Supermolecule density functional calculations on the water exchange of aquated Al(III) species in aqueous solution†

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Supermolecule density functional calculations suggest the dissociative (D) mechanism for the water exchange of aquated Al(III) species in aqueous solution and the calculated results agree well with experimental data.

The water exchange of aquated metal ions between the first hydration sphere and the bulk water is significant to understand the reactivity of metal ions in solution. Although the experimental methods can determine the water exchange rate, they are not accessible for the detailed microscopic nature of the underlying reaction mechanism.[1,2] Recent theoretical works[3–5] simulated the water exchange of metal ions using the cluster model in which the solvent was neglected or treated with self-consistent reaction fields, but this model did not reproduce properties accurately for the metal ions with strong second shell solvation such as Al(III).[6] In this communication, we simulated the water exchange on aquated Al(III) species (eqn (1)) successfully.

$$[M(H_2O)_n]^{z+} + nH_2O^* \leftrightarrow [M(H_2O^*)_n]^{z+} + nH_2O \quad (1)$$

For understanding complicated reactions and those at mineral surfaces,[7,8] the rate constants and activation parameters for water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ were determined from kinetic ^{17}O NMR experiments.[9–11] For the detailed information the water exchange mechanisms on $Al(H_2O)_6^{3+}$ were simulated based on the gas-phase cluster model.[12] The models only involved the gas-phase clusters which neglected the solvent effect. Recently, Hanauer *et al.*[13] using the gas-phase cluster model with four additional water molecules investigated the water exchange of $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$. Since their model did not consider the bulk solvent effects, their computed activation energies with the consideration of the second hydration sphere deviated from the corresponding experimental values.[10,11]

In the current study, we employed a supermolecule model on the water exchange of $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ by density functional theory calculations. In the proposed supermolecule model, six explicit solvent water molecules are added to core complexes ($Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$) for consideration of the explicit solvent effect induced by the hydrogen bonding interaction between the first and second coordinated water molecules, and the remaining solvent water is modeled as a polarizable dielectric continuum medium surrounding the supermolecular reaction system. For comparison, the gas-phase model (core complexes with one additional water molecule) calculations were also performed at the same level. All the structures of the gas-phase species and supermolecular species were fully optimized in the gas phase at B3LYP/6-311+G** level[13–16] using density functional theory, and then single-point PCM[17,18] calculations were performed in aqueous solution. E(aq) and E_s(aq) indicate bulk solvent effect on the optimized gas-phase species and supermolecular species, respectively. Vibrational frequency calculations were carried out to confirm the stable structures and the transition state. To obtain accurate energies, single-point energies were further calculated using MP2[19] at 6-311+G** level. The Gaussian 03 suite of programs was used throughout.[20] The reactants, transition states and products in the gas-phase reaction system for water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ are denoted as R1, TS1, P1, R2, TS2, and P2, respectively, and those in the supermolecular reaction system are denoted as R_s1, TS_s1, P_s1, R_s2, TS_s2, and P_s2, respectively. The parameters used for structural changes comprise average bond length between aluminium and the first coordinated water molecules r(Al–O), the bond distance between aluminium and the leaving water molecule $r(Al–O_L)$, the bond distance between the leaving water and hydrogen of the neighboring water in the first coordination sphere $r(H–O_L)$, and the sum of the distance between aluminium and the water molecules in the first and second spheres $\sum r$(Al–O).

Concerning the number of the nonbulk water molecules included in the supermolecular model to describe the explicit solvent effect, six explicit solvent water molecules were considered in the present study. Until now, the solvation sphere around hydrated metal ions has usually only been considered explicitly for the first and to some extent for the second coordination spheres, usually for only one or at most four additional water molecules.[13] For confirmation of the sufficiency of the adopted explicit structure models, we also modeled the supermolcules with the consideration of four and five explicit water molecules for the water exchange on $Al(H_2O)_6^{3+}$. As shown in Table 1, the calculated energy barriers with the consideration of five and six explicit water molecules are very close and in good agreement with the experimental data, and thereby the convergence with respect to the number of water molecules is satisfactory for $n > 5$. In addition, a large number of explicit water molecules might produce a very large number of orientations associated with local minima, which may lead to biased conclusions. Nevertheless, the supermolcular model in this study should be less effected by the orientation problem due to two reasons. Firstly, the orientations of the explicit water molecules are simply determined by the solute–solvent hydrogen-bonding. Secondly, the orientations of

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Table 1 Energy barriers (kJ mol^{-1}) with the consideration of four, five and six explicit water molecules for water exchange on $Al(H_2O)_6^{3+}$

No. waters	$n = 4$	$n = 5$	$n = 6$	($\Delta H^{\ddagger}$/kJ mol^{-1})[a]
ΔE_s(aq)/kJ mol^{-1}	83.1	74.6	70.1	73(±4)

[a] Experimental values for $\Delta H^{\ddagger}$ from ref. 10.

the six water molecules surrounding reactants, transition states and intermediates are closely connected with each other for the confirmation by IRC calculations. Therefore, we expect that our adopted supermolecule model will accurately model the water exchange on aquated Al(III) species.

