COOH}$ form 1:1 complexes with UO₂²⁺ and that the complexes have remarkably large stability constants ($\log K_{\text{UO}_2}=18.9-19.2$) with high selectivity factors ($\log(K_{\text{UO}_2}/K_{\text{M}^{2+}})=10-17$) in water.¹ Such high selectivity was attributed to the rigged skeleton of calix[*n*]arenes (*n*=5 and 6) which can provide pre-organized penta- or hexacoordination geometry for the binding of UO₂²⁺.

We investigated divalent metal ion binding properties of sodium hydroxycalix[8]arene-*p*-sulfonate, $\mathbf{1}_8$, which has eight donating groups on a more flexible macrocyclic skeleton than those of $\mathbf{1}_5$ and $\mathbf{1}_6$. We found that $\mathbf{1}_8$ forms a highly stable 1:2 ($\mathbf{1}_8$:UO₂²⁺) complex with UO₂²⁺, similar to that formed by $\mathbf{1}_5$ and $\mathbf{1}_6$ in stability. But extremely unstable 1:1 complexes were formed

Scheme 1 Sodium hydroxycalix[8]arene-*p*-sulfonate, $\mathbf{1}_8$.

with other divalent metal ions such as Ca²⁺ and Zn²⁺, according to accurate analyses of pH titration curves. There was no complex formed with Cu²⁺. In the present paper, we report acid dissociation constants of $\mathbf{1}_8$, its complex formation reactions with some divalent metal ions including UO₂²⁺ together with their stability constants, high selectivity factors for UO₂²⁺ in divalent metal ions, and the finding that $\mathbf{1}_8$ is another uranophile which has highly selective reactivity for UO₂²⁺.

Experimental

Materials

Hydroxycalix[8]arene-*p*-sulfonic acid sodium salts, $\mathbf{1}_8$ were obtained commercially from Sugai Kagaku Co.(Wakayama, Japan) and used after purification by recrystallization with water. Pure white crystals were

† To whom correspondence should be addressed.

obtained after performing recrystallization three times starting from the pale-yellow powder. The pH value of the aqueous mother solution was about 3. The white solid product was dried at 60°C under reduced pressure for 24 h, then used for titration studies.

pH titration

Procedures, instrumentation and methods for pH ($-\log[H^+]$) measurement similar to those described in our previous paper² were used for the pH titrations. The sample solution containing 0.05–0.1 mmol of **1₈** was titrated with 0.1 M carbonate free potassium hydroxide in a 50 ml water jacket cell in the presence and absence of metal ion at 25°C in a nitrogen stream. The ionic strength was adjusted to 0.1 with potassium nitrate. The pH of the sample solution was measured at every step of titration.

Spectrophotometric titration

Due to the difficulty in ascertaining which group of the multidentate ligand is deprotonated by the pH titration only, a spectrophotometric titration was carried out in the 0.1 M KCl solution simultaneously. The instrumentation used for spectrophotometric titration was basically similar to that for the pH titration. Using a micro tube pump, the sample solution in a reaction vessel was circulated at every step of titration through a small silicon tube into a Shimadzu SPD-6AV spectrophotometer equipped with a micro flow photocell. The micro flow cell was 1 cm in light-pass length and 8 μ l in volume. The optical absorbance of the reaction mixture was measured at several wavelengths between 250 nm–290 nm. At the same time, the pH of the reaction mixture was measured using a Horiba F-8AT pH meter. The same types of glass and reference electrodes were used in a similar way for pH titration.

Results and Discussion

UV spectra of **1₈**

Prior to the titration studies, the sodium and sulfur contents of **1₈** were determined by an ICP-AES method in an aqueous solutions using a Seiko-densi SPS-1200VR. Analytical results indicated that **1₈** has 1 mol of sodium per 1 mol of sulfur atoms. It was also found that no other metal cations, such as barium or potassium, nor anions such as chloride were present. This fact indicates that **1₈** is in the form of 8th sodium salts. Thus, it can be concluded that **1₈** has a maximum of 8 dissociable protons in the aqueous solution. If some of these are sulfonic protons, they would easily dissociate at relatively low pH, while if some are phenol protons, they would not dissociate even at an extremely high pH.

