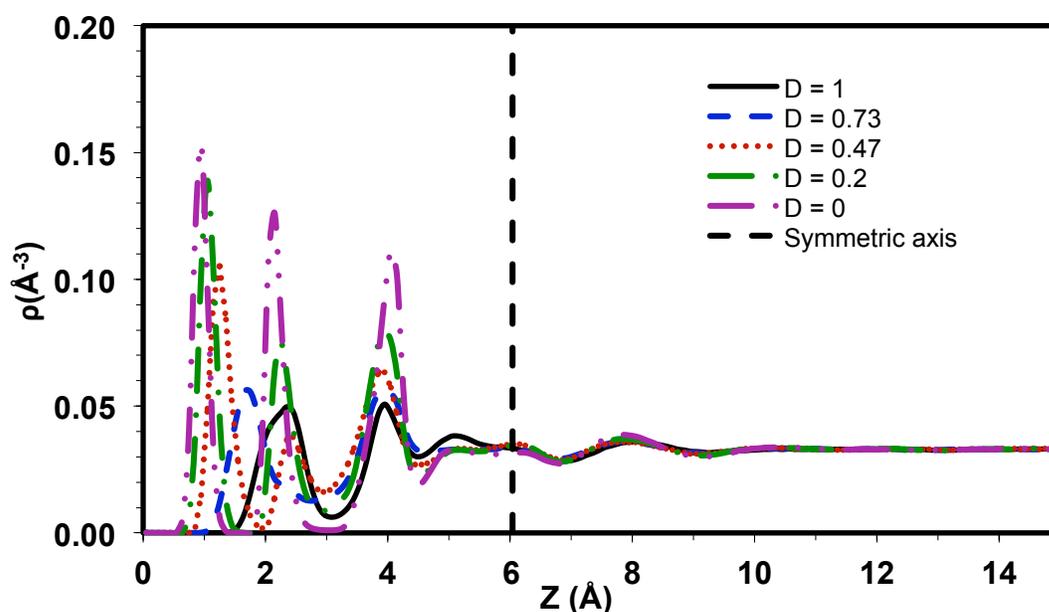


# Aqueous NaCl and CsCl Solutions Confined in Crystalline Slit-Shaped Silica Nanopores of Varying Degree of Protonation

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## Supporting information

### Part 1. Simulated system size determination.

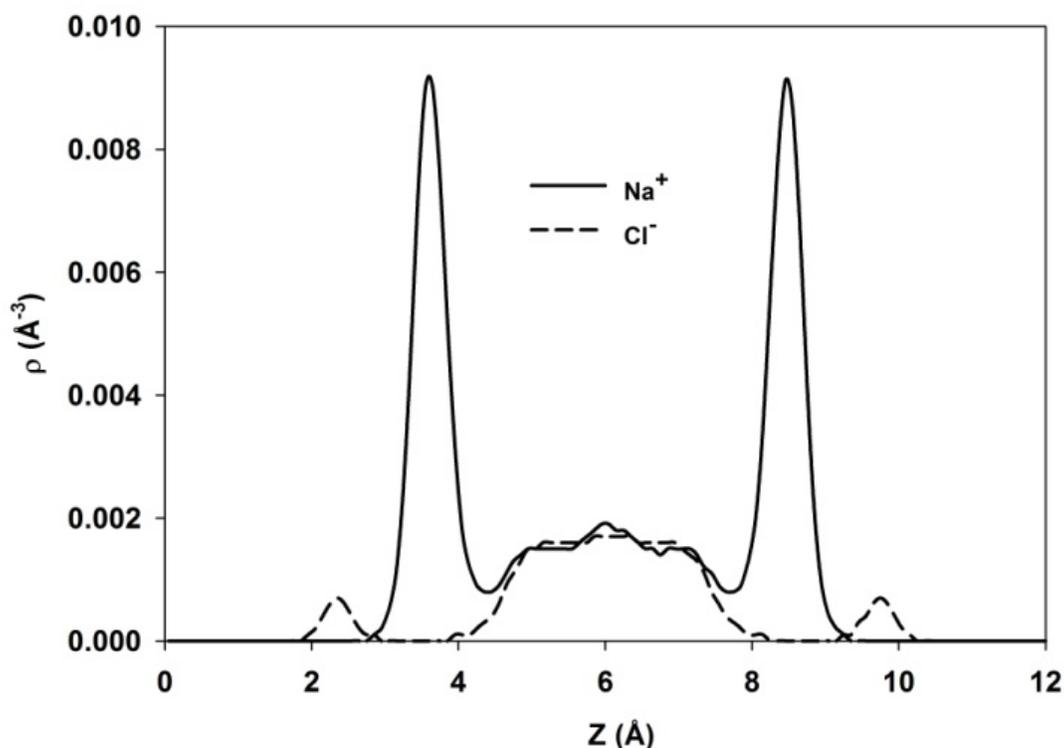


**Figure SI.1.** Atomic density profiles of water oxygen obtained from simulating a thin film of water free-standing on silica surfaces with different degrees of protonation ( $D$ ). The black dash line identifies the distance from the surface correspondent to half the width of the pores considered in this work. The number of water molecules found between the solid substrates and this dashed line is used to determine the number of water molecules within the pores.

In Figure SI.1 we present the oxygen atomic density profiles of water molecules obtained from simulating one free-standing thin film of 15,000 water molecules on the various substrates used to prepare the pores discussed in the main text. Each surface is characterized by a different degree of protonation, identified by the parameter  $D$  discussed in the main text. For the simulations of Figure SI.1 the simulation box dimensions are  $104.78 \times 100.82 \times 200 \text{ \AA}^3$ . The periodic boundary conditions are applied in all three dimensions. The simulations are conducted in the NVT ensemble at 300K, following the protocol used in our prior simulations for thin water films supported on solid substrates.<sup>1-4</sup>

The atomic oxygen density profiles of Figure SI.1 suggest that changing the surface degree of protonation affects the structure of interfacial water, in agreement with our prior simulations.<sup>1</sup> For the scopes of the present work, the simulations of Figure SI.1 are used to identify the number of water molecules located within a distance of  $6 \text{ \AA}$  from each of the surfaces considered. Because this distance is half the pore width considered in the simulations presented in the main text, twice as many water molecules as those found from Figure SI.1 are simulated within the various slit-shaped pores. The results in Figure SI.1 show that the number of water molecules found within  $6 \text{ \AA}$  from the surface considerably increases as  $D$  decreases from 1 to 0.

