Ion Exclusion and Electrokinetic Effects Resulting from Electro-Osmotic Flow of Salt Solutions in Charged Silica Nanopores

Neil R. Haria* **and Christian D. Lorenz**

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/b000000x

1 Electronic Supplementary Information

1.1 Density of ions inside of pore

The average number densities of the various ionic species inside of the pores have been determined as a function of the $z-$dimension for each of the simulated systems. The number of each species was calculated and averaged over time in bins of $\Delta z = 0.1$ nm throughout the length of the pore. The results of these calculations are shown in Figures 1 and 2 for the 0.5 M NaCl and 0.5 M $CaCl_2$ systems, respectively. While the densities are not entirely constant throughout the pores, the average values are reported in the text of the manuscript. The variation in the local densities of the various ions in solutions correlates well with the distribution of charges on the pore surface in these plots.

Generally speaking we see that in the NaCl systems the cation density is significantly larger than the anion densities, which agrees with the fact that the cations will adsorb to the interface in order to counter the surface's negative charge. Then since we do not observe overcharging by the cations there is not significant adsorption of the anions to the cation layer. Where as in the $CaCl_2$ systems, a larger concentration of Cl^- ions is observed than in the NaCl systems. This is due to the fact that charge inversion occurs in the divalent systems and so anions are bound to the positive ion layers.

Materials Research Group, Department of Mechanical Engineering & Material and Molecular Modelling, Department of Physics, King's College London, London, UK WC2R 2LS
* *E-mail: neil.haria@kcl.ac.uk*

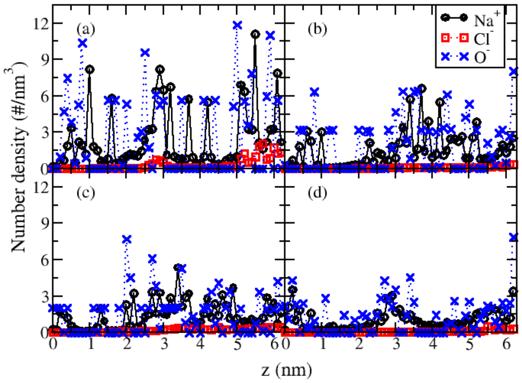

Fig. 1 Number density (#/nm^3) of the ionic species as a function of the z-dimension in the 0.5 M NaCl systems inside a pore with diameter of a) 1.5 nm, b) 2.0 nm, c) 2.5 nm and d) 3.0 nm. Different symbols are used to represent the different ionic species: black circles for Na$^+$, red squares for Cl$^-$ and blue X's for bare oxygens on silica surface.

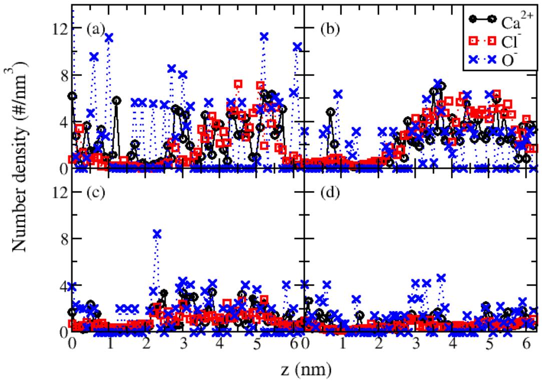

Fig. 2 Number density (#/nm^3) of the ionic species as a function of the z-dimension in the 0.5 M $CaCl_2$ systems inside a pore with diameter of a) 1.5 nm, b) 2.0 nm, c) 2.5 nm and d) 3.0 nm.Different symbols are used to represent the different ionic species: black circles for Ca^{2+}, red squares for Cl$^-$ and blue X's for bare oxygens on silica surface.

1.2 Orientation of water molecules

The average orientation of water molecules was calculated for water molecules throughout the pore system. In doing so, the orientation is defined by the angle between the vector from the oxygen atom of a water molecule and the midpoint between the two hydrogen atoms of a molecule and the vector normal to the system ([0,0,1]). As a result to the way that it is calculated, an angle of $< 90°$ represents a water molecule with the oxygen at smaller z-coordinates than the midpoint of the hydrogens, while an angle of $> 90°$ represents a water molecule with the oxygen at larger z-coordinates than the midpoint of the hydrogens. The value is averaged over the course of the production simulation and is measured for water molecules within 1 Å bins in the z-dimension. The results are displayed in Figures 3 and 4 for the NaCl and

$CaCl_2$ systems, respectively.

