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Chemical Forms of Uranium in Artificial Seawater

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The chemical forms of uranium in an artificial seawater are determined by use of the ion-association model. The data on the stoichiometric association constants of the ion pairs are used in calculation to evaluate the distribution of the major ionic species. Also, the more accurate values of the thermodynamic stability constants are used for the uranyl complexes. The calculation indicates that a dominant species of uranium is $UO_2(CO_3)_3^{4-}$ in artificial seawater at 25°C.

KEYWORDS: chemical forms, uranium, seawater, ion association model, chloride association, effective ionic strength, computer calculations, tri-carbonate complexes

I. INTRODUCTION

The oceans contain over 4 billion tons of dissolved uranium, at a concentration of 3.3 ppb, and recovery of this element from seawater is presently being considered by a number of countries[1][2]. It is indispensable to clarify how uranium is dissolved in seawater.

Ogata *et al.*[3][4] concluded that the *tri*-carbonate complex $UO_2(CO_3)_3^{4-}$ is the dominant species in seawater. Their calculation, however, has two shortcomings: (1) They calculated the concentration of the major ionic species in seawater using thermodynamic data and estimated values of activity coefficients by the Kielland equation. (2) They neglected the formation of ion pairs between chloride and the major seawater cations.

Johnson & Pytkowicz[5][6] and Sipos *et al.*[7] have recently determined the stoichiometric association constants of ion pairs present in seawater. Langmuir[8] has critically evaluated the thermodynamic stability constants of uranyl complexes. Therefore, the calculation of Ogata *et al.* should be revised to include the effects of chloride ion pairs and more accurate values of stoichiometric association constants and thermodynamic stability constants.

The purpose of this paper is to re-examine the chemical forms of uranium in seawater. An artificial seawater was chosen to minimize biological effects and to provide a reproducible solution of known composition.

II. EXPERIMENTAL

1. Preparation of Artificial Seawater

The recipes of artificial seawater are almost similar to those of Kester *et al.*[9] The composition of artificial seawater is given in **Table 1.** The artificial seawater containing uranium was prepared by mixing artificial seawater with a uranyl nitrate solution.

2. Measurement of RpH and Total Inorganic Carbon

In order to equilibrate the artificial seawater with atmospheric gases, the artificial seawater was aerated by drawing laboratory air through the solution until the pH did not

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change. The value of pH after aeration is referred to as RpH (*i.e.* Reserve pH). The total inorganic carbon was then measured by means of an infra-red spectrophotometer. The values of pH were measured at 25°C using a glass electrode pH meter. The results of these measurements are shown in **Table 2.**

The total inorganic carbon $[C]_T$ is defined to be

$$[C]_T=[CO_2]_T+[HCO_3]_T+[CO_3]_T$$
$$=\alpha P_{CO_2}\{1+K_1'/a_H(1+K_2'/a_H)\}, \quad (1)$$

where a_H is the activity of hydrogen ion, K_1' the first apparent dissociation constant of carbonic acid, K_2' the second dissociation constant, P_{CO_2} the equilibrium partial pressure of CO_2, and α the solubility coefficient. The value of α was calculated from the Weiss equation[10], and the values of K_1' and K_2' were obtained from Mehrbach *et al.*[11] By substituting the average values of RpH and $[C]_T$ into Eq. (1), the following values were obtained:

$P_{CO_2}=3.45\times10^{-4}$ atm, $[HCO_3]_T=1.88\times10^{-3}$ mol/dm³, $[CO_2]_T=2.22\times10^{-4}$ mol/dm³.

Table 1 Preparation of artificial seawater

Salt	Molecular weight	Solution (g/dm³)
NaCl	58.44	23.926
Na_2SO_4	142.04	4.008
KCl	74.55	0.738
$NaHCO_3$	84.01	0.196
$MgCl_2\cdot6H_2O$	203.33	10.831
$CaCl_2\cdot2H_2O$	147.02	1.519

Table 2 Measurements of RpH and $[C]_T$ at 25°C

U conc. in artificial seawater (μg-U/dm³)	RpH	$[C]_T$ (mM)
0	8.22	2.03
10	8.22	2.27
100	8.22	2.08
1,000	8.22	2.11
Average	8.22	2.12