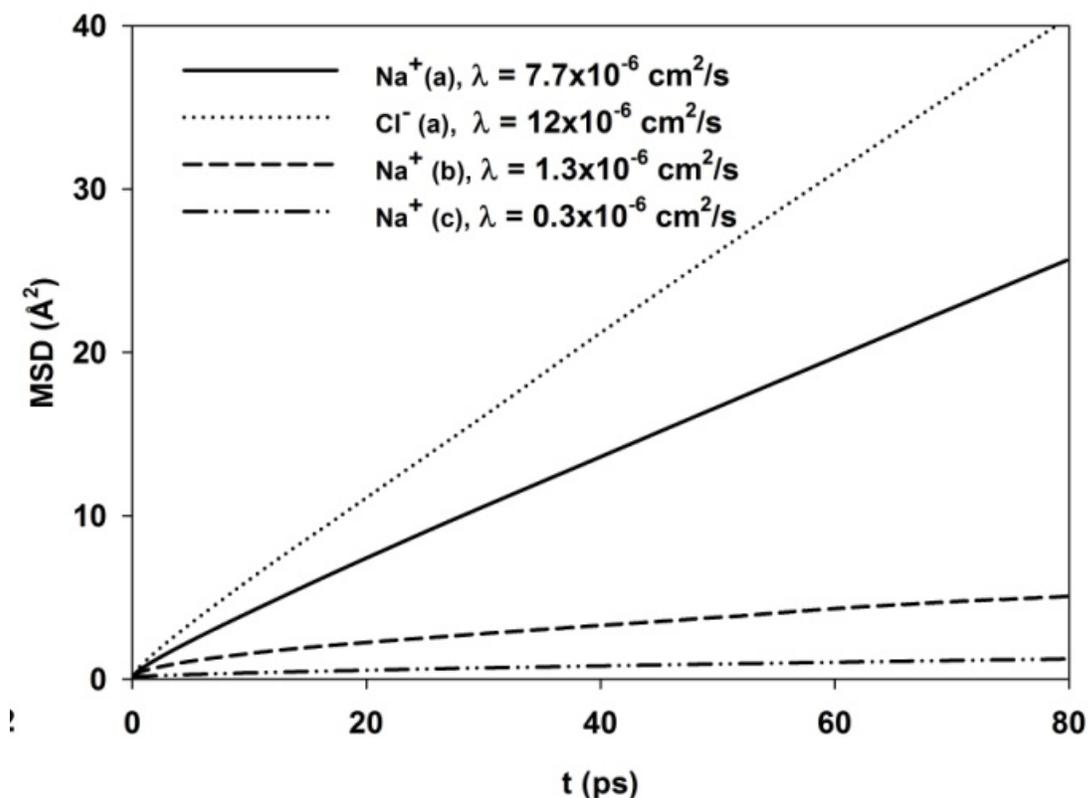
## Part 2. Effect of method used to maintain electro-neutrality on results.



**Figure SI.2.** Atomic density profiles of Na<sup>+</sup> and Cl<sup>-</sup> ions within the D=0.73 pore when the system electro-neutrality was secured by adding Na<sup>+</sup> ions. The resultant solution contained 3190 water molecules and 166 Na<sup>+</sup> and 58 Cl<sup>-</sup> ions.

The system electro-neutrality for the systems discussed in the main text was secured by adjusting the charge of a few ‘dummy’ atoms located far from the confined aqueous solutions, far enough that they would not interact significantly with the confined system. Alternatively, one could maintain the system electro-neutrality by adjusting the number of ions within the confined solution. To compare the results obtained following the two approaches we conducted additional simulations for aqueous NaCl solutions confined within the slit-shaped pore of D=0.73. Results for the atomic density profiles of Na<sup>+</sup> and Cl<sup>-</sup> ions within the pore and along the direction perpendicular to the solid surface are shown in Figure SI.2. The system considered contained 166 Na<sup>+</sup> and 58 Cl<sup>-</sup> ions. Because of the much larger number of Na<sup>+</sup> ions compared to that in the D=0.73 system discussed in the main text, the density peaks for Na<sup>+</sup> are much more intense in Figure SI.2 than in Figure 4d. In addition, and more importantly, a significant amount of Na<sup>+</sup> ions are found near the pore center. The density profile of Cl<sup>-</sup> ions in Figure SI.2 is similar to that in Figure 4d because the number of Cl<sup>-</sup> ions in the two systems is similar.

The different density distributions shown in Figure SI.2, due to the different amounts of electrolytes simulated, are likely to yield differences in the estimated ionic mobility. In Figure SI.3 we report the planar mean square displacement calculated for Na<sup>+</sup> and Cl<sup>-</sup> ions within the plane parallel to the solid substrates for the system of Figure SI.2. Results are shown for all ions, as well as for the Na<sup>+</sup> ions found within the first dense layer near the solid surfaces (dashed line). For comparison, the mean square displacement reported for Na<sup>+</sup> ions in Figure 5 of the main text is also shown (dash-dot-dot line). As expected from the density distribution results, Na<sup>+</sup> ions have a significantly larger self-diffusion coefficient within the system of Figure SI.2 than within the systems described within the main text. This is because more ions are present within the system, and a significant amount of the Na<sup>+</sup> ions are found near the pore center. Note in fact that the mean square displacement obtained for those Na<sup>+</sup> ions within the first adsorbed layer is not significantly different than that shown in Figure 5. As a consequence of the increased Na<sup>+</sup> mobility, because of ion-ion correlations, our results show that even the self-diffusion coefficient for Cl<sup>-</sup> ions in the system of Figure SI.2 is larger than that discussed in the main text.



