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Acid dissociation mechanisms of $Si(OH)_4$ and $Al(H_2O)_6{}^{3+}$ in aqueous solution

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Abstract

Silicic acid and the hexa-aqua of Al^{3+} are fundamental model aqueous species of chemical importance in nature. In order to investigate their hydroxyl dissociation mechanisms, Car–Parrinello molecular dynamics (CPMD) simulations were carried out, which allow treating the solutes and solvents on the same footing. The method of constraint was employed to trigger the reactions by taking coordination number as the reaction coordinate and the thermodynamic integration was used to obtain the free-energy profiles. The approximate transition states were located and the reactant and product states were also characterized. The free-energy changes of dissociation are found about 15.0 kcal/mol and 7.7 kcal/mol for silicic acid and Al-aqua, respectively. From the simulation results, the first p*K*as were calculated by using two approaches, which are based on the pristine thermodynamic relation and the RDF (radial distribution function)-free energy relation, respectively. Because of more uncertainties involved in the RDF way, it is suggested that the pristine way should be favored, which shows an error margin of 1 p*K*a unit. This study provides an encouraging basis for applying the present methodology to predict acidity constants of those groups that are difficult to measure experimentally.

1. INTRODUCTION

Silicon and aluminium are respectively the second and the third most abundant elements on the earth. Understanding their aqueous chemistry is critical for geochemistry, environmental sciences and material syntheses (Iler, 1979; Sigel and Sigel, 1988; Yokel, 2004). Silicic acid and the hexa-aqua of Al^{3+} are their basic forms in water and according to hydroxyl dissociation and dehydration reactions, they can evolve to a broad spectrum of species in aqueous solutions, for example, $SiO(OH)_3{}^-$ and $SiO_2(OH)_2{}^{2-}$; $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)_2{}^+$ and $Al(OH)_4{}^-$ (StÖber, 1967; Martin, 1988, 1991). Furthermore, these species can form larger polynuclear clusters through condensation reactions, which eventually lead to the crystal growths, e.g. Al/Si containing (hydr)oxides, zeolites and clay minerals (Casey and Rustad, 2007; Casey et al., 2009; Trinh et al., 2009). In all of these processes, the dissociations of the coordinated hydroxyls and waters are key reaction steps and therefore, it is obvious that the relevant acidity constants and dissociation mechanisms are central for understanding their geochemical properties (Casey et al., 2009).

In the previous studies, first-principles techniques have been applied to investigate the dissociations of hydroxyls and water of the small Al- and Si- containing clusters. For example, Rustad et al. (2000a) found a correlation between the calculated gas-phase p*K*as and the measured aqueous phase values of silicic acid; Bickmore et al. (2004, 2006) have proposed a bond–valence approach to calculate acidity constants and applied it to a broad spectrum of species. In the studies of Kubicki (2001) and Sefcik and Goddard (2001), they correlated the deprotonation

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energies with the measured p*K*as. In those calculations, the solvent effects were simplified by inserting several water molecules around or with empirical continuum models. But actually, the products of those approaches are still far from the real nature of the reactive events in condensed phases. In condensed phase reactions, the dynamical fluctuations form the basis of entropy component of free energies (Sprik, 1998). However, in the traditional quantum chemical ways, almost all analyses are based on the static calculations, e.g. geometry optimization. Therefore the results are actually obtained under absolute zero and thus the entropy contribution is hard to include. Furthermore, in the reactions involving proton transfer, the solvents effects are more significant because the solvent (e.g. water) can directly participate in the reactions as reactant or catalyst (van Erp and Meijer, 2004; Marx, 2006). These factors make it necessary to treat the explicitly solvated systems under a finite temperature and by using full quantum mechanical techniques.

In this study, we employ first-principles molecular dynamics technique to investigate the dissociation mechanisms of $Si(OH)_4$ and $Al(H_2O)_6^{3+}$. With Car–Parrinello molecular dynamics (Car and Parrinello, 1985), the solutes and solvents are simulated on the same footing. The dissociation reaction is an activated process, i.e. it is far beyond the timescale accessible to present-day CPMD simulation (i.e. tens of picoseconds). We therefore enforce the reactive event by using the method of constraints (Carter et al., 1989; Sprik and Ciccotti, 1998), and calculate the free-energy profile by thermodynamic integration of the average constraint force and derive the acidity constants.

