Molecular Dynamics Calculation of the Activation Volume for Water Exchange on Li$^+$

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The rates of water exchange around aquo ions and polynuclear complexes are fundamental to aqueous chemistry.[1] The activation volume ($\Delta V^\ddagger$), given by the pressure dependence of the rate constant, is the key indicator of the mechanism of water exchange.[2] It is generally thought that the partial molar volume of the transient exchanging water molecule controls the sign and magnitude of $\Delta V^\ddagger$. This contribution is added to the system in the case of a dissociative mechanism and taken away in the case of an associative mechanism.[2] As a corollary, the barrier to the water exchange reaction should increase with pressure for a dissociative mechanism and decrease with pressure for an associative mechanism. Since it is not a simple matter to determine the associative/dissociative character of an exchange reaction by any means other than through measurement of $\Delta V^\ddagger$, it has not been possible to test this hypothesis directly.

Furthermore, the pressure-dependence of a reaction rate can be separated into contributions arising from the effect of pressure on the barrier height and contributions arising from the effect of pressure on the coefficient of transmission across the barrier.[3] In the standard interpretation of activation volume data,[2] it is implicitly assumed that the pressure-dependence of the free energy of activation controls the pressure dependence of the reaction rate. It is not known to what extent pressure-dependent transmission effects might contribute to the $\Delta V^\ddagger$ values measured for aquo ions. Such effects have been shown to make an important contribution to $\Delta V^\ddagger$ in some systems, for example, isomerization reactions in cyclo-hexane.[3b] If the contributions are significant, then the standard interpretation of activation volume data might need revision. In this study we use molecular dynamics simulations to calculate directly, for the first time, the effect of pressure on both the barrier height and the transmission coefficient for water exchange around an aqueous ion. Previous estimates of activation volume have been indirect, based on the difference in solvent-excluded volume between the transition state and minimum energy state of the complex.[1a] We find a clear correspondence between an associative exchange mechanism and a negative activation volume, but also show that pressure-dependent transmission effects can make an important contribution to the total activation volume.

We choose Li$^+$(aq) because it has been shown that existing Li$^+$–H$_2$O potential functions provide a reasonable prediction of the zero-pressure water exchange rate.[4] The exchange mechanism, though involving a somewhat diverse set of configurations, is demonstrably highly associative for systems governed by these potential functions,[4] and also in ab initio calculations.[5] While $\Delta V^\ddagger$ has not been determined experimentally for Li$^+$(aq), an associative mechanism with a large negative activation volume, similar to the 4-fold

coordinated Be^{2+}(aq) (-13.6 cm^3/mol)[1b] is expected. For comparison Mg^{2+}(aq), which is 6-fold coordinated, has an activation volume of $+6.7$.[1b]

The methods used here follow almost exactly those used in a previous study of the water exchange rate for Li$^+$.[4a] We use the Li$^+$–H$_2$O potentials given there, as well as the reactive flux method[6] to calculate the rate of exchange of water around Li$^+$ as a function of pressure. The rate constant is taken as $k_{RF} = k_{plateau} k_{TST}$. k_{TST} is the transition state rate constant calculated from the centrifugally averaged effective potential of mean force $W_{eff}(r)$:[4]

$$k_{TST} = \sqrt{\frac{1}{2\pi\mu\beta}} \frac{\exp(-\beta W_{eff}(r^*))}{\int_0^{r^*} \exp(-\beta W_{eff}(r)) \, dr} \tag{1}$$

where r, the reaction coordinate, is the distance between the Li$^+$ ion and the exchanging water molecule, r^* is the position of the maximum in the $W(r)$, μ is the reduced mass, and $\beta = 1/k_b T$. The transmission coefficient $k_{plateau}$ is extracted from the plateau value of the time-dependent transmission coefficient as calculated from:[6]

$$k(t) = \frac{\langle \delta \, [r(0) - r^*] \, \dot{r}(0) \, \theta[r(t) - r^*] \rangle}{\langle \delta[r(0) - r^*] \, \dot{r}(0) \, \theta[\dot{r}(0)] \rangle} \tag{2}$$

$\theta[r(t) - r^*]$ differentiates reactants ($r > r^*$; $\theta[r(t) - r^*] = 1$) from products ($r < r^*$; $\theta[r(t) - r^*] = 0$).

Runs were carried out for the Li$^+$ ion in 216 water molecules at (constant) water densities of 18.01, 17.39, and 16.81 cm^3/mol which correspond to pressures of 0, 100, and 200 ($\pm$ 0.7) MPa. The Ewald method was used to calculate the charge–charge interactions. The equations of motion were solved with the velocity Verlet integrator with a time step of 1.34 fs. Constraints were enforced with RATTLE,[7] both for the rigid water and for the constrained ion–water runs. The potential of mean force was calculated using the weighted histogram analysis method (WHAM).[8] Biasing was done with a harmonic spring, $^1/_2 k_{sp}(r - r_0)^2$, with $k_{sp} = 14000$ kJ/mol/nm^2. We used 10 windows with r_0 spaced 0.01 nm apart between 0.180 and 0.290 nm. Histograms of $r_{Li-H_2O^*}$ for each window were accumulated over 670 ps. $W(r)$ was calculated on 100 bins between 0.175 and 0.300 nm. The WHAM equations were solved to a tolerance of 0.00001. Errors, estimated via Monte Carlo bootstrap analysis, were less than 0.02 kJ/mol at each bin.[9]

