Supporting Information

Ding et al. 10.1073/pnas.1400675111

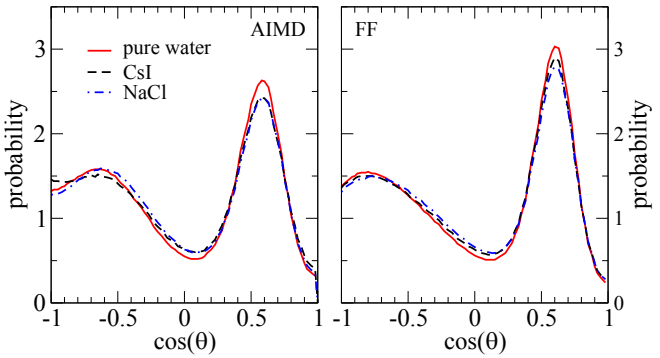

Fig. S1. Angular distributions of $\angle O_C O_N$ p in pure water (red solid line), 3 M CsI (black dashed line), and 3 M NaCl (blue dotted and dashed line) solutions (O_C is the oxygen center, whereas O_N p is the bisector of a neighboring water molecule in the first solvation shell of H_2O_C) simulated with both ab initio molecular dynamics (AIMD) (*Left*) and classical force field (FF) (*Right*), respectively.

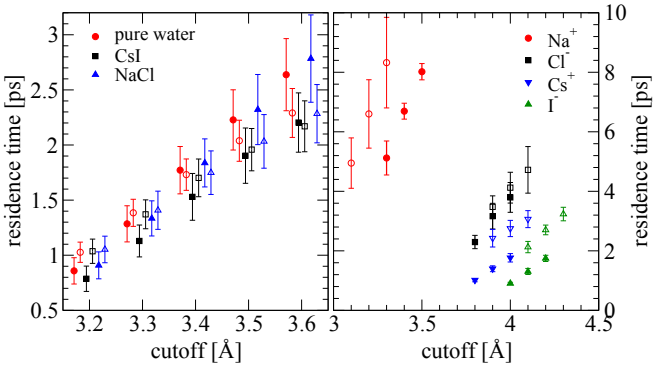

Fig. S2. Average water residence time around water (*Left*) and ions (*Right*) at different cutoffs of the solvation shell. The error bars represent the SD. For clarity, the data at the same cutoff are shifted in the left, and the chosen cutoffs are 3.2, 3.3, 3.4, 3.5, and 3.6 Å. The chosen cutoffs of the first solvation shell of ions (Table S1) ± 0.1 Å are used for the residence time calculations. Results obtained from AIMD simulations are in solid symbols, whereas those from classical simulations are in open symbols.

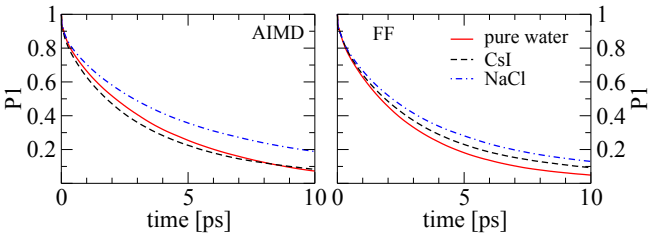

Fig. S3. P1 autocorrelation functions of water molecules in pure water (red solid line), 3 M CsI solution (black dashed line), and 3M NaCl solution (blue dashed and dotted line) obtained from AIMD (Left) and classical FF (*Right*) simulations.

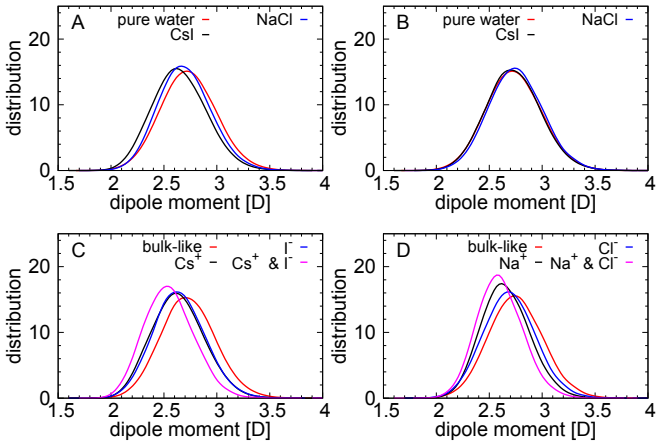

Fig. S4. Smoothed dipole moment distributions. (*A*) Distributions of all water molecules in pure water (red line), 3 M CsI (black line), and 3 M NaCl (blue line) solutions. (*B*) Distributions of all water molecules in pure water (red line), and those of waters not in the vicinities of any ions, i.e., bulk-like water in 3 M CsI (black line) and NaCl (blue line) solutions. (*C*) Distributions of water molecules in different environments of 3 M CsI solution: (1) bulk-like water (red line), (2) in the vicinity of Cs^+ (black line), (3) in the vicinity of I^- (blue line), and (4) in the vicinities of both Cs^+ and I^- ions (purple line). (*D*) Distributions of water molecules in different environments of 3 M NaCl solution: (1) bulk-like water (red line), (2) in the vicinity of Na^+ (black line), (3) in the vicinity of Cl^- (blue line), and (4) in the vicinities of both Na^+ and Cl^- ions (purple line).

Table S1. Applied cutoffs and corresponding water coordination numbers (CN) in pure water (O…O), and 3 M CsI and 3M NaCl solutions (ion…O) from both AIMD and classical simulations

	AIMD		Classical	
X...O pairs	Cutoff, Å	CN	Cutoff, Å	CN
O…O (pure water)	3.2	4.1	3.2	4.2
Cs^+…O	3.9	7.8	4.0	6.9
I^-…O	4.1	8.1	4.2	7.0
Na^+…O	3.4	6.2	3.2	4.5
Cl^-…O	3.9	8.0	4.0	6.4

The cutoffs are based on radial distribution functions, where physically meaningful coordination numbers are obtained.

Table S2. AIMD simulation time in NVE ensemble (t^{sim}), fitted water reorientation time (τ^{P1} and τ^{P2}), and hydrogen bond life time (τ^{HB}) in both AIMD and classical simulations

	AIMD (ps)				Classical (ps)		
Simulated systems	t^{sim}	τ^{P1}	τ^{P2}	τ^{HB}	τ^{P1}	τ^{P2}	τ^{HB}
Pure water	198	4.14	2.07	3.85	2.69	0.80	3.16
				18.87	6.46	1.81	16.01
3 M CsI	173	2.76	1.20	3.53	1.97	1.36	2.96
		8.33	2.61	18.16	6.17	3.61	16.60
3 M NaCl	206	3.05	1.78	3.62	3.21	1.64	3.40
		10.72	5.35	18.47	16.07	6.06	20.64

Two exponential functions are used to fit P1, P2, and HB autocorrelation functions. However, for the P1 and P2 autocorrelation functions of ab initio water, single exponential decays are observed. NVE, microcanonical ensemble.