

Sorption of UO_2^{2+} onto Goethite and Kaolinite: Mechanistic Modeling Approach

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Abstract

The sorption of UO_2^{2+} onto goethite and kaolinite under various experimental conditions was successfully interpreted using surface complexation modeling (SCM). The SCM approach used in this work is the triple-layer model (TLM) in which weakly bonded ions are modeled as outer-sphere (ion-pair) complexes and strongly bonded ions as inner-sphere (surface coordination) complexes. The change of ionic strength did not affect the U(VI) sorption onto goethite, thus the formation of inner-sphere surface complexes, $(\text{FeO})_2\text{UO}_2$ and $(\text{FeO})_2(\text{UO}_2)_3\text{OH}_5^-$ was assumed to simulate the effects of ionic strength and goethite concentration. On the other hand, the U(VI) sorption onto kaolinite showed ionic strength dependence, thus the formation of $\text{AlO}^+-\text{UO}_2^{2+}$ (outer-sphere complex) and $\text{SiO}(\text{UO}_2)_3\text{OH}_5$ (inner-sphere complex) was assumed to simulate the experimental data. In the presence of carbonates, the sorption of U(VI) onto kaolinite decreased in the weakly alkaline pH range. This was well simulated assuming the formation of a outer-sphere surface complex, $\text{AlOH}^{2+}-\text{(UO}_2)_2\text{CO}_3\text{OH}_3^-$. Since SCM approach uses thermodynamic data such as surface complexation constants, it is more predictive than empirical modeling approach in which conditional values such as partition coefficient are used.

Key Words : sorption, uranium, goethite, kaolinite, surface complexation

1. Introduction

The effect of radioactive elements and heavy metals on environmental systems has been the subject of research in many fields[1]. Interactions between radionuclide and geological material are known to be an important mechanism of radionuclide retardation in groundwater

systems[2].

Uranium is of fundamental element in the nuclear fuel cycle, where it starts as a energy source and ends as a waste component. It is a representative actinide element while it is a potential environmental pollutant. The mobility of uranium in the environment is enhanced in oxidizing environment by the formation of uranyl

ions (UO_2^{2+}). In groundwater conditions, chemical interactions with solid surfaces retard uranyl mobility. The stronger the interaction between the uranyl species and solid surfaces is, the greater the retardation in the natural groundwater system is.

Traditionally, experimental sorption data have been described by empirical means, including partition coefficients, isotherm equations, etc[3],[4]. In order to fully describe the environmental behavior of U, a quantitative model for the sorption of uranyl on natural surfaces is essential. Quantitative modeling of uranyl sorption to natural system is still in a developing stage. Nevertheless, SCM has been developed recently and applied to certain minerals to gain an understanding of the sorption mechanism involved and to describe it in a mechanistic way[5]. The fundamental concept of SCM is that sorption on solid surface takes place at specific coordination sites and can be described quantitatively by mass law equations.

In our previous paper, the sorption of Cu^{2+} onto iron oxides and kaolinite mineral has been described by SCM approach. In this study, the sorption behavior of UO_2^{2+} is simulated onto goethite and kaolinite, which are known as single minerals in natural geomedias.

2. Experimental

In the absence of carbonate, the mixtures were prepared with single minerals (12 g / L), uranyl nitrate 6-hydrate (1.0×10^{-4} M) and potassium nitrate (1.0 to 1.0×10^{-3} M) in 30 ml polypropylene bottles (Nalgene). In order to minimize the sorption of U(VI) onto reaction vessel, polypropylene bottles were used instead of glassware. In the presence of carbonate, potassium bicarbonate (1.0×10^{-3} M) was added to the mixtures above. Goethite was purchased from

High Purity Fine Chemical Inc. (Japan), and kaolinite (KGa-1b) was supplied by the Source Clays Repository of the Clays Minerals Society (Washington County, Georgia). All solutions were prepared from AR grade reagents and water with the electric resistivity of $18.3 \text{ M}\Omega\text{cm}$ (Milli-Q, Millipore).

