Supporting Information

Spectroscopic Study on Aqueous Uranyl(VI) Complexes with Methoxy- and Methylbenzoates: Electronic and Steric Effects of the Substituents

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Description on extrapolation of the equilibrium data to infinite dilution state using the specific ion interaction theory (SIT)

According to the specific ion interaction theory (SIT), the activity coefficient of ion i (γ_i) in an aqueous solution is expressed as eq. (S1). In eq. (S1), z_i is the charge of ion i, D is the Debye-Hückel term, $\epsilon(i,j)$ is the ion interaction coefficient for an ion pair (i,j), m_j is the molal concentration of ion j in the solution. For a given ionic strength of the solution in molality (I_m), the Debye-Hückel term (D) is expressed as described in eq. (S2), where A and B are the theoretical constants, and a_0 represents an ionic size of the hydrated ion i. Furthermore, the A and B constants can be calculated using eqs. (S3) and (S4), respectively. In eqs. (S3) and (S4), e is the elementary charge, N_A is the Avogadro's number, ε_r is the relative permittivity of the solution, ε_0 is the vacuum permittivity, k_B is the Boltzmann's constant, and T is the absolute temperature of the solution. As summarized in the OECD NEA's guidelines on the SIT,¹ the values of A and Ba₀ are simply considered as 0.509 kg^{1/2}·mol^{-1/2} and 1.5 kg^{1/2}·mol^{-1/2} for all ions in the solution at a pressure of 1 bar and temperature of 25 °C.

$$\log \gamma_i = -z_i^2 D + \sum_j \varepsilon(i,j) m_j \tag{S1}$$

$$D = A\sqrt{I_m}/(1 + Ba_0\sqrt{I_m})$$
(S2)

$$A = e^{3} N_{A}^{1/2} / \{ \ln 10 \times 4\pi \sqrt{2} (\epsilon_{r} \epsilon_{0} k_{B} T)^{3/2} \}$$
(S3)

20

$$\mathbf{B} = \mathbf{e} \{ 2N_{\mathrm{A}} / (\varepsilon_{\mathrm{r}} \varepsilon_{\mathrm{0}} k_{\mathrm{B}} T) \}^{1/2}$$
(S4)

In an aqueous solution, dipole-ion or dipole-dipole interactions and ionic interaction between ions of the same charge are generally negligible except for the condition with very high ionic strength. Therefore, only ionic interactions between oppositely charged ions are considered in the SIT. Besides, the equilibrium constant can be expressed either in molality (β_m) or molarity (β_M) units, and they can be simply converted to each other as given in eq. (S5). In eq. (S5), $\Sigma_r v_r$ is the sum of the stoichiometric coefficients of a chemical reaction, where the sign of the stoichiometric coefficients (v_r) is positive for the products and negative for the reactants. ρ is a factor for the conversion of molarity to molality of background electrolyte, and the ρ factor for aqueous 0.1 M NaClO₄ medium is 1.0075, which is calculated using the reported empirical parameters of the density of aqueous solution.²

$$\log \beta_{\rm m} = \log \beta_{\rm M} + \sum_{\rm r} v_{\rm r} \log \varrho \tag{S5}$$

Finally, the equilibrium constant at zero ionic strength (β°) is expressed as described in eq. (S6), where Δz^2 is the difference of sum of the square of the charge between the products and reactants (eq. (S7)) and $\Delta \epsilon$ is the difference of sum of the ion interaction coefficient between the products and reactants (eq. (S8)). In the case of the chemical equilibrium involving H₂O as a reactant or product (e.g. hydrolysis reaction), the activity of water (a_{H_2O}) is also considered in eq. (S6), and p represents the stoichiometric coefficient of water in the reaction. The sign of p is positive when water is a reactant, and it is negative for the opposite. For 0.1 M NaClO₄ aqueous medium, the

activity of water is 0.9966 at 25 °C according to the OECD NEA's guidelines.¹ Table S1 summarizes the reported ion interaction coefficients of the relevant ion pairs in this study, and Table S2 provides the previously reported log β° of the UO₂OH⁺ and (UO₂)₂(OH)₂²⁺ species. Finally, the hydrolysis constants in molarity unit (log β_{M}) at I = 0.1 M NaClO₄ are calculated to be -5.44 ± 0.24 for UO₂OH⁺ and -5.84 ± 0.04 for (UO₂)₂(OH)₂²⁺. Figure S1 shows the resulted distribution of the hydrolyzed U(VI) species at –log [H⁺] < 3.5.