III. CALCULATIONS

1. Stoichiometric Association and Stability Constants

Ions are considered to exist in the form of free ions, ion pairs or complexes. The stoichiometric association constant of an ion pair M_mX_x is defined to be

$$K^*_{MX}=[MX^{(m-x)+}]/[M^{m+}][X^{x-}], \quad (2)$$

where the brackets indicate the molarity of the species. The stoichiometric association constants were obtained from Johnson & Pytkowicz[5][6] and Sipos *et al.*[7]

The stoichiometric stability constants of uranyl complexes can be related to the corresponding thermodynamic stability constants by activity coefficients, as shown in the following way. The stoichiometric stability constant of UO_2Cl^+ was estimated from the equation:

$$\beta^*_{UO_2Cl^+}=\beta^t_{UO_2Cl^+}(\gamma_{UO_2^{2+}}\gamma_{Cl^-}/\gamma_{UO_2Cl^+}), \quad (3)$$

where β^* represents the stoichiometric stability constant, and β^t the thermodynamic stability constant of the subscripted species, and γ is the activity coefficient of each species. The thermodynamic stability constants of uranyl complexes were obtained from Langmuir[8].

The data for the activity coefficient, which are necessary to convert β^t to β^*, of Cl^-, SO_4^{2-}, CO_3^{2-} and OH^- were obtained from Whitfield[12]. The activity coefficients for uranyl ion and uranyl complexes were calculated from the Helgeson trace activity coefficient equation[13]:

$$\log\gamma_i=-\frac{AZ_i^2\sqrt{I_e}}{1+a_iB\sqrt{I_e}}+B'I_e, \quad (4)$$

where a_i and Z_i are the distance closest approach and the charge of ion i, respectively. The values of A, B and B' are 0.5095, 0.3284 and 0.041 at 25°C. **Table 3** shows the assumed values of a_i. The effective ionic strength is defined to be

$$I_e=\frac{1}{2}\sum_i C_i Z_i^2. \qquad (5)$$

Table 3 Assumed values of a_i

Species	a_i	γ_i†
UO_2Cl^+	3.5	0.661
$UO_2(SO_4)_2^{2-}$	4.0	0.185
$UO_2(CO_3)_2^{2-}$	4.0	0.185
$UO_2(CO_3)_3^{4-}$	4.0	0.00101
UO_2OH^+	3.5	0.661
$(UO_2)_2(OH)_2^{2+}$	10.0	0.385
$(UO_2)_3(OH)_5^+$	10.0	0.817

†: γ_i's are calculated at $I_e=0.520$.

2. Calculation Procedures

To calculate the distribution of chemical species, mass-balance equations are written for each constituent in artificial seawater containing uranium, as listed in **Table 4.** The concentration of ion pair or complex in Table 4 can be expressed in terms of its stoichiometric association constant or its stoichiometric stability constant and the free concentrations.

Table 4 Mass balance equations for defining distribution of ions

$$[Na]_T=[Na^+]+[NaCl^0]+[NaSO_4^-]+[NaHCO_3^0]+[NaCO_3^-]$$
$$[Mg]_T=[Mg^{2+}]+[MgCl^+]+[MgSO_4^0]+[MgHCO_3^+]+[MgCO_3^0]$$
$$[K]_T=[K^+]+[KCl^0]+[KSO_4^-]$$
$$[Ca]_T=[Ca^{2+}]+[CaCl^+]+[CaSO_4^0]+[CaHCO_3^+]+[CaCO_3^0]$$
$$[H]_T=[H^+]+[HCl^0]+[HSO_4^-]$$
$$[UO_2]_T=[UO_2^{2+}]+[UO_2Cl^+]+[UO_2SO_4^0]+[UO_2(SO_4)_2^{2-}]+[UO_2CO_3^0]+[UO_2(CO_3)_2^{2-}]$$
$$+[UO_2(CO_3)_3^{4-}]+[UO_2OH^+]+2[(UO_2)_2(OH)_2^{2+}]+3[(UO_2)_3(OH)_5^+]$$
$$[Cl]_T=[Cl^-]+[NaCl^0]+[MgCl^+]+[KCl^0]+[CaCl^+]+[HCl^0]+[UO_2Cl^+]$$
$$[SO_4]_T=[SO_4^{2-}]+[NaSO_4^-]+[MgSO_4^0]+[KSO_4^-]+[CaSO_4^0]+[HSO_4^-]+[UO_2SO_4^0]+2[UO_2(SO_4)_2^{2-}]$$
$$[HCO_3]_T=[HCO_3^-]+[NaHCO_3^0]+[MgHCO_3^+]+[CaHCO_3^+]$$
$$[CO_3]_T=[CO_3^{2-}]+[NaCO_3^-]+[MgCO_3^0]+[CaCO_3^0]+[UO_2CO_3^0]+2[UO_2(CO_3)_2^{2-}]+3[UO_2(CO_3)_3^{4-}]$$
$$[NO_3]_T=[NO_3^-]$$
$$[OH]_T=[OH^-]+[UO_2OH^+]+2[(UO_2)_2(OH)_2^{2+}]+5[(UO_2)_3(OH)_5^+]$$