Due to the phenols, the UV absorption peak usually shifts to a longer wavelength side and the absorbances increase when a hydroxyphenol dissociates to form a phenolate ion by an increase in pH. In contrast, the

absorbance of the solution containing phenolate ion may decrease and the absorption peak may shift to the shorter wavelength side by an addition of acids.

Two absorption peaks were observed in the UV spectrum of **1₈** in water at 275 and 283 nm. They moved to the longer wavelength side where the absorbance increased with an increase in pH. At pH<2, the absorbance is constant regardless of the change in pH, as shown in Fig. 1. Thus we can conclude that no acid dissociation of any hydroxyl proton takes place at pH<2. This evidence indicates the presence of a phenol group and the absence of a phenolate ion. As a result, the presence of sodium sulfonates for all sulfonic groups in **1₈** is indicated, because no other metal ions were present. This means that all of the dissociable protons in **1₈** are from the phenol groups. This is supported by the fact that sodium hydroxycalix[4]arene-*p*-sulfonate, **1₄**, which was obtained by recrystallization from water (pH *ca.* 3), was also in a form of tetrahydroxytetrasodiumsulfonate.²

The results of the elemental analyses and IR spectra suggest the presence of water in **1₈**. The presence of water is also reported elsewhere.³ The complete removal of water was difficult without the decomposition of **1₈**. The presence of water does not interfere with the titration study in the aqueous system; thus the experiments were carried out using samples containing water.

Titration curves of calixarenes

The titration curve for 0.110 mmol of **1₈** in a 40 ml of aqueous solution is shown in Fig. 2. The number on the abscissa, *a*, indicates the molar ratio of KOH added to an amount of **1₈**. The titration curve has a pH buffer region from *a*=0 to *a*=4, indicating an inflection at *a*=2

Fig. 1 Variation in absorbance due to the deprotonation of **1₈** at 283 nm as a function of pH. $\mu=0.1$ with KCl at $2 < \text{pH} < 12$, **1₈** = 2.5×10^{-5} M, initial volume of the sample solution = 40 ml, light-pass length = 1 cm.

Fig. 2 pH titration curve for **1₈** with 0.1 M KOH at 25°C. [**1₈**]=2.76 mM, μ =0.1 with KNO₃, initial volume=40 ml, a =molar ratio of KOH added/**1₈**

and another small one at $a=3$. This indicates that **1₈** dissociates two protons up to $a=2$ in a weakly acidic solution of $\text{pH}<6$, one of the remaining two protons up to $a=3$ at about $\text{pH}=8$, and the other up to $a=4$ at about $\text{pH}=10$.

Acid dissociation constants

Acid dissociation constants were computed using the titration data for various amounts of **1₈** using the computer program PKAS;⁴ the results are shown in Table 1. When the quantity of titratable protons in **1₈** is presumed to be 4, the best agreement obtained for calculated pH values and those measured over all points of titrations gave the smallest σ values⁴, where $\sigma = (\sum W \cdot (\text{pH}_{\text{obs}} - \text{pH}_{\text{calc}})^2 / \sum W)^{1/2}$, $W = (\text{pH}_{i+1} - \text{pH}_{i-1})^{-2}$ and i is the number of titration points. The smaller the σ value, the larger the degree of agreement between the calculated and measured pH values. From the resultant pK_{a} values shown in Table 1, the mean values were calculated for each pK_{a} and the acid dissociation constants of **1₈** were determined to be $\text{pK}_{\text{a}1}=3.73 \pm 0.05$, $\text{pK}_{\text{a}2}=4.39 \pm 0.05$, $\text{pK}_{\text{a}3}=8.07 \pm 0.02$, and $\text{pK}_{\text{a}4}=10.1 \pm 0.1$.

The sulfonate ion of **1₈** (H_4L^{8-}) dissociates two protons in the acidic solution, while the third deprotonation can

Table 1 Acid dissociation constants, pK_{a} , of hydroxyl groups in **1₈** at 25 °C and $\mu=0.1$ with KNO₃

1₈ /mmol ^a	$\text{pK}_{\text{a}1}$	$\text{pK}_{\text{a}2}$	$\text{pK}_{\text{a}3}$	$\text{pK}_{\text{a}4}$
0.06481	3.67	4.46	8.09	10.1
0.06530	3.68	4.37	8.08	10.2
0.1104	3.77	4.33	8.05	10.1
Mean	3.73 ± 0.05	4.39 ± 0.05	8.07 ± 0.02	10.1 ± 0.1

a. Initial volume=40 ml.