The fully optimized structures of the species involved in the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ for the supermolecular reaction system are shown in Fig. 1. For the reactant R_s1, six additional solvent water molecules simultaneously form strong hydrogen bonds with the first coordinated water molecules. Detaching one of the first coordinated water molecules leads to the transition state TS_s1. In the transition state TS_s1, the leaving water molecule forms one hydrogen bond, $r(H–O_L)$ = 1.911 Å, with one of the coordinated water molecules and is located between the first and second coordination spheres at a distance of 2.847 Å. On lengthening the distance between aluminium and the leaving water molecule, the leaving water molecule becomes part of second coordination sphere, and the product P_s1 forms. As depicted in Fig. 1, the leaving water molecule in P_s1 forms one hydrogen bond with one neighboring coordinated water molecules in the linear way and is located in the second coordination sphere at a distance of 3.964 Å. From Table 2, it can be seen that the average bond length between aluminium and the coordinated water molecules decreases from 1.930 Å in R_s1, to 1.880 Å in TS_s1, and finally to 1.871 Å in P_s1 as the reaction proceeds. The overall difference of this mean bond length between reactant and product is obvious, about ~0.06 Å, which can be interpreted as bond strengthening induced by the decrease of the coordinated water molecules.

For the reactant R_s2, as a result of the strong *trans*-activating effect of the hydroxyl ligand, the coordinated water molecule *trans* to the hydroxyl is easier to leave than the others. On lengthening the distance between the leaving water molecule and center Al(III) to 2.741 Å, the leaving water molecule forms one hydrogen bond in a linear way, $r(H–O_L)$ = 2.044 Å, with one of the first coordinated water molecules, and then transition state TS_s2 forms. In the product P_s2, the distance between the leaving water molecule and the center aluminium is lengthened to 4.050 Å. As shown in Table 2, as a result of decrease of the coordination number, the mean Al–O bond length stepwise decreases as the reaction proceeds.

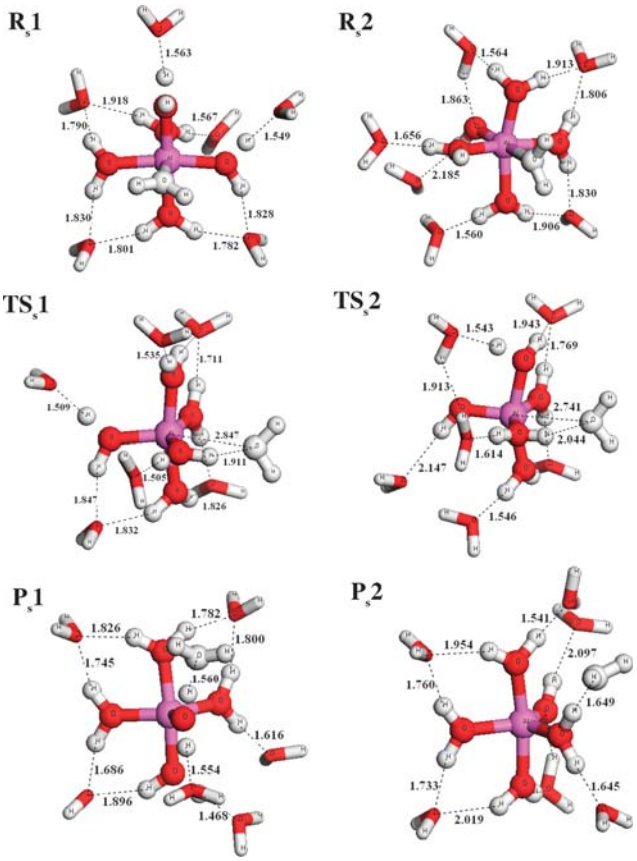

Fig. 1 Optimized structures for water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ in the supermolecular reaction system. The oxygen atom of the leaving water molecule is colored with white to differ from the others.