The mixtures were allowed to stand overnight, and the pH of the samples was then adjusted by the addition of KOH or HNO_3 . After a week of equilibrium period, the final pH was determined, and an aliquot of the samples was withdrawn with a 10 ml plastic syringe and then filtered using a $0.45\mu\text{m}$ syringe filter (Whatman). The uranium concentration in the filtrate was determined using ICP-AES (JY 50 P, Jobin yvon).

3. Results and Discussion

3.1 Surface Complexation Modeling

The sorption of metal ions onto mineral surfaces has been described by SCM approach. In the SCM, the surface is considered to be composed of specific functional groups that react with dissolved metal ions to form coordinative complexes or ion pairs in a manner similar to complexation reactions in solution[7]. The SCM used in this work is the modified version of the triple-layer model (TLM), which allows model analogues of both inner-sphere (placed in the o-plane) and outer-sphere (placed in the β -plane) complexes to be formulated (see Figure 1)[8],[9],[10]. In the TLM, weakly bonded ions are modeled as outer-sphere (ion-pair) complexes and strongly bonded ions as inner-sphere (surface coordination) complexes.[11]

The surface complexation constant ($\log K_{sc}$) of UO_2^{2+} for goethite and kaolinite was fitted by the FITEQL program. The FITEQL is a computer program for the determination of chemical

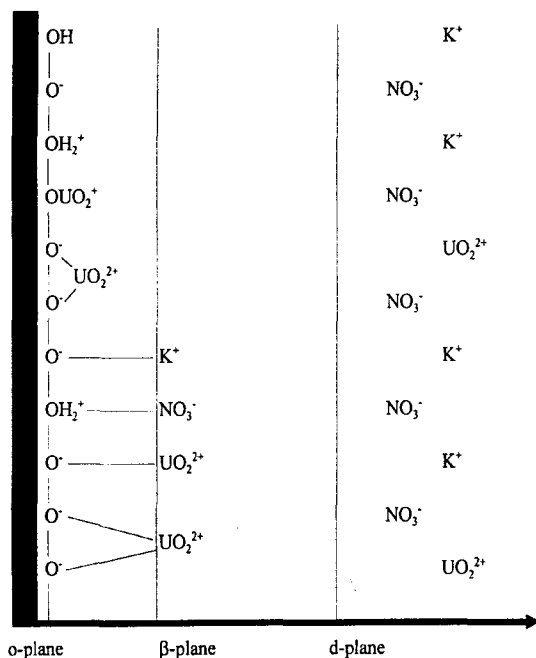
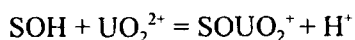


Fig. 1. Schematic Representation of Inner- and Outer-sphere UO_2^{2+} Complexes Considered in this Work; o-plane is Mineral Surface and Location of Inner-sphere Complex. β -plane is Location of Outer-sphere Complex. d-plane is Distance of Closest Approach for Freely Moving Ions in the Diffuse Layer.

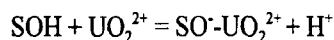
equilibrium constants from experimental data[12]. For each data set (around 15 data points), the goodness of fit was estimated as the overall variance that is the weighted sum of the square residuals divided by the degree of freedom, SOS/DF. The K_{sc} is defined as follows:

Inner-sphere complex



$$K_{sc} = \frac{[\text{SOUO}_2^+][\text{H}^+]}{[\text{UO}_2^{2+}][\text{SOH}]} \exp(F\Psi_o / RT)$$

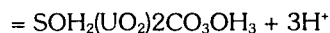
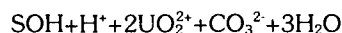
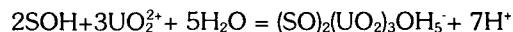
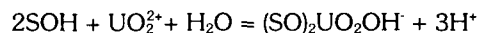
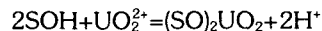
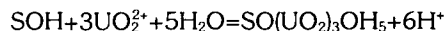
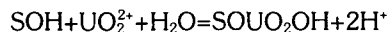
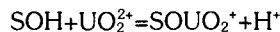
Outer-sphere complex



$$K_{sc} = \frac{[\text{SO}^-\text{UO}_2^{2+}][\text{H}^+]}{[\text{UO}_2^{2+}][\text{SOH}]} \exp(F(\Psi_o - 2\Psi_\beta) / RT)$$

where SOH is surface functional group, F the Faraday constant (96485 C/mol), R the molar gas constant (8.314 J/molK), T the absolute temperature (K), Ψ_o the potential at the o-plane (V), and the potential at the β -plane (V). In the above equations, $[]$ represent concentrations and $\{ \}$ represent activities. The activity coefficients for surface species such as SOH, SOUO_2^+ and $\text{SO}^-\text{UO}_2^{2+}$ are assumed to be same.

