



Research paper

Rate theory on water exchange in aqueous uranyl ion

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ABSTRACT

We report a classical rate theory approach to predict the exchange mechanism that occurs between water and aqueous uranyl ion. Using our water and ion-water polarizable force field and molecular dynamics techniques, we computed the potentials of mean force for the uranyl ion–water pair as a function of different pressures at ambient temperature. These potentials of mean force were used to calculate rate constants using transition rate theory; the transmission coefficients also were examined using the reactive flux method and Grote-Hynes approach. The computed activation volumes are positive; thus, the mechanism of this particular water-exchange is a dissociative process.

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1. Introduction

Understanding the behavior of aqueous complexes such as uranyl ions in the condensed phase is fundamentally and technologically important because of its direct relevance to the nuclear fuel cycle. Knowledge of solvent-exchange and the kinetic properties of aqueous uranyl ions is essential for the development and improvement of solvent extraction processes used to recover these ions from spent nuclear fuels [1–5].

Significant progress has been made in this particular research area. Wipff and coworkers generated force field parameters for uranyl ions–water from free energy calculations, and reported on molecular dynamics (MD) simulation studies of the complexation and hydration behavior of aqueous uranyl ions [6]. More recently, Kerisit and Liu modified Wipff's ion–water potential parameters and carried out studies on the structure, free energy, and kinetics of the uranyl ion using a variety of theoretical methods [7]. Maginn and co-workers developed classical force field parameters for aqueous actinyl cations using quantum mechanical calculations and validated their results against static properties as well as the dynamical properties of the water–actinyl ion system [8].

The main goal of our work is to advance the understanding of the water-exchange mechanism around the actinyl ion. Knowledge of free energy profiles and rate theory evaluations are important for understanding a wide range of physical and chemical phenomena for these ionic systems. Information from those sources also provides a challenging test of the accuracy of the information derived from force field models. Our work is distinguished from earlier contributions by the methodology and to the extent to

which we have exploited rate theory approaches. The most important values of this work are (1) polarization effects are explicitly included in the potential models, (2) pressure dependence and solvent response to the rate constant were evaluated, and (3) activation volume can be calculated from the rate constants as the function of pressures and this quantity can be compared directly to the experimental measurements. The remainder of this paper is organized as follows. In Section 2, we describe the potential models and simulation methods used. Results and discussion are presented in Section 3, and our conclusions discussed are in Section 4.

2. Potential models, simulations, and methods

For water–water interactions, we employed the Dang–Chang (DC) polarizable water model [9]. Because of uncertainties in the hydration number and hydration energy [7,8], we expended substantial effort in developing the polarizable force field parameters for UO_2^{2+} –water interactions. The functional form that describes the UO_2^{2+} –water interactions is the same as used in the DC model as shown below. The total interaction energy of the system is summarized as follows:

$$U_{\text{tot}} = U_{\text{pair}} + U_{\text{pol}} \quad (1)$$

$$U_{\text{pair}} = \sum_i \sum_{j>i} \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right) \quad (2)$$

and

$$U_{\text{pol}} = -\sum_{i=1}^N \mu_i \cdot E_i^0 - \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \mu_i \cdot T_{ij} \cdot \mu_j + \sum_i \frac{|\mu_i|^2}{2\alpha_i} \quad (3)$$

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Table 1

Optimized potential parameters for water–water [9] and uranyl–water interactions used in the MD simulation. The terms σ and ε are the Lennard-Jones parameters, q is atomic charge, and α is the molecular polarizability.

Atom type	$\sigma(\text{\AA})$	ε (kcal/mol)	$q(e)$	α (\AA^3)
O	3.2215	0.1825	0.0000	0.0000
H	0.0000	0.0000	0.5190	0.0000
M	0.0000	0.0000	−1.0380	1.4440
U	3.3498	0.0270	3.1250	1.0000
O(U)	3.2963	0.4380	−0.5625	0.0000

Table 2

Hydration properties of the UO_2^{2+} - H_2O .

	Coordination number	Hydration enthalpy	First maximum
MD	5.0 ± 0.1	-406 ± 3 kcal/mol	2.40 ± 0.05 \AA
Expt.	4.9 ± 0.4	−397 to 418 kcal/mol	2.40 to 2.42 \AA

Here, r_{ij} is the distance between site i and j , q is the charge, and σ and ε are the Lennard-Jones parameters, E_i^o is the electric field at site i produced by the fixed charges in the system, μ_i is the induced dipole moment at atom site i , and T_{ij} is the dipole tensor. The first term in Eq. (3) represents the charge-dipole interaction, the second term describes the dipole-dipole interaction, and the last term is the energy associated with the generation of the dipole moment μ_i . During molecular dynamics simulations, a standard iterative self-consistent field procedure is used to evaluate the induced dipoles.

We performed several MD simulations to optimize the Lennard-Jones potential and the polarizability parameters for the UO_2^{2+} molecule. The final parameters that reproduce the experimental hydration number and hydration enthalpy are summarized in Tables 1, 2, and Fig. 1.

