Association of Uranyl Ions with Amino Functional Groups

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We investigated the adsorption of uranyl ions (UO_2^{2+}) on amino functional groups at various pH values using amino group-modified silica particles. We found that uranyl ions were associated with the amino groups by forming 1:2 uranyl amino group complexes.

Uranium is one of the most concerning heavy elements in the environment because of its potential release from nuclear accidents, nuclear weapons tests, and waste disposal.[1,2] Uranium typically occurs as aqueous hexavalent uranyl complexes in oxic environments.[3] The mobility of U^{VI} is determined by its interactions with soils and subsoils composed of abiotic and biotic components, principally minerals and bacteria, respectively.[4,5]

Bacterial cell surfaces have high adsorption capacities for UO_2^{2+} ions.[5–7] Surface complex modeling has been applied to the adsorption of UO_2^{2+} ions on cell surfaces and well estimates the adsorption.[8–10] This modeling assumes the phosphoryl and carboxyl functional groups to be the dominant complexation sites. Though amino groups are one of the three major functional groups, the complexation with amino groups has been disregarded because of their protonation at low pH.[11]

This letter examines the adsorption of UO_2^{2+} ions on amino groups using amino group-modified silica particles. Unmodified silica particles (unmodified silica), the silica particles on which $–NH_2$ was fixed (NH_2–silica), and the silica particles on which $–NH_2$ and hydroquinone (quinone–silica) were fixed were purchased from Corefront Corporation, Japan. The amino groups were fixed on the silica particles by condensation of 3-aminopropyltriethoxysilane (($C_2H_5O)_3SiC_3H_6NH_2$) to give a structure of $>Si–CH_2–CH_2–CH_2–NH_2$. On the quinone–silica particles, quinone ($C_6H_4(OH)_2$) molecules were bound to the amino groups that had been fixed on the silica beforehand. The quinone–silica particles were used to test the adsorption on amino groups with different proton-binding constants ($\log K$). These particles were approximately 15 μm in diameter. The densities of the functional groups on these silica particles were determined by potentiometric acid–base titration analysis using an automated burette assembly. The particles and a known amount of HCl were introduced into 70 mL of a 0.1 M NaCl solution, and base titrations with a CO_2-free 0.1 M NaOH solution were conducted from pH 3.5 to 10.0 under vigorous stirring and Ar gas bubbling. Duplicate experiments were performed.

A solution was prepared to have a U^{VI} concentration of 4×10^{-6} M (C_0) by adding a stock solution of $UO_2(OCOCH_3)_2$ to a 0.01 M aqueous NaCl solution. Silica particles were dispersed in the U^{VI} solution with a pH between 2 and 7 in a centrifuge tube at a solid-to-liquid ratio of 4 g/L. After standing for 4 h at 25 °C, the liquid phase was collected by centrifugation at 10000 rpm for 5 min. The U concentration in the supernatant (C_S) was determined with a liquid scintillation analyzer. We utilized the program FITEQL 2.0[12] to determine the functional group site concentrations, $\log K$, and the U^{VI} binding stability constants ($\log K_n$) by fitting the experimental data. Activity coefficient corrections were performed within FITEQL using the Davies equation. After the adsorption experiments, the solid phases were put in contact with a 1 M KCl solution twice and then with a 1 M HCl solution.[13] The former was to extract the U^{VI} (Q_{KCl}/mol) weakly adsorbed by mechanisms like electrostatic interaction. The latter was to forcibly extract the remaining U^{VI} (Q_{HCl}/mol).

The best-fit result obtained for the titration data of the unmodified silica particles indicates that these particles have two hydroxy (silanol) groups with different $\log K$ values (Table 1). For the NH_2–silica particles, a fraction of the hydroxy groups was assumed to be unbound to amino groups ($>Si–CH_2–CH_2–CH_2–NH_2$). For the quinone–silica particles, the presence of hydroxy groups with a somewhat different $\log K$ value (reaction H) was assumed and these hydroxy groups were assigned to the hydroxy groups of the quinone moieties, but the presence of the silica matrix hydroxy groups unbound to amino groups was not assumed. The best-fit results (Table 1) indicate that the other two proton-binding sites assigned to amino groups were present on the NH_2–silica and quinone–silica particles, respectively (reactions C, D, F, and G). The $\log K$ values of the amino groups on the quinone–silica particles were somewhat larger than those on the NH_2–silica particles, which would result from the binding of quinone molecules to the amino groups on the former particles.

The fractions of the U^{VI} adsorbed on the tested silica particles increased with pH, forming characteristic adsorption edges (Figure 1). The adsorption edge on the unmodified silica particles appeared around pH 4. The adsorption edges on the NH_2–silica and the quinone–silica particles appeared around pH 2 and 3, respectively, which was lower than that for the unmodified silica particles. The adsorption on the NH_2–silica and the quinone–silica particles below pH 4, where U^{VI} is not adsorbed on the silica matrix (unmodified silica particles), is due to the association of U^{VI} with amino groups. Below pH 4, a larger frac-

Table 1. Proton-binding stability constants ($\log K$) and functional groups site concentrations (C_f) for the silica particles, which were obtained from the best-fit result for the titration data[a]