Scheme 2 Proposed intramolecular hydrogen bondings for H_2L^{10-} which appear similar to bis-deprotonated **1₄**.

Scheme 3 Proposed intramolecular hydrogen bondings for L^{12-} in which 4 hydroxyl protons were dissociated alternately.

only take place in the alkaline solution. This fact suggests that ionic species H_2L^{10-} is considerably stabilized due to the formation of intramolecular hydrogen bonds in its macro cyclic ring, as shown in Scheme 2. This species seems similar to a biscalix[4]arene, bis-**1₄**, where 1 mol of **1₈** dissociates 2 mol of protons and forms a stable bis-tetramer. After the fourth deprotonation took place, no more deprotonation was observed in the higher alkaline solution. So we believe the neighboring phenol and phenoxide ions formed four couples of hydrogen bonds alternately, as indicated in Scheme 3, and the ionic molecule also stabilized. Thus it can be concluded that **1₈** in an aqueous solution is a tetrabasic acid in the form of $\text{Na}_8\text{H}_4\text{L}$.

Complex formation of **1₈** with divalent metal ions

The formation of metal complex, $\text{M}_m\text{L}_l\text{H}_h$ and its stability constant, β_{mlh} were determined using the computer program BEST⁴ from the analyses of the pH titration curves of **1₈** which were measured in the presence of divalent metal ions.

$$\beta_{mlh} = [\text{M}_m\text{L}_l\text{H}_h] / [\text{M}]^m [\text{L}]^l [\text{H}]^h \quad (2)$$

In Eqs. (1) and (2), the charges of metal ion, ligand and

complex species are omitted in order to more simply express the equations.

1_8 - UO_2^{2+} complexes and their stability constants

Some pH titration curves for 1_8 ($R=\infty$) and 1_8 - UO_2^{2+} mixtures ($R=2.1-0.53$) are shown in Fig. 3, where R is $1_8/M^{2+}$ in molar ratio. Compared to 1_8 alone, the presence of UO_2^{2+} decreases pH values considerably in proportion to the amount of UO_2^{2+} present, *i.e.*, with decreasing R values in the sample solution. Therefore, it is clear that 1_8 forms some complexes with UO_2^{2+} by dissociating protons even in the acidic solution. From the inflection points of each titration curve, we were able to calculate the amount of hydrogen ions released from 1 mol of UO_2^{2+} , followed by complex formation with 1_8 , and found it to be 3.5 mmol.

All pH titration data were analyzed by using the computer program BEST¹¹ under the above presupposition

Fig. 3 pH titration curves for 1_8 ($\circ$, $R=\infty$) and 1_8 - UO_2^{2+} mixture solutions (R : $\blacktriangle$, 2.1; $\square$, 1.3; $\triangle$, 0.71; $\blacksquare$, 0.53) with 0.1 M KOH at 25°C. $\mu=0.1$ with KNO_3 . Initial volume of sample solution=40 ml.

Table 2 1_8 - UO_2^{2+} species and their stability constants, $\log \beta_{mlh}$ at 25 °C

R^b	Amount of UO_2^{2+} and 1_8 /mmol ^c		$\log \beta_{mlh}$	
	UO_2^{2+}	1_8	112	21-3
0.53	0.207	0.110	23.27	12.34
0.71	0.155	0.110	22.97	12.31
1.1	0.104	0.110	22.71	12.11
1.3	0.0518	0.0648	22.11	12.19
2.1	0.0518	0.110	22.56	11.71
Mean			22.72 $\pm$ 0.39	12.13 $\pm$ 0.23

a. $\mu=0.1$ with KNO_3 .

b. R =molar ratio of 1_8 to UO_2^{2+} in sample solution.

c. Initial volume=40 ml.

to obtain complex species mlh and their stability constants, β_{mlh} . The resultant species and their stability constants are summarized in Table 2. The same complex species and similar stability constants could be obtained from different titration data which were measured on the different sample solutions of R values. In these calculations, pH_{obs} and pH_{calc} agreed well with each other over the entire pH range, giving the smallest σ . As the analytical results seem to be reliable, it is concluded that two kinds of complexes, **112** and the binuclear **21-3**, are formed. Their stability constants were evaluated and found to be $\log \beta_{112}=22.72$ and $\log \beta_{21-3}=12.13$, respectively.