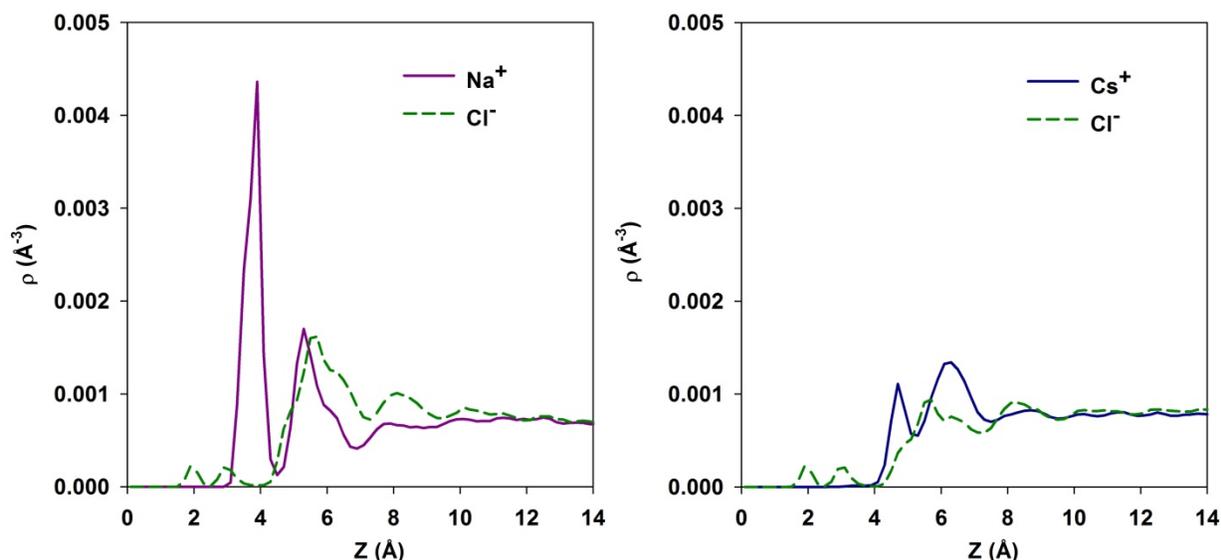
**Figure SI.3.** Mean square displacement and corresponding self-diffusion coefficient of Na<sup>+</sup> and Cl<sup>-</sup> ions within the D=0.73 pore of Figure SI.2. The solid and dot lines are for all Na<sup>+</sup> and Cl<sup>-</sup> ions inside the pore, respectively. The dash line is for Na<sup>+</sup> ions within the first Na<sup>+</sup> peak near the solid substrate. For comparison, the results for Na<sup>+</sup> ions reported in Figure 5 are also shown (dash-dot-dot line).