$$\log \beta_{\rm m} = \log \beta^{\circ} + \Delta z^2 D - \Delta \varepsilon I_{\rm m} + p \log a_{\rm H_2O}$$
 (S6)

$$\Delta z^2 = \sum z_{\text{products}}^2 - \sum z_{\text{reactants}}^2$$
(S7)

$$\Delta \varepsilon = \sum \varepsilon_{\text{products}} - \sum \varepsilon_{\text{reactants}}$$
(S8)

Table S1. Ionic interaction coefficients of the relevant ion pairs in this study

Oppositely charged ion pairs	Value (kg·mol ⁻¹)
ε(H ⁺ , ClO ₄ ⁻)	0.14 ± 0.02^{a}
$\epsilon(Na^+, C_6H_5COO^-)$	$0.17\pm0.05^{\rm b}$
$\epsilon(\mathrm{UO}_2^{2+},\mathrm{ClO}_4)$	0.46 ± 0.03^a
$\epsilon(UO_2OH^+, CIO_4^-)$	-0.06 ± 0.40^{a}
$\epsilon((\mathrm{UO}_2)_2(\mathrm{OH})_2^{2+}, \mathrm{ClO}_4)$	$0.57\pm0.07^{\rm a}$
$\epsilon(UO_2C_6H_5COO^+, ClO_4^-)$	$0.22\pm0.07^{\mathrm{b}}$

^a Taken from reference¹

^b Taken from reference³

Hydrolysis reaction of U(VI)	$\log \beta^{\circ}$
$UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+$	-5.25 ± 0.24^{a}
$2 \text{ UO}_2^{2+} + 2 \text{ H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2(\text{OH})_2^{2+} + 2 \text{ H}^+$	-5.62 ± 0.04^{a}

Table S2. Stability constants of the hydrolyzed uranyl species used in this study

^a Taken from reference⁴



Figure S1. Calculated distribution of the hydrolyzed uranyl species at $-\log [H^+] < 3.5$ (I = 0.1 M NaClO₄).

Factor analysis of UV-Vis absorption spectra of the U(VI)-substituted



benzoate complexations in aqueous solutions

Figure S2. Factor analysis of UV-Vis absorption spectra of the U(VI)-substituted benzoate complexations in aqueous solutions (I = 0.1 M NaClO₄): (A) 2-Methoxybenzoic acid, (B) 3-Methoxybenzoic acid, (C) 4-Methoxybenzoic acid, (D) 2-Methylbenzoic acid, (E) 3-Methylbenzoic acid, (F) 4-Methylbenzoic acid. The absorption by the ligands is negligible in the given spectral range. For all complexations, the eigenvector of the third component in blue is pointlessly noisy, and the corresponding singular value is negligible, indicating that there are only two major uranyl species (free uranyl and a uranyl complex) in the aqueous solutions. The resulted eigenvectors of the first and second components are a linear combination of the single component spectra of the absorbing species, but the coefficients of the linear combinations cannot be

determined by factor analysis alone. Thus, the eigenvectors do not look like the single component spectra of the absorbing species.

Species distribution of the U(VI)-substituted benzoates and hydrolyzed species

in aqueous solutions



Figure S3. Species distribution of all U(VI) species at $-\log [H^+] < 3.3$ (I = 0.1 M NaClO₄): (A) 2-Methoxybenzoic acid, (B) 3-Methoxybenzoic acid, (C) 4-Methoxybenzoic acid, (D) 2-Methylbenzoic acid, (E) 3-Methylbenzoic acid, (F) 4-Methylbenzoic acid. In order to describe the experimental conditions, where the stability constants were determined, the concentrations of both uranium and the ligands are considered to be similar to the samples for spectrophotometric measurements; 2 mM of U(VI) was considered, and the concentrations of the ligands were considered to be 8 mM for ortho- and meta-substituted benzoic acids and 2 mM for parasubstituted benzoic acids.



Figure S4. Species distribution of all ligand species at $-\log [H^+] < 3.3$ (I = 0.1 M NaClO₄): (A) 2-Methoxybenzoic acid, (B) 3-Methoxybenzoic acid, (C) 4-Methoxybenzoic acid, (D) 2-Methylbenzoic acid, (E) 3-Methylbenzoic acid, (F) 4-Methylbenzoic acid. The concentrations of U(VI) and the ligands were considered to be the same, as described in Figure S3.

REFERENCES

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