

Solvent Electronic Polarization Effects on $\text{Na}^+ - \text{Na}^+$ and $\text{Cl}^- - \text{Cl}^-$ Pair Associations in Aqueous Solution

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Supporting Information (SI) Figures S1-S5.

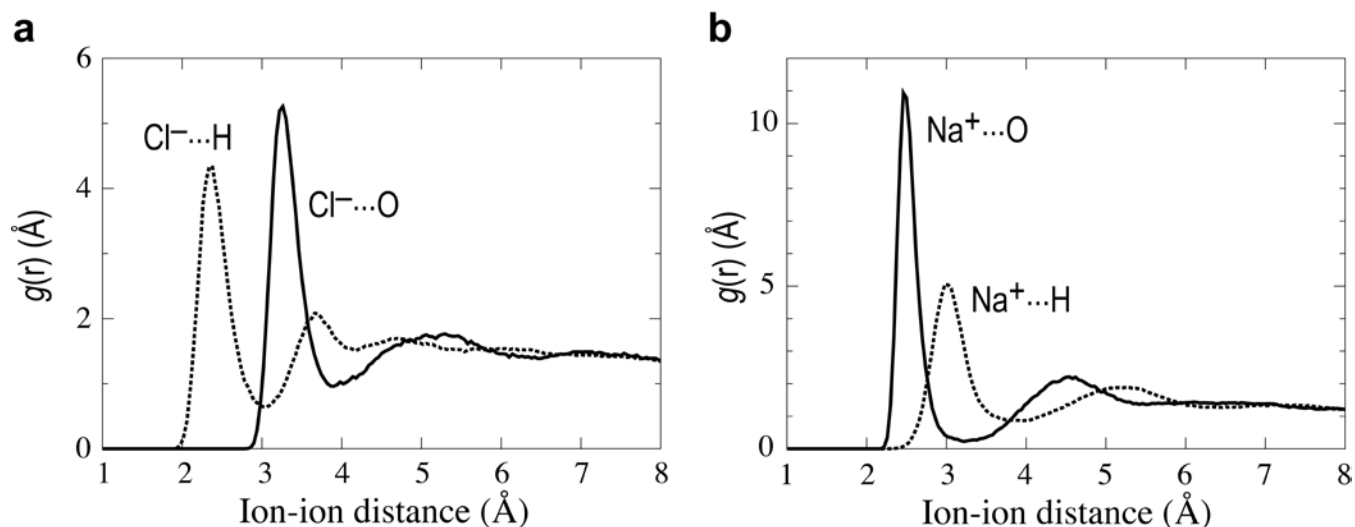


Figure S1. Radial distribution functions, $g(r)$, of ion–water interactions obtained from QM/EFP MD simulations: **(a)** Cl^- –water and **(b)** Na^+ –water interactions. Trajectories from the umbrella sampling windows with the largest ion separation (the window for the ion-ion separation of 9\AA) were used to obtain $g(r)$.