As for the total concentration of constituents, the following considerations may be applied. The total concentrations $[Na]_T$, $[Mg]_T$, $[K]_T$, $[Ca]_T$, $[UO_2]_T$, $[Cl]_T$, $[SO_4]_T$ and $[NO_3]_T$ are known. The total concentrations $[H]_T$ and $[OH]_T$ were calculated from the following equation:

$$[H]_T=a_H/f_H, \qquad [OH]_T=K_W^{SW}/[H]_T. \qquad (6)$$

The values of f_H and K_W^{SW} are 0.71 and 6.32×10^{-14} from Culberson & Pytkowicz[14], respectively.

Thus, a system of mass-balance equations extended to all constituents was solved for the equilibrium concentrations of free ions. The calculation procedures were similar to those of Kester & Pytkowicz[15]. However, an iterative calculation was used in this study, because the stoichiometric association constants of the ion pairs HCl^0, $NaCl^0$, KCl^0, $MgCl^+$ and $CaCl^+$, and the activity coefficient depend upon the effective ionic strength which was not known initially.

IV. Results and Discussions

1. Chemical Forms of Major Constituents

Table 5 shows the results of the calculation of the distribution of major constituents over various species. Although the total uranyl concentration $[UO_2]_T$ varied from 3.3 to 1,000 ppb, the concentration of major constituents except for carbonate was not changed in calculation. In Table 5, the distributions obtained by Sipos *et al.*[7] and Ogata *et al.*[4] are also shown in brackets and in parentheses for comparison, respectively. The percentages of CO_3^{2-} species are shown in **Table 6.** It is found that the resulting distribution is in good agreement with that of Sipos *et al.*, although they did not take uranium into account. The distribution is quite different from that of Ogata *et al.* The free concentrations are lower in this study, with the exception of free bicarbonate ion. The large differences between the value by Ogata *et al.* and that by this study are considered to be the result of chloride association.

Table 5 Results of calculation of distribution of major ionic species

Total molarity [M]		Free (%)	M-Cl (%)	M-SO_4 (%)	M-HCO_3 (%)	M-CO_3 (%)	M-OH (%)
Na	0.468	83.1	13.2	3.7	0.0	0.0	
	[0.482]	[82.8]	[13.4]	[3.7]	[0.0]	[0.0]	
	(0.470)	(98.5)		(1.4)			
Mg	0.0533	48.3	42.1	9.2	0.2	0.2	0.0
	[0.0549]	[47.7]	[42.8]	[9.1]	[0.2]	[0.2]	[0.0]
	(0.0536)	(85.3)		(13.6)	(0.6)	(0.4)	
K	9.90×10^{-3}	78.5	17.2	4.3			
	$[1.06\times10^{-2}]$	[78.1]	[17.6]	[4.3]			
	(9.96×10^{-3})	(97.7)		(1.3)			
Ca	0.0103	43.7	46.3	9.2	0.3	0.5	
	[0.0106]	[43.1]	[47.1]	[9.5]	[0.3]	[0.4]	
	(0.0102)	(86.1)		(12.9)	(0.7)	(0.3)	
H	8.49×10^{-9}	92.2	7.8	0.0			
	$[7.94\times10^{-9}]$	[92.2]	[7.9]	[0.0]			

Total molarity [M]		Free (%)	Na-X (%)	Mg-X (%)	K-X (%)	Ca-X (%)	H-X (%)
Cl	0.547	83.5	11.3	4.1	0.3	0.9	0.0
	[0.566]	[83.2]	[11.5]	[4.2]	[0.3]	[0.9]	[0.0]
	(0.548)	(100.0)					
SO_4	0.0282	16.2	61.6	17.4	1.5	3.4	0.0
	[0.0291]	[15.8]	[62.0]	[17.2]	[1.6]	[3.5]	[0.0]
	(0.0282)	(45.0)	(22.9)	(25.9)	(0.8)	(4.7)	
HCO_3	1.88×10^{-3}	81.7	10.6	6.3		1.5	
	$[2.10\times10^{-3}]$	[81.4]	[10.8]	[6.3]		[0.2]	
	(1.94×10^{-3})	(63.8)	(12.3)	(19.6)		(4.3)	
OH	7.45×10^{-6}	100.0					
	$[2.14\times10^{-6}]$	[99.5]		[0.0]			