For UO_2^{2+} sorption modeling, different combinations of possible equilibria have been tested. These equilibria are:

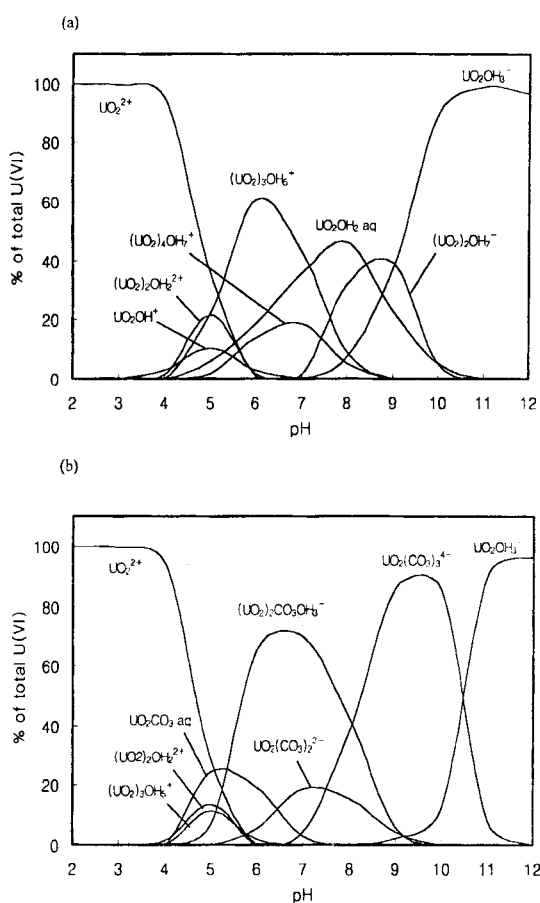


The surface complexes were selected under the assumption that dominant aqueous U(VI) species are adsorbed onto the minerals in the pH range where UO_2^{2+} is most strongly adsorbed. The distribution of aqueous U(VI) species as a function of pH was calculated using the program MINTQA2 (see Figure 2)[15]. The thermodynamic data used in the calculation were taken from the work of Grenthe et al. Using the surface reactions above, the best fit to the experimental data was obtained by the program FITEQL. The

Table 1. The Input Parameter Values of the FITEQL Program

Parameter	Goethite	Kaolinite	
Surface reactions (log K)		Aluminol	Silanol
$\text{SOH} + \text{H}^+ = \text{SOH}_2^+$	6.6	2.33	NC
$\text{SOH} - \text{H}^+ = \text{SO}^-$	-12.2	-5.28	-8.23
$\text{SOH} + \text{K}^+ - \text{H}^+ = \text{SO}^- \text{K}^+$	-10.63	-0.9	-1.75
Inner-layer capacitance (F/m^2)	1.1		1.1
Outer-layer capacitance (F/m^2)	0.2		0.2
Surface area (m^2/g)	48.0		8.68
Site density (mol/L)	1.607×10^{-2}	1.65×10^{-4}	2.85×10^{-4}

NC not considered

**Fig. 2. Distribution of Major U(VI) Species (a) in the Absence of Carbonate (b) in the Presence of Carbonate (Total Carbonate Concentration of $1.0 \times 10^{-3} \text{ M}$)**

input parameters used for the FITEQL fitting are shown in Table 1. These parameters were taken from literature[17],[18],[19].