Comparing the mean Al–O bond lengths of reactants, transition states and products between the gas-phase reaction system and supermolecular reaction system, we found that the mean Al–O bond lengths in supermolecular reaction system are shorter and closer to the available experimental data[21] (1.90 Å for R_s1) than those in gas-phase reaction system, demonstrating the consideration of a second coordination sphere can describe the structural parameters more accurately. As shown in Table 2, the changes of the sum of Al–O bond length between the transition state and reactant for the supermolecular reaction system are positive, which are consistent with the change of available activation volume (+5.7 cm^3 mol^{-1} for $Al(H_2O)_6^{3+}$)[9] and suggest the D mechanism[1] for the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$.

The computed energy barriers for the gas-phase reaction system and the supermolecular reaction system for the water

Table 2 Selected structural parameters (Å) for water exchange on $A(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$

Complex	r(Al–O$_L$)/Å	r(H–O$_L$)/Å	r(Al–O)/Å	$\sum r$(Al–O)/Å	r(Al–O)/Å[a]
R_s1	—	—	1.930	35.141	1.90
TS_s1	2.847	1.911	1.880	35.661	—
P_s1	3.964	1.560	1.871	36.581	—
R_s2	—	—	1.939	35.170	—
TS_s2	2.741	2.044	1.883	35.551	—
P_s2	4.050	1.649	1.870	37.002	—

[a] Experimental values for r(Al–O) from ref. 21.

Table 3 Selected relative energies (kJ mol^{-1}) for water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$

Complex	ΔE(g)/kJ mol^{-1}[a]	ΔE(aq)/kJ mol^{-1}[b]	ΔE_s(g)/kJ mol^{-1}[c]	ΔE_s(aq)/kJ mol^{-1}[d]	($\Delta H^{\ddagger}$/kJ mol^{-1})[e]
TS1/TS$_s$1	63.0	88.9	38.8	70.1	73(±4)
P1/P$_s$1	48.7	79.2	10.5	61.2	
TS2/TS$_s$2	40.3	55.2	20.0	36.7	36.4(±5)
P2/P$_s$2	2.2	37.1	−4.9	23.9	

[a] For the gas-phase reaction system. [b] Bulk solvent effect on the gas-phase species. [c] For the supermolecular reaction system. [d] Bulk solvent effect on the supermolecules. [e] Experimental values for $\Delta H^{\ddagger}$ from refs. 10 and 11.

exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ are summarized in Table 3. As shown in Table 3, The energy barriers for the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ in the gas-phase reaction system are 63.0 and 40.3 kJ mol^{-1}, respectively. However, after accounting for the bulk solvent effect the energy barrier for water exchange on $Al(H_2O)_6^{3+}$ is increased to 88.9 kJ mol^{-1}, while the energy barrier for water exchange on $Al(H_2O)_5(OH)^{2+}$ is increased to 55.2 kJ mol^{-1}. With the experimental conclusion in mind, one can see that the energy barriers from gas-phase reaction system deviate largely from the corresponding experimental data, indicating that gas-phase models can not correctly describe the energies of the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$.

From Table 3, one can note that for the supermolecular reaction system, the energy barriers are decreased to 38.8 and 20.0 kJ mol^{-1} relative to the gas-phase reaction system for the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$, respectively, indicating that the involvement of the second hydration sphere is important to promote the water exchange reactions. It is interesting to note that the reaction barriers are increased substantially after accounting for the bulk solvent effects by PCM. With the consideration of the bulk solvent effects, the energy barriers for the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ are increased to 70.1 and 36.7 kJ mol^{-1}, respectively, and the reaction energies are also increased to 61.2 and 23.9 kJ mol^{-1}, respectively, which underscores the importance of the long-range electrostatic interactions. Comparing the results listed in Table 3, we found that both the explicit water effects and bulk water effects have great shifts on the values of energy barriers, and that the explicit water effects reduce the energy barriers while the bulk effects increases the energy barriers.

Upon comparing the calculated energy barriers for water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ with the experimental $\Delta H^{\ddagger}$ values, we found that the calculated values are in good agreement with the experimental values, namely, the calculated values 70.1 kJ mol^{-1} and 36.7 kJ mol^{-1} compared with the experimental values 73 (±4) kJ mol^{-1} and 36.4 (±5) kJ mol^{-1}, respectively.[10,11]

We have investigated the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ in aqueous solution by density functional theory calculations. Our results support the conclusion that the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ proceeds *via* a D mechanism.[1] The computed activation energies $\Delta E^{\ddagger}$ for $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ are in good agreement with the experimental values for $\Delta H^{\ddagger}$. Our calculated results indicate that both the explicit water molecules in the second hydration sphere and bulk solvent water have great influence on the energy barriers. It is interesting that the involvement of the explicit water molecules decreases the energy barriers for the water exchange reactions, while the bulk solvent effect increase the energy barriers.

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