Supplementary Information

Molecular Understanding of Ion Rejection in the Freezing of Aqueous Solutions

Shuang Luo[1], Yakang Jin[1], Ran Tao[1], Haiyang Li[2], Chu Li[3], Jun Wang[2,1], and Zhigang Li[1,2]

[1]*Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

[2]*Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry of Education, Beijing University of Technology, Beijing 100124, P.R. China*

[3]*Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

[1] jwang@bjut.edu.cn
[2] mezli@ust.hk

PMF Calculations for Different Number of Constrained Ice Molecules

For the PMF calculation in the main text, the temperature is set at 260 K and the molecules in all the six bilayers of the ice slab are constrained at their lattice sites. Calculations are also performed at 250 K with a fraction of ice molecules in the slab constrained. Figures S1a and S1b show the free energy profiles for the case with 4 ice bilayers close to the vacuum constrained. Figures S1c and S1d plot the free energy profiles for the case, where 3 ice bilayers close to the vacuum are constrained.
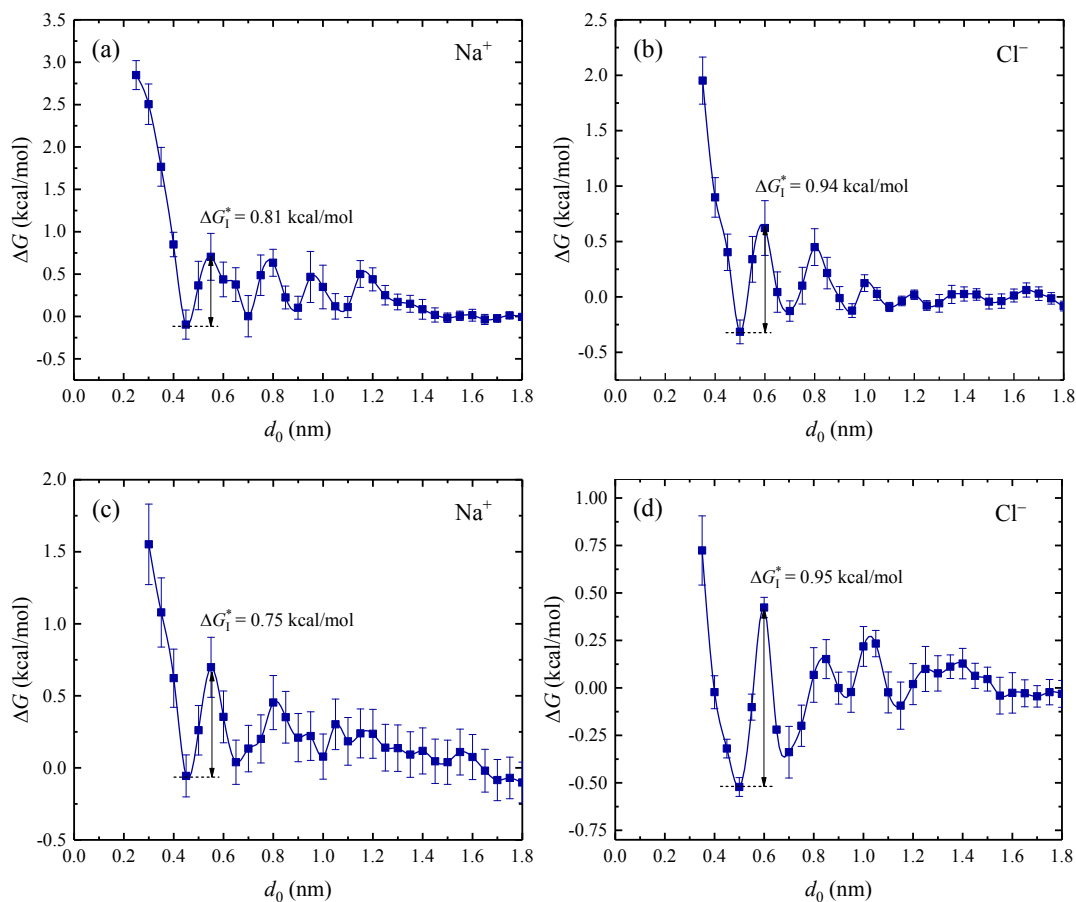

Figure S1 Free energy profiles as a function of distance, d_0, from the ice surface for Na$^+$ and Cl$^-$ with different numbers of constrained ice molecules. (a) and (b) Ice molecules in the 4 bilayers in contact with the vacuum are constrained. (c) and (d) Ice molecules in the 3 bilayers in contact with the vacuum are constrained.