3.2. UO_2^{2+} Sorption onto Goethite

The sorption of UO_2^{2+} as a function of pH and goethite concentration is shown in Figure 3. The sorption increased from near zero at pH 3.0 to greater than 99% of the total U(VI) at pH 5.5. At a given pH, the sorption increased when additional goethite was present. This is caused by the increase of surface binding sites. The result confirms that the concentration of dissolved U(VI) was not controlled by the solubility of U(VI) precipitates, since the addition of goethite would not affect dissolved U(VI) in that case. The effect of ionic strength on the sorption of UO_2^{2+} onto goethite is shown in Figure 4. The change of ionic strength did not influence the sorption significantly. This means that uranyl ions (UO_2^{2+}) are strongly sorbed onto the goethite surface (o-plane), thus weakly sorbed ions such as potassium ions (K^+), which are located at β -plane, do not interfere the sorption.

The existence of bidentate surface complex of UO_2^{2+} on ferrihydrite was observed using EXAFS (Extended X-ray Absorption Fine Structure) analysis. Based on the crystal radii of uranyl ions,

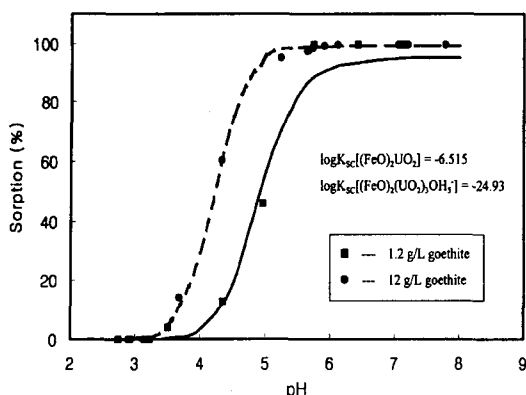


Fig. 3. Uranium(VI) Sorption onto Goethite as a function of pH and Goethite Concentration at a Ionic Strength of 0.01 M KNO₃. Points are Experimental Data, and Lines are Simulation Results.

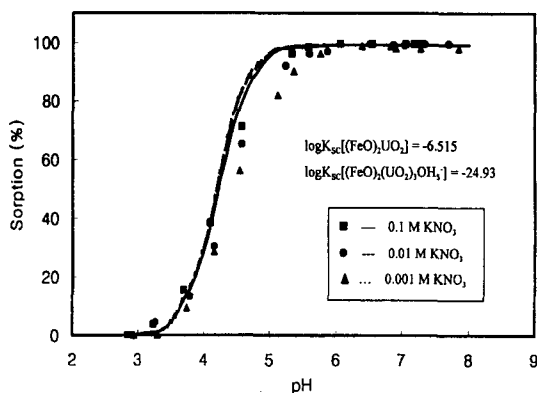


Fig. 4. Uranium(VI) Sorption onto Goethite as a Function of pH and Ionic Strength at a Goethite Concentration of 12g/L. Points are Experimental Data, and Lines are Simulation Results.

Table 2. The FITEQL Fitting of U(VI) Sorption onto Goethite as a Function of pH and Goethite Concentration

Case No.	Surface complexes (log K _{sc})			SOS/DF
	(FeO) ₂ UO ₂	(FeO) ₂ UO ₂ OH ⁻	(FeO) ₂ (UO ₂) ₃ OH ₅ ⁻	
1	-6.370	-	-	8.66720
2	-	-14.07	-	42.94529
3	-	-	-24.17	17.38165
4	O	O	-	NC
5	-6.515	-	-24.93	5.22258
6	-	-14.83	-24.47	7.23553
7	O	O	O	NC

NC not converged

O included in the modeling but not determined because of no convergence

the sorbed (UO₂)₃OH₅⁺ complex has a minimum cross-sectional diameter of 0.6-0.8 nm[13]. However, the cross-sectional area of each surface functional group is only 0.06 nm² based on the site density of goethite (16.8 sites / nm²). The above observations support the exclusion of the formation of monodentate surface complexes.

The experimental data were fitted with bidentate inner-sphere complexes only using the FITEQL

program. In the preliminary work, we found that the best fit to the data of ionic strength effect did not successfully simulate the data of goethite concentration effect, thus the data of goethite concentration effect were fitted first and the best fit was used to simulate the data of ionic strength effect. The fitting results are given in Table 2. Several combinations of surface complexes explained the experimental data equally well. On

the basis of SOS/DF value, a combination of bidentate species $(\text{FeO})_2\text{UO}_2$ and $(\text{FeO})_2(\text{UO}_2)_3\text{OH}_5$ gave the best fit to the data (see Figure 3).