Particles		Reaction	$\log K$	C_f/mol g^{-1}
Unmodified silica	(A)	$–OH \rightarrow –O^- + H^+$	-7.42 ± 0.05	$(1.60 \pm 0.18) \times 10^{-4}$
	(B)	$–OH \rightarrow –O^- + H^+$	-9.29 ± 0.10	$(6.85 \pm 1.05) \times 10^{-4}$
NH_2 –silica	(C)	$–NH_2 + H^+ \rightarrow –NH_3^+$	5.57 ± 0.15	$(2.75 \pm 0.28) \times 10^{-4}$
	(D)	$–NH_2 + H^+ \rightarrow –NH_3^+$	8.23 ± 0.07	$(3.17 \pm 0.03) \times 10^{-4}$
	(E)	$–OH \rightarrow –O^- + H^+$	-9.30[b]	$(2.56 \pm 0.33) \times 10^{-4}$
Quinone –silica	(F)	$–NH_2 + H^+ \rightarrow –NH_3^+$	6.82 ± 0.05	$(1.44 \pm 0.37) \times 10^{-4}$
	(G)	$–NH_2 + H^+ \rightarrow –NH_3^+$	5.15 ± 0.55	$(1.29 \pm 0.02) \times 10^{-4}$
	(H)	$–OH \rightarrow –O^- + H^+$	-8.60 ± 0.11	$(1.75 \pm 0.05) \times 10^{-4}$

[a]Each of the silica particles also has proton-binding sites with a $\log K$ of 3.0, where the adsorption of protons on the silica matrixes occurs. [b]Taken front reaction (B).
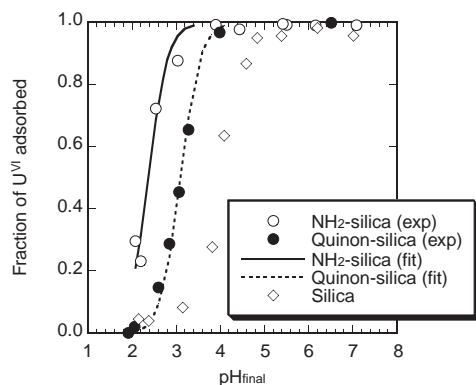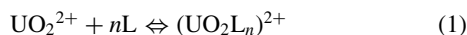
Figure 1. Fractions of U^{VI} adsorbed on silica particles.

tion of U^{VI} was adsorbed on the NH_2–silica particles than on the quinone–silica particles, which is accounted for by the concentration of the amino groups on the NH_2–silica particles being more than twice that on the quinone–silica particles.

Below pH 4, U^{VI} was calculated using the program, the Geochemist's Work Bench®,[14] to be UO_2^{2+} ions. The interaction between UO_2^{2+} ions and amino groups (L) to form surface complexes is expressed by the following equation.

$$UO_2^{2+} + nL \Leftrightarrow (UO_2L_n)^{2+} \tag{1}$$

The stability constant, K_n, for the reaction is given by

$$K_n = \frac{[(UO_2L_n)^{2+}]}{[UO_2^{2+}][L]^n} \tag{2}$$

where $[(UO_2L_n)^{2+}]$ is the concentration of the 1:n uranyl–amino complex, $[UO_2^{2+}]$ is the activity of uranyl ions in solution, and [L] is the concentration of amino groups on the silica particles. The best-fitted adsorption edge was obtained when 1:2 uranyl–amino complexes were assumed, shown by solid and dashed lines in Figure 1. The estimated adsorption edge was not reproduced when we assumed 1:1 complexes. These results strongly suggest that uranyl ions are associated with amino groups in a molar ratio of 1 to 2.

Each of the NH_2–silica and the quinone–silica particles had two amino groups (L_a and L_b) with two different $\log K$ values. The $\log K_2$ values were estimated when 1:2 complexes of $(UO_2L_{a2})^{2+}$ and $(UO_2L_{b2})^{2+}$ were assumed to form simultaneously (Figure 2). The possible $\log K_2$ values range from approximately 7 to 16, and the value increases with $\log K$ of the amino groups. The $\log K_2$ values for $(UO_2L_aL_b)^{2+}$ are 13.6 and 12.4 for the NH_2–silica and the quinone–silica particles, respectively.

None of the UO_2^{2+} ions adsorbed at pH below 4 on the NH_2–silica and the quinone–silica particles were extracted by exchange with 1 M K^+ ions, while the adsorbed UO_2^{2+} ions on those silica particles were quantitatively extracted with a 1 M HCl solution and the mass balances during the whole adsorption–extraction experiments were very good ($C_0 \cdot V/(C_S \cdot V + Q_{KCl} + Q_{HCl}) \approx 1$, where V (l) is the volume of solution). The former result indicates that the association of UO_2^{2+} ions with amino groups is not weak but firm. The formation of stable inner-sphere complexes, with direct binding of ions to complexation sites on the surface with no intervening water molecules, may account for this result.
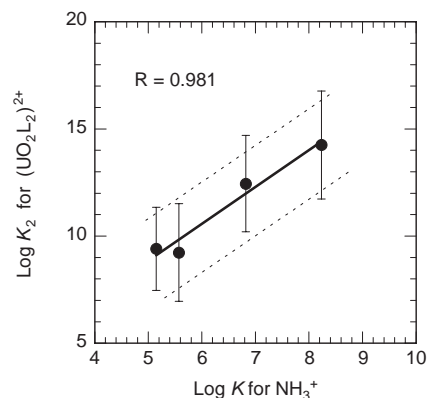

Figure 2. Relation between the proton-binding constants ($\log K$) of amino groups and the U^{VI} binding stability constants ($\log K_2$). The black circles show the averaged values of the possible range of $\log K_2$ values. The correlation coefficient was obtained from the regression line for the averaged $\log K_2$ values.

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