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Equilibrium and Transport Properties of Aqueous Electrolytes within Narrow Slit-Shaped Pores: from Molecular Dynamics Results to Nanofluidics Devices

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We report equilibrium molecular dynamics simulation results for structural and dynamic properties of aqueous electrolyte solutions confined within narrow pores. The slit-shaped pores are carved from cristobalite silica. The pore width is in the range 0.8 – 1.0 nm. The aqueous solutions contain NaCl and CsCl at 1M.
Equilibrium simulations are performed at ambient conditions within the NVT ensemble. The results are analyzed for both water and electrolytes in terms of density profiles away from the solid substrates, self diffusion coefficients in the direction parallel to the solid substrate, and residence time at contact with the solid substrate.
The data suggest the formation of layered structures. Because the self-diffusion coefficient is faster as the distance from the solid increases, the ions that are at the pore center diffuse more quickly through the pore than those adsorbed closer to the wall. Thus our results could be used to design membranes to separate, e.g., aqueous NaCl from CsCl solutions.

1. Introduction

The understanding of aqueous solutions near charged surfaces continues to attract great attention due to fast advances in applications including nanofabrication,(Quake and Scherer, 2000) water desalination,(Fornasiero et al., 2008a, Argyris et al., 2010) and nano-fluidics. Properties of water at the solid-liquid interface play an important role in ion adsorption/desorption processes on solid substrates, diffusion of ions in nanopores, biological membranes, and ion channels.(Hille, 2001 , Fornasiero et al., 2008) A number of experimental(Mamontov et al., 2008) and theoretical(Kerisit et al., 2008, Argyris et al., 2008, Giovambattista et al., 2009, Argyris et al., 2009b) studies have provided molecular-level insights on the behavior of interfacial water. It has been reported that the structural and dynamics properties of interfacial water are significantly affected by the solid substrate characteristics, resulting in different behavior compared to that of water in the bulk.(Argyris et al., 2009a) In general, these effects occur at short distances from the solid substrate.(Godawat et al., 2009) Experimental investigations on interfacial water are carried out using, for example, backscattering spectroscopy,(Mamontov et al., 2008) quasi-elastic neutron scattering, attenuated total reflectance infrared spectroscopy, X-ray reflectivity measurements, and ultrafast

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infrared spectroscopy.(Fenn et al., 2009) The experimental investigations are often enriched by theoretical studies conducted with the aid of computer simulations for structural and dynamical properties of interfacial water. In this report we extend our prior investigations towards understanding the relationship between local water structure and dynamics at interfaces and observable quantities such as the diffusion of electrolytes. We limit the discussion in this manuscript to the structural and dynamical behavior of water within narrow slit-shaped silica pores.

2. Simulation Details

Slit-shaped pores were used in our simulations. Two silica substrates with identical surfaces were placed at a distance of 8-11 Å along the z-axis. The (1 1 1) crystallographic face of β-cristobalite(Schmahl et al., 1992) was used to model the solid substrate. The surface area of each periodic system is 104.8×100.8 $Å^2$ (x-y plane) with plate thickness 10.3 Å; details on the surface preparation can be found elsewhere.(Puibasset and Pellenq, 2003) To obtain a chemically realistic surface all the non-bridging oxygen atoms are hydroxylated. The resulting surface hydroxyl group density is ~4.5 OH/nm^2, which corresponds to experimental densities observed in silica surfaces.(Zhuravlev, 2000) To represent pH effects we manipulate the percent of non-bridging O atoms that are hydroxylated. The percent of hydroxylated non-bringing O atoms ranges from 100% to 40%. Correspondingly, the surface charge density is highest (0.31 C/m^2) on the 100% hydroxylated surface, and decreases as the degree of hydroxylation decreases. The CLAYFF force field(Cygan et al., 2004) was implemented to model the silica surface. All other simulation details can be found in our prior report.(Argyris et al., 2010) The total simulation time for all cases was 400 ns.
Three different electrolyte solutions, each including several thousand water molecules, were confined between the two identical silica substrates. The three electrolyte mixtures consisted of pairs of either NaCl or CsCl, and pairs of both NaCl and CsCl, respectively. The number of ions changed to keep the ionic strength in all systems at 1 M. The system temperature was maintained at 300 K by using the Nosé-Hoover thermostat with a relaxation time of 100 fs.