For 12 g/L goethite data, the model gave a good agreement, while it underpredicted the UO_2^{2+} sorption above pH 5 for 1.2 g/L goethite data. Considering the high loading of U(VI) on the surface, the deviation might be caused by the formation of polynuclear U(VI) species on the surface, which are not formed in bulk solution. The surface complexation constants which were obtained by fitting the data of goethite concentration effect were used to predict the effect of ionic strength on UO_2^{2+} sorption (see Figure 4). The sorption edge (narrow range where sorption goes from near zero to almost complete sorption) of the prediction shifted slightly to a lower pH than that of the experimental data. Considering no fitting to the experimental data of ionic strength effect, however, the model predicts the experimental data extraordinarily well.

3.3. UO_2^{2+} Sorption onto Kaolinite

The effect of ionic strength on UO_2^{2+} sorption onto kaolinite is shown in Figure 5-a. Increasing the ionic strength substantially reduced the sorption of UO_2^{2+} in the acidic conditions. This is quite similar to the previous work of Cu^{2+} sorption onto kaolinite.⁶ This indicates the existence of weakly bound uranyl complexes. Thus the formation of inner- and outer-sphere complexes was assumed in the modeling. Kaolinite is a representative layered aluminosilicate mineral with the structure of tetrahedral (Si center) and octahedral (Al center) sheet in a 1 : 1 ratio[22]. Sorption of metal ions and development of surface charge are controlled mainly by amphoteric reactions at oxygen sites on aluminol and siloxane surfaces that are conceptually similar to surface reactions on oxide minerals[23]. Because the

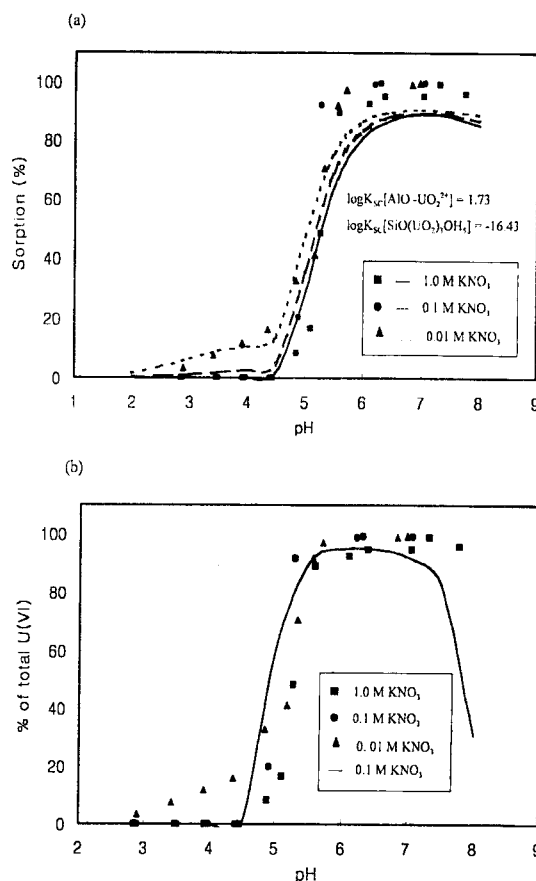


Fig. 5. Uranium(VI) Sorption onto Kaolinite as a Function of pH and Ionic Strength at a Kaolinite Concentration of 12g/L. (a) Simulation by Considering Sorption Only (b) Simulation by Considering Precipitation only. The Precipitate is Schoepite ($\text{UO}_2^{2+} + 3\text{H}_2\text{O} = \beta\text{-UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O} + 2\text{H}^+$, $\log\beta = -4.844$). Points are Experimental Data, and Line is Simulation Result

kaolinite surface is composed of Al and Si sites, a two-site model was also used to fit the experimental data. And the silanol groups were assumed not to protonate at the pH values of the experiment[19]. Thompson et al suggested the existence of inner-sphere complex on the Si site through the EXAFS analysis[24]. Thus the

Table 3. The FITEQL Fitting of U(VI) Sorption onto Kaolinite at an Ionic Strength of 0.01 M KNO₃