### Part 3. Comparison to supported thin films of aqueous electrolyte solutions.

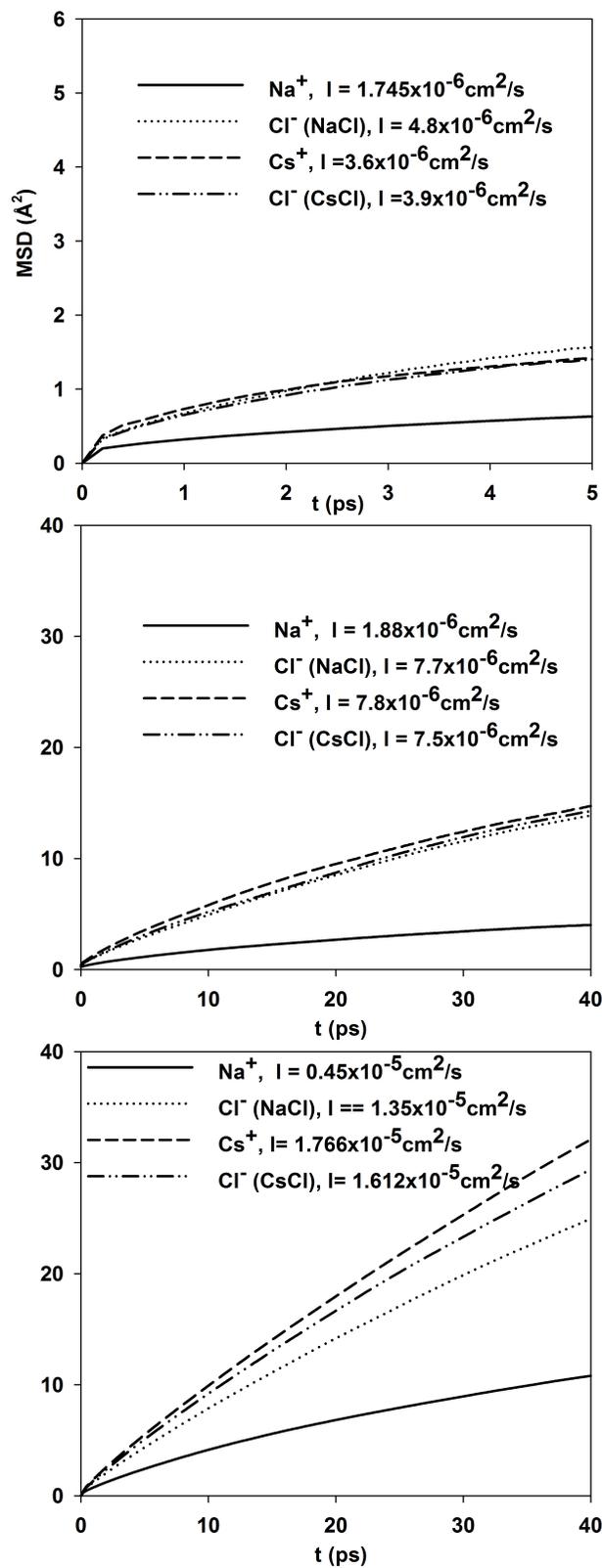
The results in the main text show significant differences in ionic distribution and mobility within narrow slit-shaped pores. It is of interest to quantify the role of confinement on such results. For comparison, we simulated thin films of 1M aqueous solutions of either NaCl or CsCl (7296 water molecules and 132 NaCl or CsCl) supported on a flat silica substrate characterized by  $D=0.47$ . Simulations are analogous to those of Figure SI.1, except for the presence of the electrolytes. The simulation box dimensions are  $104.78 \times 100.82 \times 200 \text{ \AA}^3$ ,  $T=300\text{K}$ , and periodic boundary conditions are applied along the three dimensions. It should be pointed out that, because a water-vacuum interface is now present, polarizable force fields should be implemented. However the results at the water-solid interface can be compared to those presented in the main text.

In Figure SI.4 we report the atomic density distribution along the direction perpendicular to the surface for NaCl (left) and CsCl (right). The results show a uniform density distribution of all ions at distances larger than  $\sim 1.2$  nm from the solid, suggesting that bulk-like properties have been reached at such distances. Pronounced density layers are observed closer to the surface, and these are different depending on the ion of interest. Comparing the results in Figure SI.4 to those obtained under confinement we note that the positions of the various peaks are similar in the two cases, but the density of the various peaks obtained near the surface in Figure SI.4 are lower than those obtained under confinement, because a significant amount of ions is found far from the surfaces.

To assess the mobility of the ions within the system of Figure SI.4 we calculated the mean square displacement along planes parallel to the surface for ions located at different distances from the surface. From the mean square displacement, the self-diffusion coefficient can be estimated. The results are shown in Figure SI.5, and clearly show that the ions mobility increases as their distance from the  $D=0.47$  surface increases. In all cases considered the planar self-diffusion coefficients shown in Figure SI.5 are larger than those obtained within the  $D=0.47$  slit-shaped pores considered in the main text.