The species distribution curves for these complexes were drawn using the computer program SPE⁴ in accordance with the above species and their stability constants as a function of pH; the results are given in Fig. 4. This shows that **112** is the minor species which has a limited existence in a narrow pH range of 2-3, while **21-3** is the stable and main species; its formation starts at pH 2.5, then 1 mol of 1_8 form a complex with 2 mol of UO_2^{2+} almost quantitatively at pH 3.5. The resultant complex exists in a wide pH range when R is larger than 0.5.

Shinkai *et al.*¹ have reported that both 1_5 and 1_6 associate with UO_2^{2+} at a 1:1 molar ratio. Recently, we found that the UO_2^{2+} - 1_4 complex is at a 1:2 (M:L) molar ratio.⁵ Thus, it can be concluded that the binding ratio of UO_2^{2+} to 1_n is subject to the hole size of the ligand and molecule, 1_n .

Spectrophotometric study of 1_8 - UO_2^{2+} complex formation

Colorless 1_8 forms a red-orange complex with UO_2^{2+} . By using the light absorption resulting from the 1_8 - UO_2^{2+} complex, the binding ratio of 1_8 with UO_2^{2+} was also determined by the continuous variation method at 450 nm. The results are shown in Fig. 5. The maximum absorption is obtained at a concentration ratio of $[UO_2^{2+}]/([1_8]+[UO_2^{2+}])=0.66$ in the pH 4.7 and 7.6 solu-

Fig. 4 Fractional diagrams of 1_8 - UO_2^{2+} system calculated on the basis of $\beta_{112}=22.73$, $\beta_{21-3}=12.13$, $[UO_2^{2+}]=5.3$ mM, $R=0.53$.

Fig. 5 Determination of the binding ratio of 1_8 - UO_2^{2+} by the continuous variation method at 450 nm. Light-pass length=1 cm; pH: Δ , 4.7; $\square$, 7.6; $\circ$, 12.1.

tions and at 0.63 in the pH 12.1 solution. This result indicates that the complex having $\text{UO}_2^{2+}:1_8=2:1$ is formed over a wide pH range, in agreement with the result obtained by the pH titration method. The absorbances at each peak of the curves are almost constant, regardless of the differences in pH value of the sample solution. This also indicates that **21-3** is almost completely formed even in an acidic solution at pH 4.7. This experimental result agrees well with the result from the species distribution curve shown in Fig. 4.

At pH 2–3, a part of 1_8 forms the complex with UO_2^{2+} at a 1:1 molar ratio, as shown in Eq. (3) to gave **112**:

At pH>3.5, the **21-3** species is formed according to Eq. (4):

It has been reported¹ that cyclic pentamers and cyclic hexamers act as excellent ligands for UO_2^{2+} , but that cyclic tetramers do not. In addition to the above ligands, we found that the cyclic octamer, 1_8 can also act as an excellent ligand for UO_2^{2+} , forming the binuclear complex, **21-3**. Although the structure of the **21-3** complex could not be established, we estimated a bis-tetrameric coordination arrangement of 1_8 with two UO_2^{2+} ions. The remaining coordination site of UO_2^{2+} must be combined with water and the excess protons released in Eq.(4) should be those dissociated from the coordinated water of UO_2^{2+} in the complex.

Complex formation of 1_8 with other divalent metal ions

Figure 6 shows pH titration curves of 1_8 in the

Fig. 6 pH titration curves for 1_8 ($\circ$, $R=\infty$) and 1_8 - Ca^{2+} (Δ , $R=1.0$) mixture solutions with 0.1 M KOH at 25°C. $\mu=0.1$ with KNO_3 . Initial volume of sample solution=40 ml.