3. Results

As we discussed in our early publications, the structure of interfacial water is important in determining macroscopic properties such as electrolytes adsorption and diffusion near a surface. In Figure 1 we present the density distribution of oxygen and hydrogen atoms of water within the pores considered. The direction z is perpendicular to the solid substrate. Because of the slit-shape geometry of the pore, we notice the accumulation of water near both surfaces. By comparing the density distribution of oxygen and hydrogen atoms it is possible to obtain insights regarding the orientation of interfacial water, as discussed earlier. (Argyris, 2008, Kerisit et al., 2008) The results in Figure 1 are obtained on 100% hydroxylated surfaces. In Figure 2 we quantify the changes in the structure of interfacial water as the degree of hydroxylation decreases from 100% to 40%. It appears that as the degree of hydroxylation decreases form 100% to 40% the

dense layer of interfacial water formed at contact with both surfaces becomes denser and the peak shifts at shorter separation. It also appears that the surface hydroxylation affects the orientation of interfacial water molecules, in qualitative agreement with observations obtained for thin water films on free-standing silica-based surfaces.(Argyris et al., 2009b).

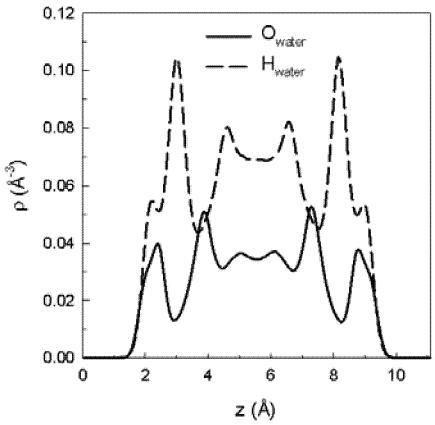

Figure 1: Atomic density profiles of water oxygen (solid line) and hydrogen (dashed line) as a function of distance from the fully hydroxylated silica surfaces.

For the scopes of the present work it is important to understand the distribution of aqueous electrolytes (Na^+, Cs^+ and Cl^-) within the silica-based slit-shaped pores considered in Figures 1 and 2. In Figure 3 we report the density distribution in the direction perpendicular to the solid substrate observed for the three electrolytes within the 100% hydroxylated silica pores of width ~0.8 nm. Because of the pronounced positive surface charge density, and in agreement with our results on wider pores,(Argyris et al. 2010) we observe that the negatively charged Cl^- ions accumulate predominantly near the two solid surfaces. On the contrary, both Cs^+ and Na^+ ions accumulate in the pore center. The preferential distribution of Na^+ and Cs^+ ions within the pores is however different. We attribute these differences to the different size of the two ions, and possibly to differences in their hydration structure. As the degree of hydroxylation changes, the preferential distribution of the electrolytes within the pores also changes (not shown for brevity).

As shown by a number of simulation studies,(Argyris et al., 2009a) water molecules possess more pronounced mobility the farther they are from the silica substrates. Thus it is expected that, because of the different preferential distribution within the pores shown in Figure 3, left, the different ions will have different mobility within the silica pores considered here. To quantify this expectation, we calculated the self-diffusion coefficient for the various electrolytes in the direction parallel to the solid substrate. The results are shown in Figure 3, right, as a function of the surface degree of hydroxylation. As can be seen, when the surfaces are 100% hydroxylated Cs^+ ions move much faster than Na^+ ions, while Cl^- ions are strongly adsorbed on the pore surfaces and do not

move. As the degree of hydroxylation decreases the mobility of both Cs^+ and Na^+ ions decreases, while that of Cl^- ions increases. When the degree of hydroxylation is 40% our results suggest that Cl^- ions move faster than Na^+ ones, but still more slowly than Cs^+.