2. Chemical Forms of Uranium

The three assumptions were required in our calculations:

(1) The stoichiometric stability constants of the uranyl complexes were related to the corresponding thermodynamic stability constants by activity coefficients estimated from the Helgeson equation[13].

(2) The UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$ were considered as the uranyl hydroxy complexes[8].

(3) The various uranyl complexes with phosphate and fluoride were ignored.

Table 6 Distribution of carbonate species (%) $[CO_3]_T = 2.22 \times 10^{-4}$ (mol/dm³)

Species	Total U conc. (μg-U/dm³)			Ogata[4] *et al.*†	Sipos[7] *et al.*††
	3.3	300	1,000		
CO_3^{2-}	9.2	9.1	8.7	8.44	8.08
$NaCO_3^-$	18.1	17.8	17.1	16.88	16.25
$MgCO_3^0$	48.7	47.9	46.0	64.94	43.31
$CaCO_3^0$	24.1	23.7	22.7	9.74	21.38
$UO_2CO_3^0$	0.0	0.0	0.0		
$UO_2(CO_3)_2^{2-}$	0.0	0.1	0.3		
$UO_2(CO_3)_3^{4-}$	0.0	1.6	5.2		

† : $[CO_3]_T = 3.60 \times 10^{-4}$ (mol/dm³)
††: $[CO_3]_T = 1.877 \times 10^{-4}$ (mol/dm³)

Table 7 Distribution of uranyl species (%)

Species	Total U conc. (μg-U/dm³)			Ogata *et al.*[3]
	3.3	300	1,000	
$UO_2CO_3^0$	0.1	0.1	0.1	
$UO_2(CO_3)_2^{2-}$	8.1	8.2	8.5	0.38
$UO_2(CO_3)_3^{4-}$	91.8	91.7	91.4	97.88

Table 7 shows the results of the calculation of the distribution of uranium over various species. The dominant chemical species of uranium are $UO_2(CO_3)_3^{4-}$ (92%) and $UO_2(CO_3)_2^{2-}$ (8%). All of the other uranium species considered in this study are negligible.

The distribution obtained by Ogata *et al.*[3] is also shown in Table 7 for comparison. The differences are not dramatic. However, the evaluation of the chemical forms of uranium in seawater has been revised as follows:

(1) The experimentally determined stoichiometric association constants of the ion pairs, corrected for chloride ion-pairing, were used to evaluate the major ionic species present in seawater. Therefore, this removes the estimation of the activity coefficients of ion pairs and single ions.

(2) The calculation procedure in this study makes it possible to predict the chemical forms of uranium when the total uranium concentration is increased.

This result will be applied to the discussion on the multi-component diffusion in artificial seawater containing uranium[16]. Furthermore, the chemical forms of uranium in artificial seawater will be experimentally verified by the measurement of diffusion coefficient[17].

[NOMENCLATURE]

A: Constant relating to solvent, Eq. (4)
a_i: Distance of closest approach of ion i (Å)
a_H: Activity of hydrogen ion on NBS scale
B: Constant relating to solvent, Eq. (4)
B': Deviation function, Eq. (4)
C_i: Concentration of ion i (mol/dm³)
f_H: Total activity coefficient of hydrogen ion
I_e: Effective ionic strength (mol/dm³)
K^*: Stoichiometric association constant
K_1': Apparent first dissociation constant of carbonic acid
K_2': Apparent second dissociation constant of carbonic acid
K_W^{SW}: Ion product of water in seawater (mol²/dm⁶)
P_{CO_2}: Equilibrium partial pressure of CO_2 (atm)
pH: $-\log a_H$
RpH: Reserve pH
Z_i: Charge of ion i
α: Solubility coefficient
β^t: Thermodynamic stability constant
β^*: Stoichiometric stability constant
γ_i: Activity coefficient of ion i
[ ]: Concentration
(Subscript)
T: Total

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