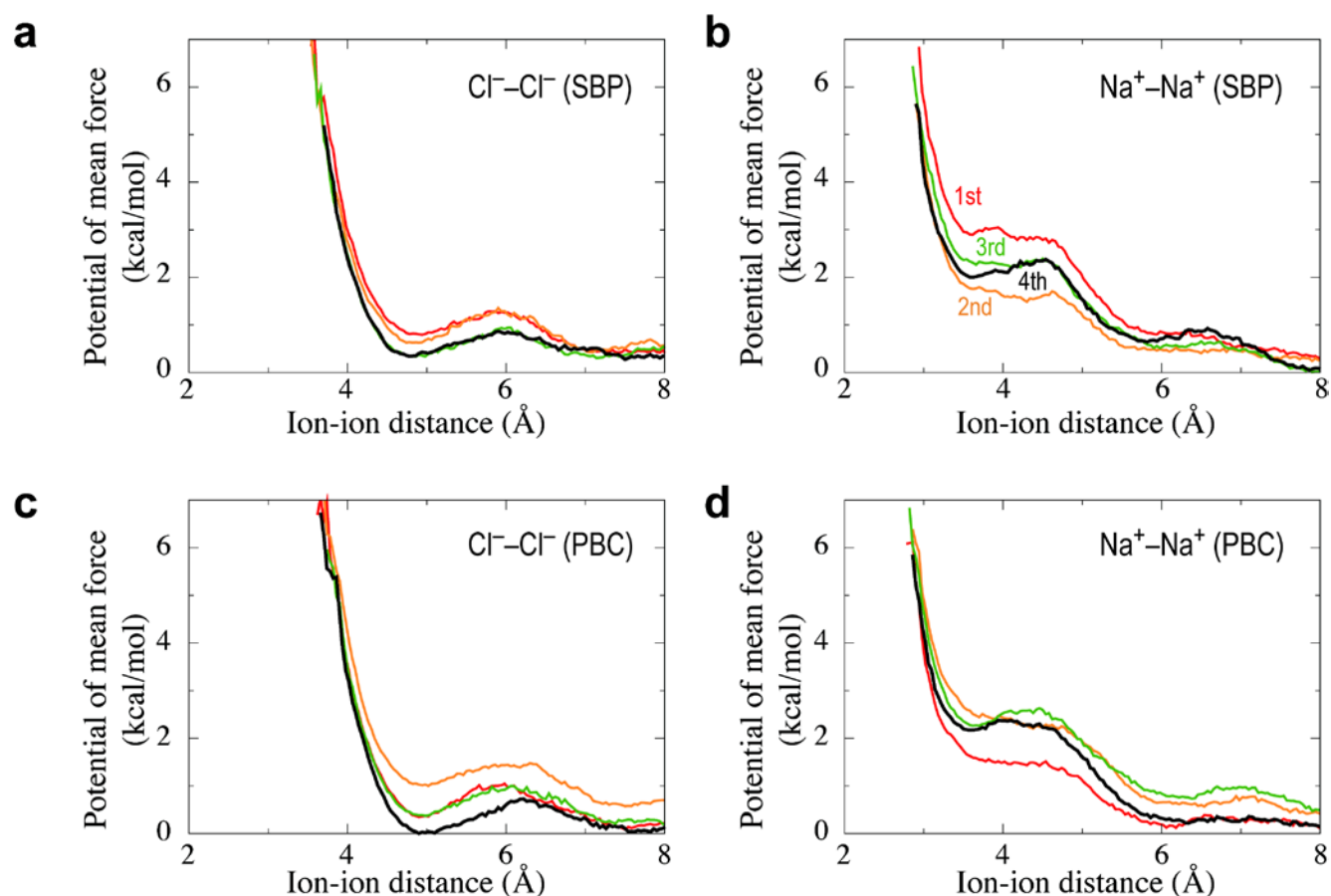


Figure S2. Convergence of the PMFs obtained from the classical MD simulations: **(a)** Cl^- – Cl^- using SBP, **(b)** Na^+ – Na^+ using SBP, **(c)** Cl^- – Cl^- using periodic boundary conditions with PME, and **(d)** Na^+ – Na^+ using periodic boundary conditions with PME. Red, orange, green, and black colors designate forward (1st), backward (2nd), forward (3rd), and backward (4th) umbrella sampling calculations,

respectively .

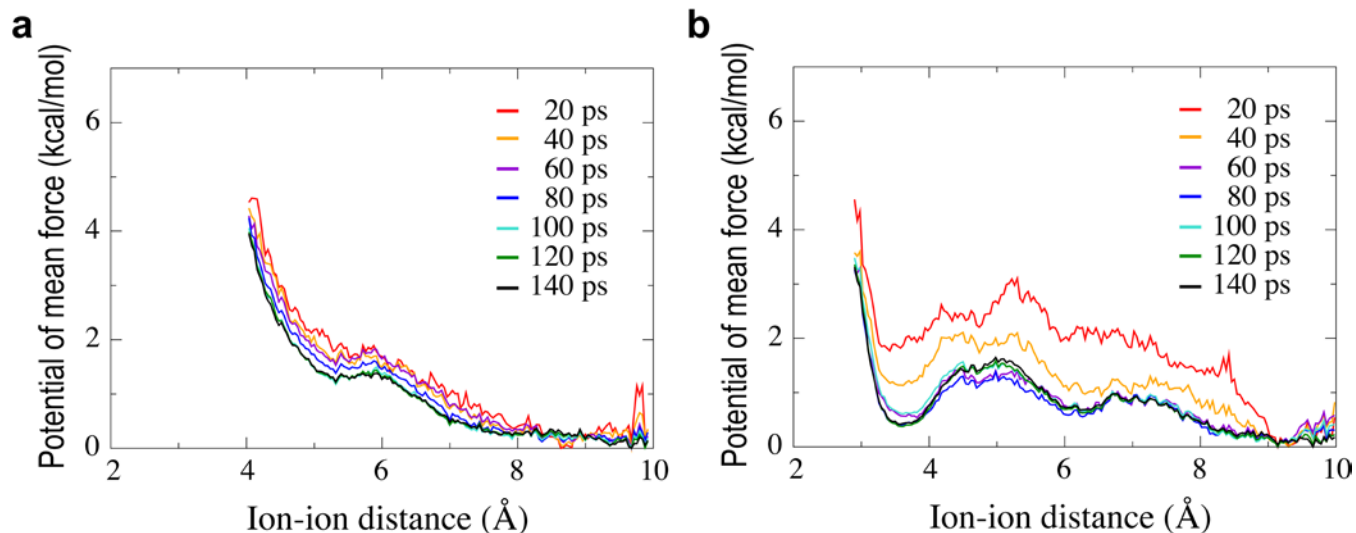


Figure S3. PMFs obtained from QM/EFP MD simulations with seven different simulation lengths: (a) Cl⁻-Cl⁻ and (b) Na⁺-Na⁺ pairs.