Table 3 1_8 - M^{2+} species and their stability constants, $\log \beta_{mlh}^a$ at 25°C

R^b	Amount of M^{2+} and $1_8/\text{mmol}^c$		$\log \beta_{mlh}$			
	M^{2+}	1_8	112	111	110	11-1
1.2	Mg 0.0520	0.0648	—	11.92	3.39	-8.31
0.51	Ca 0.216	0.110	20.1	12.5	3.4	—
1.0	Ca 0.108	0.110	20.1	12.6	3.4	—
1.2	Ca 0.0540	0.0648	20.6	12.9	3.7	—
1.2	Co 0.0558	0.0648	20.4	12.9	—	—
1.3	Mn 0.0495	0.0648	20.7	13.4	—	—
1.2	Ni 0.0552	0.0648	20.1	12.7	—	—
1.2	Zn 0.0531	0.0648	20.3	13.4	—	—

a. $\mu=0.1$ with KNO_3 .

b. R =molar ratio of 1_8 to M^{2+} in sample solution.

c. Initial volume=40 ml.

absence ($R=\infty$) and presence of Ca^{2+} ($R=1$). Both curves have similar pH values to each other at each titration point. This indicates that the degree of complex formation between 1_8 and Ca^{2+} is very weak. Similar pH titration curves were also obtained for other divalent metal ions such as Mg^{2+} , Co^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} . Table 3 shows the complex species and the stability constants computed for these divalent metal ions. Three kinds of 1:1 species, *i.e.*, **112**, **111**, and **110** were formed for Ca^{2+} , while the last two species, **111** and **110**, were formed for Mg^{2+} in addition to **11-1**. The formations of the first two species, **112** and **111**, were found for other divalent metal ions. These metal complexes have stabilities similar to each other. Figure 7 shows species distribution curves for Mg^{2+} complex as a function of pH. At pH<8, almost all Mg^{2+} is uncomplexed. This means that these divalent metal ions do

Fig. 7 Fractional diagrams of 1_8 - Mg^{2+} system calculated on the basis of $\beta_{111}=11.9_2$, $\beta_{110}=3.2_9$, $\beta_{11-1}=-8.3_1$, $[Mg^{2+}]=1.3$ mM, $R=1.25$.

not form stable complexes with 1_8 . Thus in the acidic solution no complex is formed; divalent metal ions are present as uncomplexed metal ions.

Furthermore, the facts that the pH titration curve of a 1_8 - Cu^{2+} mixture ($R=1$) solution overlapped completely with that for 1_8 alone ($R=\infty$) up to $a=2$ and also that copper hydroxide was produced at $a>2$ indicate that no copper complex was formed at all with 1_8 .

Selective reactivity of 1_8 for UO_2^{2+}

As discussed above, 1_8 can form a stable complex only with UO_2^{2+} ; some other divalent metal ions form extremely unstable complexes and Cu^{2+} does not form any 1_8 -complex. The concentrations of trivalent metal ions in seawater are lower by far than those of divalent metal ions. Thus when studying the complex formation of metal ions with 1_8 in seawater, we can exclude the presence of trivalent metal ion complexes. Among the divalent metal ions, Mg^{2+} is the highest in concentration; thus the selective reactivity of UO_2^{2+} to Mg^{2+} , $Sr(UO_2/Mg)$, was calculated as the concentration ratio of these metal ions complexed with 1_8 .

As indicated in the present study, 1_8 forms **21-3** species with UO_2^{2+} at pH 8.0, and its overall stability constant, $\beta_{21-3}(UO_2)$ is given by Eq. (5):

$$\frac{[(UO_2)_2LH_3]/[UO_2^{2+}]^2[L][H]^{-3}}{\beta_{21-3}(UO_2)} = 10^{12.13} \quad (5)$$

On the other hand, Mg^{2+} forms only **111** species at pH 8.0 and its overall stability constant, $\beta_{111}(Mg)$, is given by Eq. (6):

$$[MgLH]/[Mg^{2+}][L][H] = \beta_{111}(Mg) = 10^{11.92} \quad (6)$$

From Eqs. (5) and (6), we obtain Eq. (7):

$$\frac{Sr(UO_2/Mg) = [(UO_2)_2LH_3]/[MgLH]}{\beta_{21-3}(UO_2)/\beta_{111}(Mg) \cdot [UO_2^{2+}]^2 \cdot [Mg^{2+}]^{-1} \cdot [H^+]^{-4}} \quad (7)$$

The selective reactivity, $Sr(UO_2/Mg)$, i.e., the concen-

tration ratio of UO_2^{2+} to Mg^{2+} in the 1_8 -complexes, $[(UO_2)_2LH_3]/[MgLH]$, is a function of pH, UO_2^{2+} and Mg^{2+} concentrations in seawater. These are already known to be $[UO_2^{2+}]=1.5 \times 10^{-8}$ M, $[Mg^{2+}]=5.2 \times 10^{-2}$ M, and $[H^+]=1.0 \times 10^{-8}$ M, respectively. Thus the value we obtained for $Sr(UO_2/Mg)$ was 7.0×10^{17} .