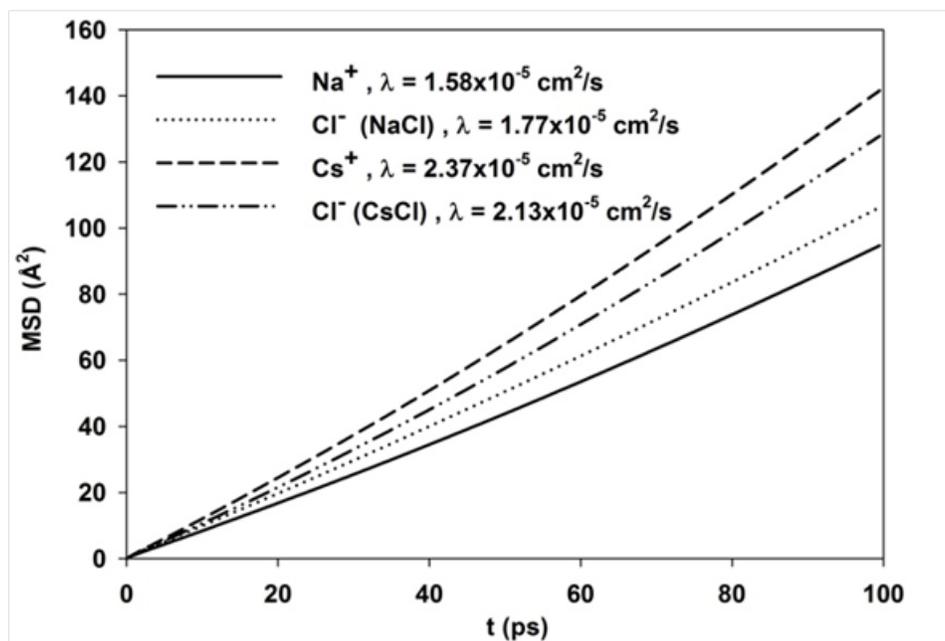


**Figure SI.4.** Left: Atomic density profiles of  $\text{Na}^+$  (solid purple line) and  $\text{Cl}^-$  (green dash line) ions obtained from simulating a thin film of 1M aqueous NaCl solution supported on one surface characterized by  $D=0.47$ . Right: Atomic density profiles of  $\text{Cs}^+$  (solid blue line) and  $\text{Cl}^-$  (green dash line) ions obtained from simulating a thin film of 1M aqueous CsCl solution supported on the same  $D=0.47$  surface.



**Figure SI.5.** Planar mean square displacement, and corresponding self-diffusion coefficient  $\lambda$ , obtained for ions in systems such as those of Figure SI.4. The three panels are for ions found at 6 Å (top panel), 8 Å (middle), and 12 Å (bottom) from the surface, respectively.

#### Part 4. Comparison to bulk 1M solutions.



**Figure SI.6.** Three-dimensional mean square displacement, and corresponding diffusion coefficient  $\lambda$ , for ions in bulk 1M aqueous NaCl and CsCl solutions. The systems consist of 15,000 water molecules and 270 NaCl or CsCl ions (1M). Simulations are conducted in the NPT ensemble at 300 K and 1 bar.

To compare the properties of aqueous NaCl and CsCl systems obtained under confinement and discussed in the main text, we also simulated 1M aqueous solutions of NaCl and CsCl in the bulk at ambient conditions for 6ns. The NPT ensemble was used ( $P=1\text{bar}$ ,  $T=300\text{K}$ ). Results for ion-ion radial distribution functions are presented in the main text (Figure 7). Those for the three-dimensional mean square displacement, and the correspondent self-diffusion coefficients, are shown in Figure SI.6. The results, in qualitative agreement with literature data, confirm that the ionic mobility for  $\text{Cs}^+$  is larger than that for  $\text{Na}^+$  ions in the bulk, and that bulk self-diffusion coefficients are larger than those obtained under confinement for the systems considered here.

#### References

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