Eq. (4) was used to calculate the ion–water mean force as an average over the different solvent configurations [10]:

$$F(r) = \frac{1}{2} \langle \vec{r}_u \cdot (\vec{F}_A - \vec{F}_B) \rangle. \quad (4)$$

In this expression, F_A and F_B are the forces acting on the solutes. The term, \vec{r}_u , which is a unit vector along the A–B direction, is defined as:

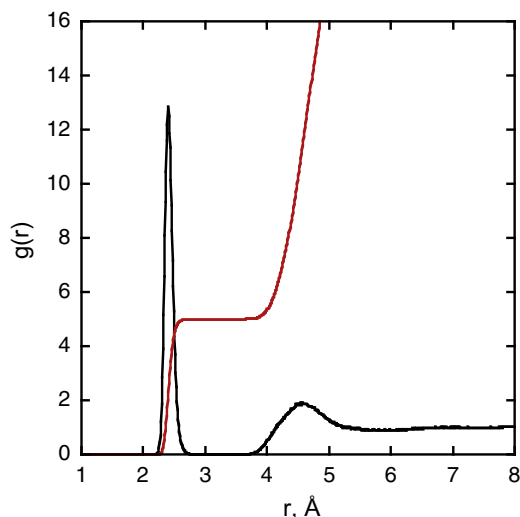


Fig. 1. Computed rate density function and corresponding running coordination number for U–O at ambient conditions.

$$\vec{r}_u = \vec{r}_{AB}/|r_A - r_B| \quad (5)$$

The potential of mean force (PMF), $W(r)$, is calculated as:

$$W(r) = - \int_{r_0}^{r_s} \langle F(r) \rangle dr. \quad (6)$$

We evaluated PMFs along the center-of-mass separation between the UO_2^{2+} - H_2O interactions with the separation between them incremented by 0.1 \AA. At each center-of-mass separation, the average $F(r)$ was determined from a 2-ns simulation time, preceded by a 500-ps equilibration period. The uncertainties of the PMFs were ± 0.05 kcal/mol as estimated by determining the force averaged (the corresponding PMFs) over four equally spaced time frames during the production. The systems investigated consisted of one UO_2^{2+} in 1066 water molecules. All simulations were performed in an NVT ensemble at 300 K, with periodic boundary conditions applied in all three directions and a time step of 2 fs. To compute the ΔV^\ddagger , we carried out three studies at pressures of 0, 2, and 4 kbar, which correspond to cubic box lengths of 31.8, 31.2, and 30.7 \AA, respectively. We used a modified version of the Amber 9 software package to perform all MD simulations [11]; the Ewald summation technique to handle long-range electrostatic interactions [12]; and the SHAKE algorithm to fix the internal water and UO_2^{2+} geometries [13].

3. Results and discussions

We start with the PMFs for the UO_2^{2+} - H_2O pair at pressures of 0, 2, and 4 kbar, and then continue with rate theory results using the transition state theory (TST) [14], reactive flux (RF) [15], Grote-Hynes (GH) [16], and Impey, Madden, and McDonald (IMM) methods [17]. We end the section with the computed activation volume, ΔV^\ddagger . Fig. 2 shows the computed PMF values obtained at 300 K for the three pressures normalized to the contact UO_2^{2+} - H_2O pair free energy minimum at 0 bar. As expected, the shapes of the computed PMFs are very similar, and the changes are small but noticeable. We observe two effects: (1) an increase in pressure stabilizes the contact UO_2^{2+} - H_2O pair and (2) the free energy barrier for escaping the first hydration shell increases from 6.82 ± 0.05 kcal/mol at 0 bar to 7.20 ± 0.05 kcal/mol at 4 kbar. These changes are accompanied by a small change in the transition state distance from 3.25 \AA to 3.24 \AA. For a given PMF, the rate constant for the exchange process can be computed using TST as follows [14]:

$$k^{\text{TST}} = \sqrt{\frac{k_b T}{2\pi\mu}} \frac{(r^*)^2 e^{-\beta W(r^*)}}{\int_0^{r^*} r^2 e^{-\beta W(r)} dr} \quad (7)$$

where r^* is defined as the position of the barrier top, μ is the ion–water reduced mass, k_b is the Boltzmann constant, and T is the temperature. Using the computed PMFs and transition state distances, we computed the rate constant, k^{TST} , for the exchange process using Eq. (7); the results for k^{TST} are 1.48×10^{-4} , 1.09×10^{-4} , and 0.85×10^{-4} ps $^{-1}$ at 0, 2, and 4 kbar, respectively. These results are summarized in Table 3. We found k^{TST} increases with increasing pressure, and this trend would be expected by examining at the PMFs and the barrier heights. Eq. (8) gives the pressure dependence of the rate constant at constant temperature [18].

$$\Delta V^\ddagger = -RT \left(\frac{\partial \ln(k)}{\partial P} \right)_T \quad (8)$$

where ΔV^\ddagger is the activation volume, T is the temperature, R is the gas constant, k is the rate constant, and P is the pressure. An approximate solution to Eq. (8) can be obtained using Eq. (9):

$$\ln \left(\frac{k_p}{k_0} \right) = -\Delta V^\ddagger \frac{P}{RT} \quad (9)$$

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