The value $k(t)$ was calculated by harvesting configurations 6.7 ps apart from constant-temperature runs (298.15 K, thermostat of Berendsen and co-workers;[10] coupling constant = 0.125 ps) of 5.36 ns with r_{Li-O^*} constrained at 0.265 nm. Each harvested configuration was integrated forward and backward for 2 ps in constant-energy simulations, with the Li–O* constraint removed, to find the plateau value of $k(t)$. The value of $k_{plateau}$ was taken from the average of $k(t)$ over the last 1 ps of simulation. The final value of $k_{plateau}$, at

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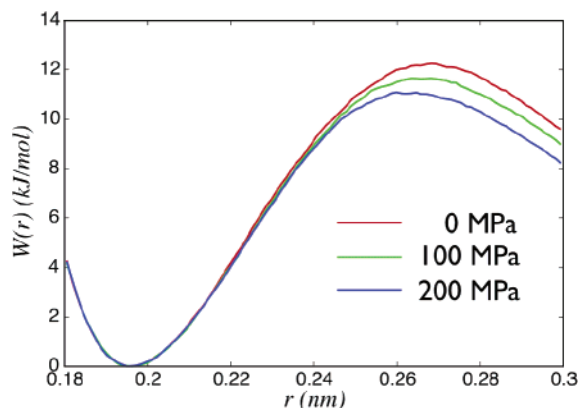‡ Georgia Institute of Technology.

Figure 1. Pressure dependence of the potential of mean force $W(r)$. Uncertainties in the barrier are not shown because they are less than 0.02 kJ/mol

Table 1. Pressure Dependence of Activation Barriers and Rate Coefficients

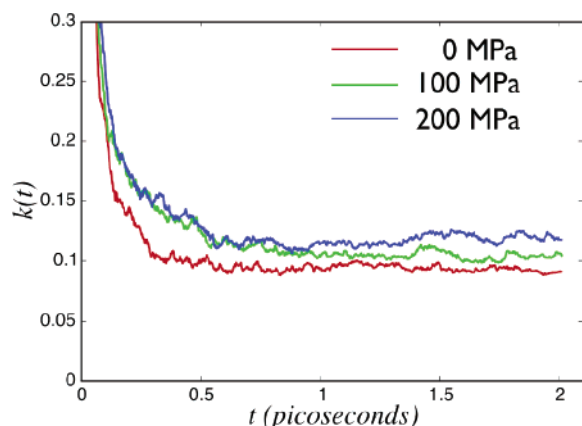| pressure (MPa)	$W(r^*)$ (kJ/mol)	k_{TST} (ns^{-1})	k	k_{RF} (ns^{-1})
0	12.25	52.9	0.094	4.97
100	11.64	66.8	0.104	6.94
200	11.07	84.1	0.118	9.92
$\Delta V^{\ddagger}$ (cm^3/mol)		−5.7		−8.5

Figure 2. Pressure dependence of the transmission coefficient $\kappa(t)$. Errors in the final value, $\kappa_{plateau}$ are ±0.01.

each pressure, was averaged over four repetitions of this procedure (3200 configurations total).

The pressure dependence of the potential of mean force is shown in Figure 1. Barriers are reported in Table 1 and have an error less than 0.02 kJ/mol. The barrier decreases by about 0.6 kJ/mol with every 100 MPa increase in pressure. The numerical data in Table 1 can be used to estimate an activation volume through the equation $\Delta V^{\ddagger} = -RT[\partial \ln(k/k_0)/ \partial P]$. If k is taken as k_{TST}, $\Delta V^{\ddagger}_{TST} = -5.7$ cm^3/mol.

The calculated pressure dependence of the transmission coefficient in given in Figure 2. The numerical data are noisy but clearly establish a trend of increasing transmission with increasing pressure. Thus, the pressure dependence of the barrier height is, in the case of this model Li$^+$ system, reinforced by the pressure dependence of the transmission coefficient. ‡ It is evident from Figure 2 that the ∼100 ns used here to obtain the rate should be regarded as a minimum computational time to define the pressure-dependence of the transmission coefficient.

The numerical data allow several questions to be answered for this model system. The calculated $\Delta V^{\ddagger}$ is indeed negative, in line with both the expected associative character of the exchange mechanism and the observations of individual trajectories[4a]. Thus, for the first time, there is direct verification of the correspondence between an associative exchange reaction and a negative $\Delta V^{\ddagger}$.

The calculations indicate that the pressure dependence of the transmission coefficient can make an important contribution to $\Delta V^{\ddagger}$; 2−3 cm^3/mol can be significant considering that experimentally determined activation volumes for aquo ions range from −13 to +13 cm^3/mol[1b]. The precise contributions to $\Delta V^{\ddagger}$ from the barrier height and transmission coefficient may depend on the chosen reaction coordinate (which is arbitrary in the reactive flux method), but the effect of pressure on the barrier height is not, in general, sufficient to predict $\Delta V^{\ddagger}$. It would be useful to search for a better choice of reaction coordinate (with a higher transmission coefficient) using transition-path approaches.[11] Nevertheless, accurate calculation of $\Delta V^{\ddagger}$ will require dynamical simulation; calculations based entirely on volume estimation[1a] will not address the transmission effects at all. Whether the transmission effects would always contribute negatively to $\Delta V^{\ddagger}$ is an interesting question for further investigation. The effects of explicit solvent polarization, here ignored, might also be expected to make an important contribution.

These calculations imply that inferring mechanistic information from the sign of the activation volume could be problematic for water exchange rates on polynuclear clusters[12] where $\Delta V^{\ddagger}$ can be small (+3 ± 1 cm^3/mol for GaO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}^{7+}$$_{aq}$) and where transmission effects would be expected to be very different from octahedral aquo ions. Surface environments would present similar difficulties.[13]

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