Another goal of this study is to test the methodology of p*K*a prediction. If the technique can be calibrated on these known small systems, it should be transferable to predicting the acidities of more complex systems of (geo)chemical importance, which are usually difficult to measure experimentally. For example, hydroxyls and chemically-adsorbed water widely distribute on the edge surfaces of clay minerals and (hydro)oxides (e.g. Si, Al, Mn, Fe-containing), which are highly chemically reactive and play active roles in many interfacial reactions (Rustad et al., 1999, 2000b, 2001; Bickmore et al., 2003; Churakov, 2006, 2007; Liu et al., 2008; Casey et al., 2009). For these systems, the broken surfaces are complicated by themselves and the electrostatics of the substrates spread into the solution phases, and therefore, the first-principle MD simulation seems the only possible way to tackle the dissociation mechanisms of the surface groups.

2. METHODOLOGY

2.1. Car–Parrinello MD

The simulation cell is a periodically repeated cubic box of side length 10.5 Å. The $Si(OH)_4$ and Al-aqua systems contain 34 and 38 water molecules, respectively, which reproduce the density of water under ambient condition. The electronic structures are calculated in the framework of density functional theory and the exchange-correlation is described by BLYP functional (Becke, 1988; Lee et al., 1988), which has been proven able to accurately describe the behaviors of water and proton (e.g. Laasonen et al., 1993; Marx et al., 1999). The norm-conserving Martins–Troullier pseudopotentials (Troullier and Martins, 1991) are used to describe the interaction of the valence electrons and the core states and the Kleinman–Bylander scheme (Kleinman and Bylander, 1982) is applied. The orbitals are expanded in plane wave basis sets with a kinetic energy cutoff of up to 70 Ry. For the $Al(H_2O)_6^{3+}$ system, a neutralizing background charge is added.

The molecular dynamics simulations are performed by using the CPMD package (CPMD version 3.11). The hydrogen is assigned a mass of deuterium. The fictitious electronic mass is set to 1200 au and the equation of motion is integrated with a time step of 0.168 fs, which maintains the adiabatic conditions. The temperature is controlled at 300 K with the Nosé–Hoover thermostat. For each constrained simulation, MD is carried out with the reaction coordinate fixed at the desired value. Each unconstrained/constrained MD trajectory includes a production step of 6 ps and a prior equilibration run lasting 3 ps. The statistics are collected every 6 steps for all simulations.

2.2. Method of constraint

The reaction event is enforced by the method of constraint and the relative free energies (ΔF) are obtained by integrating the averaged force (f) along the reaction coordinates via the thermodynamic integration relation,

$$\Delta F(Q) = -\int_{Q_0}^{Q} dQ' f(Q') \tag{1}$$

The reaction coordinate Q is some geometric parameter which represents the progress of the reaction path. It is an analytical function of the cartesian coordinate ($\mathbf{r}^N$), for example, bond-length, bond angle, torsion angle and coordination number.

For the distance constraint, it has been shown that the averaged force equals the Lagrange multiplier (λ) and for more general types, the force has the following form (Sprik and Ciccotti, 1998),

$$f(Q') = \frac{\langle Z^{-1/2}[\lambda - k_B T G]\rangle_{Q'}}{\langle Z^{-1/2}\rangle_{Q'}} \tag{2}$$

The bracket means the time-average over the MD trajectory by setting Q to the desired value and the first time derivative to 0. k_B and T are the Boltzmann constant and temperature, respectively. The weighting factor Z and the correction term G are defined as,

$$Z = \sum_{i}^{N} \frac{1}{m_i}\left(\frac{\partial Q}{\partial r_i}\right)^2 \tag{3}$$

$$G = \frac{1}{Z^2}\sum_{ij}^{N} \frac{1}{m_i m_j}\frac{\partial Q}{\partial r_i}\frac{\partial^2 Q}{\partial r_i \partial r_j}\frac{\partial Q}{\partial r_j} \tag{4}$$

where N means the number of the involved atoms and m denotes the atomic mass.

In the acid dissociation simulation, the coordination number (CN) of the reactive hydroxyl oxygen is chosen as