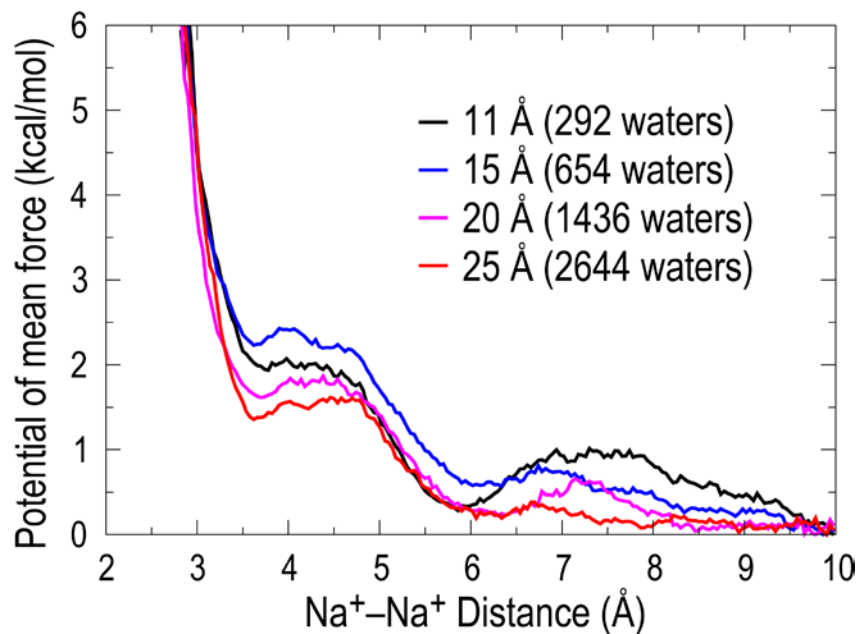


Figure S4. The Na⁺-Na⁺ PMFs of classical MD simulations as a function of sphere radius. During the simulations, extended electrostatics was not applied to make a fair comparison. The short distance regions between 3 and 5 Å of PMFs show a repulsive potential regardless of the sphere radius, although larger spheres tend to slightly reduce them. The origin of the slight size dependency may be a surface polarization. The changes in PMF due to the sphere size are not as significant as the quantum mechanical effects in QM/EFP MD. Therefore even if a large water sphere is used, a clear local minimum is predicted by QM/EFP MD that is not reproduced by classical MD simulations. Furthermore, sphere size effects change the PMFs of both classical and QM/EFP MD equally. Therefore, any relative differences in the PMFs of classical and QM/EFP MD at the same sphere size, mainly come from the differences between classical force fields and QM/EFP.

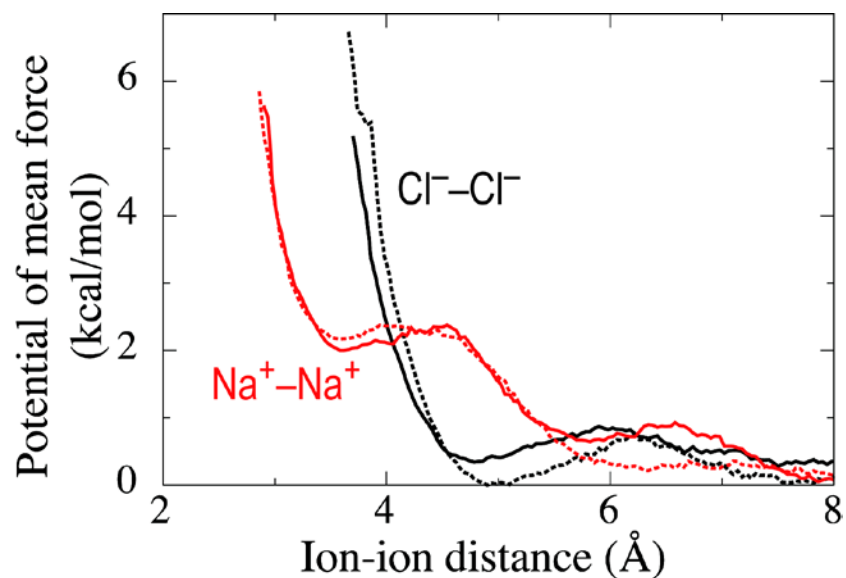


Figure S5. PMFs obtained from the classical MD simulations of Cl^- - Cl^- (black) and Na^+ - Na^+ (red) pairs either using the spherical boundary potential (two ions with 292 water molecules) (solid) or the periodic boundary condition (two ions with 201 water molecules in a cubic box of 19.3 \AA^3) (dashed). In the former, a cutoff of 50 \AA for the non-bonded interactions was used (all interactions were included). In the latter simulation, the long-range electrostatic force was calculated using the particle-mesh Ewald summation (PME) method with a grid size of less than 1 \AA .