Ion Rejection Rate on the Basal Surface of Ice

To explore the effect of the surface crystal orientation on the ion rejection rate, simulations for the basal surface are also performed. Fig. S2a shows the simulation system, where the basal plane {0001} of the ice surface is in contact with the solution. The ice slab contains 1280 water molecules and the NaCl solution includes 5120 water molecules and 54 pairs of Na^+ and Cl^-, which make the salt solution equal to 0.6 M. The snapshot for an ice crystallization process is depicted in Fig. S2b. It is seen that there are more Cl^- trapped in the ice than Na^+. Fig. S3 plots the ion rejection rate versus temperature. On average, the ion rejection rate for the basal plane is approximately 10% higher than that for the second prismatic plane.
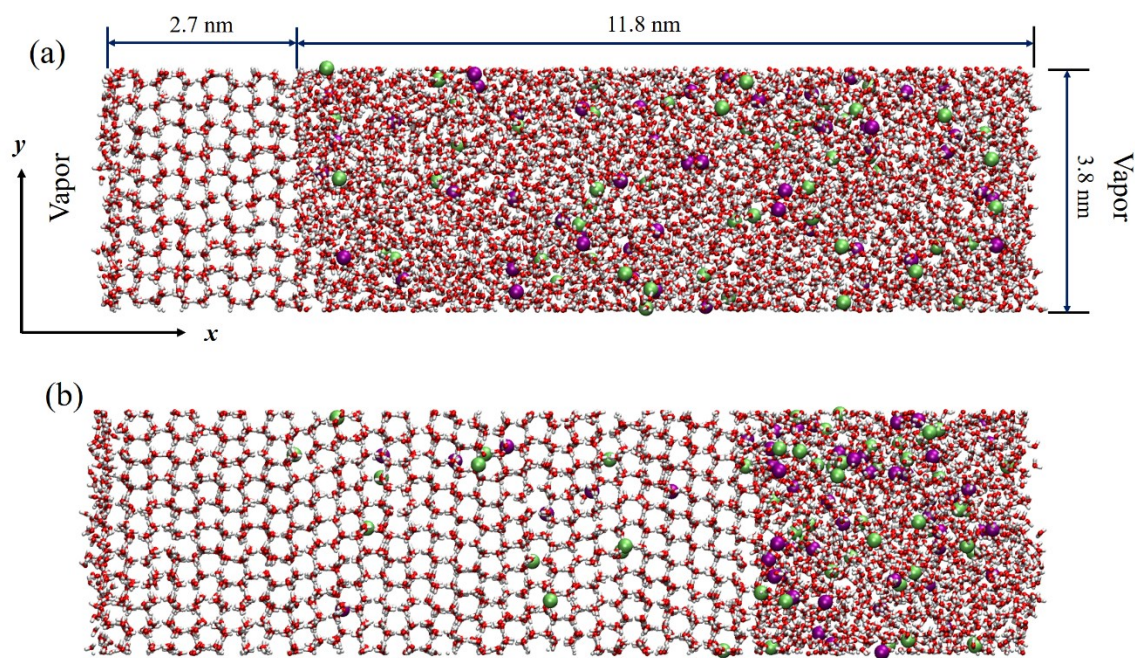

Figure S2 Molecular dynamics simulation system and ice crystallization process for the basal plane. (a) Simulation system. The basal plane of ice is in the *xy* plane. The lengths in the *x*, *y*, and *z* directions are 16.8 nm, 3.8 nm, and 3.5 nm, respectively. (b) Snapshot for an ice crystallization process after 500 ns at 230 K.
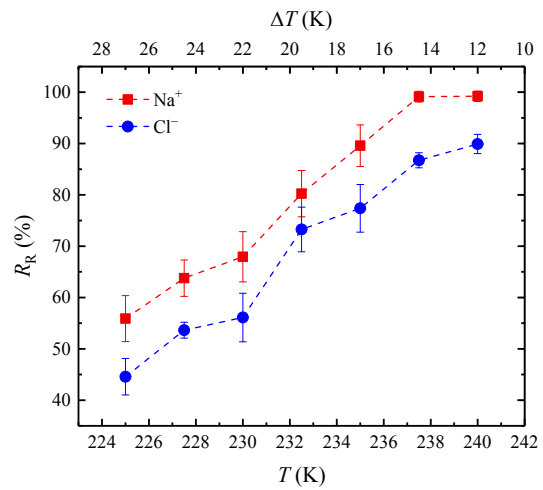
Figure S3 Ion rejection rate for the basal surface as a function of temperature.