Case No.	Surface complexes (log K _{sc})						SOS/DF
	SiOUO ₂ ⁺	AlO ⁻ -UO ₂ ²⁺	SiOUO ₂ OH	AlO ⁻ -UO ₂ OH ⁺	SiO(UO ₂) ₃ OH ₅	AlO ⁻ -(UO ₂) ₃ OH ₅ ⁺	
1	O	O	-	-	-	-	NC
2	-	-	O	O	-	-	NC
3	-	-	-	-	O	O	NC
4	O	-	-	O	-	-	NC
5	-1.281	-	-	-	-	-14.44	153.11419
6	-	O	O	-	-	-	NC
7	-	-	O	-	-	O	NC
8	-	0.8103	-	-	-16.27	-	51.45035
9	-	-	-	-4.463	16.32	-	62.42156
10	O	O	O	O	O	O	NC

NC not converged

O included in the modeling but not determined because of no convergence

formation of inner-sphere complex on the Si site and outer-sphere complex on the Al site was assumed in the modeling.

The modeling results of ionic strength dependence are given in Table 3. Similar to the fitting results of UO₂²⁺ sorption onto goethite, several models gave a reasonable fit to the experimental data. On the basis of SOS/DF values, the best fit to the experimental data was obtained with a combination of AlO⁻-UO₂²⁺ (outer-sphere complex) and SiO(UO₂)₃OH₅ (inner-sphere complex). The model did well explain the effect of ionic strength in the low pH region, however, underpredicted the experimental data above pH 5 (see Figure 5-a). The very steep (near vertical) slope of sorption edge for 1.0 M and 0.1 M KNO₃ data is a contrast to the distinctive 'S' curve which is observed in numerous experiments in which sorption appears to be the major process. Therefore, precipitation of U(VI) solid species might occur in the conditions studied[25]. Assuming the formation of solid U(VI) species only, the agreement between model and experiment is surprisingly good between pH 5 and

pH 7 (see Figure 5-b). Thus, in the pH range above, the experimental data may be well simulated with the precipitation reaction of U(VI) included in the FITEQL fitting.

The experimental results for the effect of carbonate concentration on UO₂²⁺ sorption onto kaolinite are shown in Figure 6-a. The sorption decreased in the weakly alkaline pH range. This is due to the formation of aqueous U(VI)-carbonato complexes. U(VI), as uranyl (UO₂²⁺), is a 'hard' cation that readily forms solution complexes with a number of 'hard' ligands (mostly O-donor ligand).

Under the assumption that no uranyl carbonates were sorbed onto kaolinite, the model failed to explain the experimental data completely (see Figure 6-b model 1) because aqueous U(VI)-carbonato complexes were predominant in the experimental condition. This indicates that uranyl carbonates are also sorbed onto goethite surface in the pH range where U(VI) sorption takes place. Thus three uranyl carbonates (UO₂(CO₃)₂²⁻, UO₂(CO₃)₃⁴⁻, (UO₂)₂CO₃OH³⁻) were assumed to be sorbed as outer-sphere complex on the Al site[27]. The FITEQL fitting results are given in Table 4.

Table 4. The FITEQL Fitting of U(VI) Sorption onto Kaolinite in the Presence of Carbonate ($C_T = 1.0 \times 10^{-3} \text{ M}$) at an Ionic Strength of 0.01 M KNO_3

Case No.	Surface complexes (log K _{sc})			SOS/DF
Outer-sphere complex on the Al site				
	AlOH ₂ ⁺ ·{UO ₂ } ₂ CO ₃ OH ₃ ⁻	AlOH ₂ ⁺ ·UO ₂ (CO ₃) ₂ ²⁻	AlOH ₂ ⁺ ·UO ₂ (CO ₃) ₃ ⁴⁻	
1	9.863	-	-	20.18605
2	-	30.76	-	285.00579
3	-	-	O	NC
4	O	O	-	NC
5	O	-	O	NC
6	-	O	O	NC
7	O	O	O	NC