It has been reported¹ that 1_6 has a high selective reactivity with UO_2^{2+} and its UO_2^{2+} selectivity factor for other divalent metal ions, $Sf(UO_2/M^{2+})$ was 10^{11-17} , where $Sf(UO_2/M^{2+})$ was the ratio of the association constants of UO_2^{2+} to that of M^{2+} , $K_{16-UO_2}/K_{16-M^{2+}}$. The value for selective reactivity, $Sr(UO_2/Mg)$, in the present study happened to agree with the value for this selectivity factor, although there is no relation between these two selectivities. Furthermore the ratio of overall stability constants for these complexes, $\beta_{21-3}(UO_2)/\beta_{111}(Mg)$, is meaningless in the present study. The value for the selective reactivity of UO_2^{2+} to Cu^{2+} , $Sr(UO_2/Cu)$, will be infinite because Cu^{2+} does not form any complex with 1_8 .

The concentration factor of UO_2^{2+} to Mg^{2+} with 1_8 , the factor defined as $([UO_2LH_3]/[UO_2])/([MgLH]/[Mg])$, is also a function of pH and concentration of UO_2^{2+} . This value was calculated as indicated in Eq. (8) and found to be 2.0×10^{24} .

$$\frac{([UO_2LH_3]/[UO_2])/([MgLH]/[Mg])}{10^{0.21}[UO_2^{2+}][H^+]^{-4}} = 2.0 \times 10^{24} \quad (8)$$

Since the stabilities of a series of 1_8 - M^{2+} complexes were found to be similar to those of Mg^{2+} complexes and the concentrations of divalent metal ions in seawater are lower by far than that of Mg^{2+} , we can conclude that 1_8 essentially only forms the complex with UO_2^{2+} in seawater.

Effect of carbonate ion

Since, almost all UO_2^{2+} in seawater is present in the form of the bicarbonate complex, $UO_2(CO_3)_2^{2-}$, due to the presence of carbonate ion, we studied the influence of carbonate ion on the formation of a 1_8 - UO_2^{2+} complex.

The sample solutions were prepared by adding a given amount of 1_8 to the sodium carbonate solutions containing a given amount of UO_2^{2+} , where the carbonate- UO_2^{2+} solutions were left beforehand for 24 h to complete the formation of bicarbonate- UO_2^{2+} complex, $UO_2(CO_3)_2^{2-}$. Then, the visible absorption spectra of the sample solutions were measured at given time intervals at 25°C. Identical absorption spectra were recorded for each solution having various amounts of carbonate ion with constant amounts of 1_8 and UO_2^{2+} and including a carbonate-free solution. The pH value of the solutions was kept at 8.0 by using 0.01 M 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) (Dojin Chemical Co., Japan). The absorbances at 450 nm measured after 24 h are given in Fig. 8 as a function of the carbonate concentration at pH 8.0. This figure indicates that no influence on the sta-

Fig. 8 Influence of carbonate ion concentration on the absorbance of **18**-UO₂²⁺ complex at 25°C. [UO₂(NO₃)₂]=2.00×10⁻⁴ M, [**18**]=1.05×10⁻⁴ M, pH=8.0 with [HEPES]=0.01 M, reaction time =24 h, wavelength=450 nm, light-pass length=1 cm, reference=water.

bility of **18**-UO₂²⁺ complex can be observed up to 4×10⁻³ M. When carbonate concentration is smaller than 3×10⁻³ M, the absorbances reached values almost identical to those in Fig. 8 at least in 1 h. In the 4×10⁻³ M solution, the absorbances were about 95% of those

given in Fig. 8. This means the presence of a large amount of carbonate ion only decreases the rate of the complex formation reaction between **18** and UO₂²⁺ to a greater or lesser degree.

The present study indicates that **18** is also a selective uranophile equal to or higher in efficiency than **16**, **15**, and their hexacarboxylate derivatives¹ and also indicates its possible use as functional group of an adsorbent for the selective extract of UO₂²⁺ from seawater.⁶

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