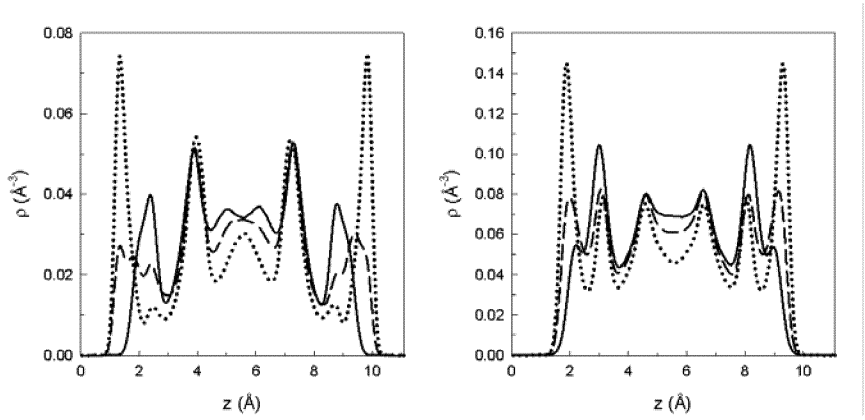

Figure 2: Atomic density profiles for oxygen water (left panel) and hydrogen water (right panel) at fully hydroxylated (solid curve), 70% hydroxylated (dashed line) and 40% hydroxylated silica (dotted line) surfaces.

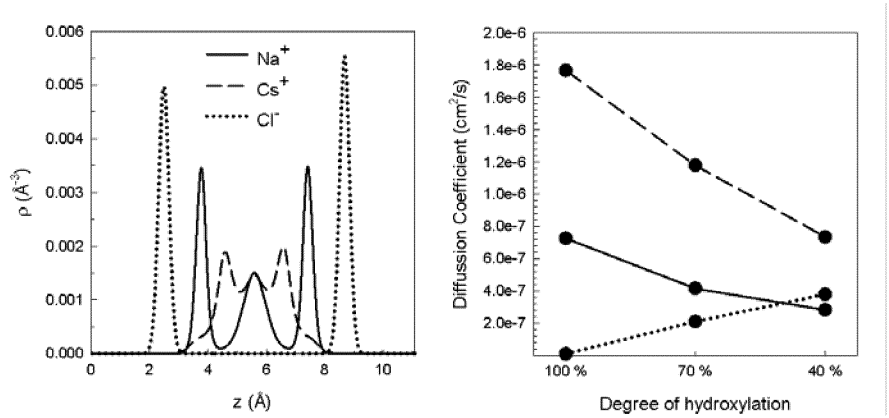

Figure 3: Left: Atomic density profiles for Na^+, Cs^+, and Cl^- ions in fully hydroxylated silica pore are shown in solid, dashed, and dotted curves. Right: Self-diffusion coefficient of Na^+, Cs^+, and Cl^- shown in solid, dashed and dotted curves, respectively, as a function of silica surface degree of hydroxylation.

4. Conclusions

Aqueous electrolyte solutions confined within silica nanopores were studied by means of all-atom molecular dynamics simulations. Long (400 ns) molecular dynamics simulations were conducted to reach equilibrium and capture the structural and dynamical aspects of the adsorption process. We calculated density profiles and in-plane diffusion coefficients. Strong ion-specific behavior is reported for both the equilibrium ion distribution and mobility. Our results suggest that the observed difference in mobility for each ionic species is determined by the equilibrium distributions within the pores. As the surface charge density changes (which can be altered by titrating the solution pH), the preferential location of the ions within the pores also changes, resulting in very different mobility. Quantification and generalization of such observations will lead to the design of innovative separation techniques that could be used for nuclear waste management, and also for water desalination.

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