NC not converged

O included in the modeling but not determined because of no convergence

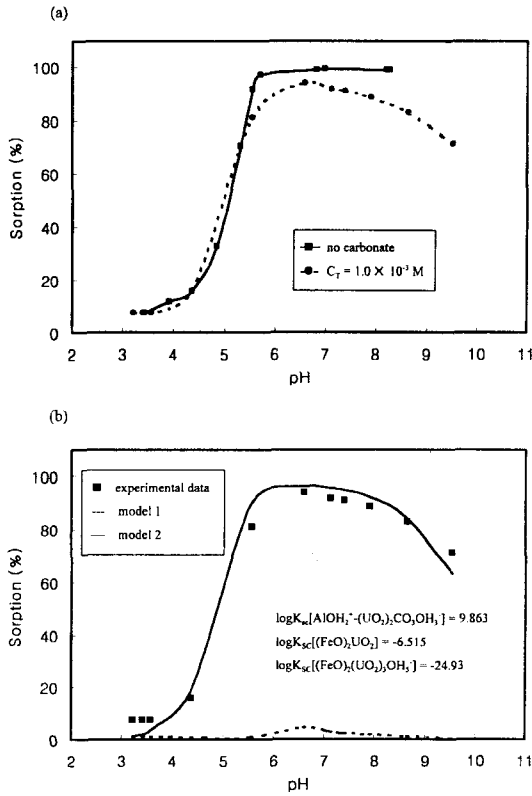


Fig. 6. Uranium(VI) Sorption onto Kaolinite (12g/L) at a Ionic Strength of 0.01M KNO_3 (a) Experimental Results; the Effect of Carbonate, Total Carbonate (C_T) = $1.0 \times 10^{-3} \text{ M}$. (b) Simulation Results; $(\text{UO}_2)_2\text{CO}_3\text{OH}_3^-$ is Assumed to be Sorbed in Model 2 and not to be Sorbed in Model 1

The best fit was obtained with a sorbed species of $\text{AlOH}_2^+ \cdot (\text{UO}_2)_2\text{CO}_3\text{OH}_3^-$. Since $(\text{UO}_2)_2\text{CO}_3\text{OH}_3^-$ is predominant aqueous species in the pH range where the sorption of U(VI) occurs, this species may be sorbed rather than $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$ species. The agreement between the model and the data is quite good considering no fitting of the log K_{sc} values for $\text{AlO}-\text{UO}_2^{2+}$ and $\text{SiO}(\text{UO}_2)_3\text{OH}_5$ complexes (see Figure 6-b model 2). These values were predetermined in the study of ionic strength effect (see Table 3). In the absence of carbonates, the model underpredicted the sorption of UO_2^{2+} above pH 5 (see Figure 5-a), but the model based solely on the sorption process explained the experimental data successfully in the presence of carbonates. In the latter case, the formation of U(VI) solid species could not occur because of the high affinity of carbonates for U(VI).

4. Conclusions

In this work, two different minerals were compared with respect to the sorption behavior of UO_2^{2+} . The sorption showed that the change of

ionic strength affected the sorption of UO_2^{2+} onto kaolinite while it did not on goethite. This difference provides indirect evidence for the formation of inner-sphere complex (strong bond) or outer-sphere complex (weak bond). In the presence of carbonate, the sorption decreased in the weakly alkaline condition. This indicates the competition between carbonates and surface functional groups for UO_2^{2+} .

The ability of SCM to explain the complex behavior of sorption was investigated. On the basis of available spectroscopic evidence such as EXAFS analysis, the sorption of UO_2^{2+} onto goethite and kaolinite under various experimental conditions was successfully modeled using a SCM approach, TLM, in a consistent manner. Since ionic forms of oxide and clay surface affect the structure and properties of surface complexes, it should be taken account in the sorption models[28]. In the case of goethite, the formation of bidentate inner-sphere complexes ($(\text{FeO})_2\text{UO}_2$ and $(\text{FeO})_2(\text{UO}_2)_3\text{OH}_5$) well explained the effects of ionic strength and goethite concentration on the sorption. For kaolinite, the formation of monodentate inner-sphere and outer-sphere complexes ($\text{AlO}^--\text{UO}_2^{2+}$, $\text{SiO}(\text{UO}_2)_3\text{OH}_5$ and $\text{AlOH}_2^+(\text{UO}_2)_2\text{CO}_3\text{OH}_3$) well simulated the effects of ionic strength and carbonate concentration.

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