In both the NaCl and $CaCl_2$ systems, the same general trend is observed in the orientation of the water molecules as it moves from $z = 0$ Å (analogous to the anode of the system) to $z = 115$ Å (cathode of the system). At $z = 0$ Å, the average orientation of water molecules is 90°, which means that on average the orientation is perpendicular to the z-axis. Then as z increases, the average orientation changes to smaller angles, meaning that the waters orient themselves such that at least one of the hydrogen atoms of the water molecules is generally nearer the bottom silica interface than the oxygens of the water molecules. Therefore, the positive end of the water dipole is preferentially interacting with the residual negative charge of the silica interface in the case of the NaCl systems and the presence of the Cl^- layer in the $CaCl_2$ system. Then as the water molecules move through the pore (30 Å $\geq z \leq$ 85 Å) their average orientation angle increases but remains less than 90°, meaning that the waters still have the general orientation of the hydrogen atoms leading them through the pore, but that they are less strongly oriented with relation to the z-axis due to the electrostatic interactions of the pore walls. At the top silica interface, the water molecules generally adopt an orientation that is greater than 90°, meaning that the water molecules rotate such that at least one of hydrogen atoms are nearer to the silica interface than are their oxygen atoms. Finally at $z > 100$ Å the water molecules again demonstrate an average orientation of $\sim 90°$.

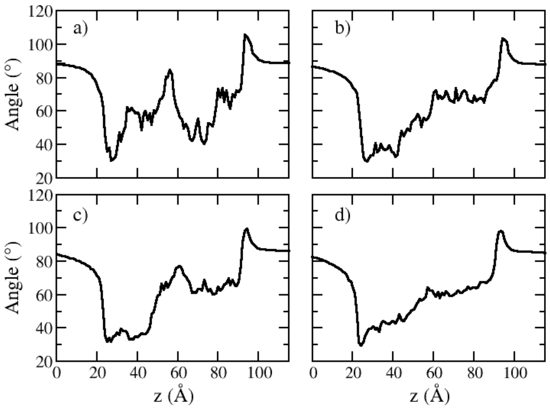

Fig. 3 Orientation of the water molecules as a function of the z-coordinate for 0.5 M NaCl system in a pore with diameter of a) 1.5 nm, b) 2.0 nm, c) 2.5 nm and d) 3.0 nm.

When comparing the behaviour as a function of pore size, there is one noticeable trend. The average orientation of the water molecules increases more gradually with increase of z-coordinate within the pore (30 Å $\geq z \leq$ 85 Å) as the pore diameter increases. This is probably due to the larger available space inside the pores as diameter increases. In the case of the 1.5 nm diameter pore, the water molecules do not change orientation throughout the length of the pore. However, in the 2.0 nm and 2.5 nm pores, at the midpoint ($z \sim 60$ Å) of the pore there is a significant change (from $\sim 40°$ to $\sim 60°$) in the average orientation of the water molecules.

Finally, when comparing the average orientations of the water molecules in the NaCl and $CaCl_2$ systems, the general trend is the same. However, there is a difference in the magnitude of the peak orientations of the water molecules near the interfaces. The water molecules near the bottom interface of the silica pore of the NaCl systems show an angle of $\sim 25°$, while the average orientation of the water molecules in the $CaCl_2$ systems show an angle of $\sim 40°$. At the top interface, the average orientation of the water molecules

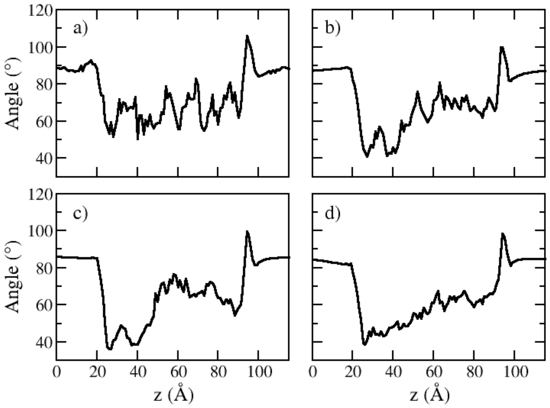

Fig. 4 Orientation of the water molecules as a function of the *z*-coordinate for 0.5 M $CaCl_2$ system in a pore with diameter of a) 1.5 nm, b) 2.0 nm, c) 2.5 nm and d) 3.0 nm.

in the NaCl systems is $\sim 110°$ and the average orientation of the water molecules in the $CaCl_2$ systems is $\sim 98°$. Therefore, in both cases the water molecules in the NaCl systems are oriented such that their dipole is more perpendicular to the silica interfaces than the water molecules in the $CaCl_2$, which generally means they are more strongly oriented. This is due to the fact that in the $CaCl_2$ systems, there is only a small amount of charge inversion observed near the silica interfaces, which would then diminish the strength of electrostatic interactions between the atoms of the water molecules and the cations that are adsorbed to the silica interface.

1.3 Velocity profiles of ions

The average velocity in the *z*-dimension of the cations and anions within the pores was measured as a function of distance from the centre of the pore. The distance was divided into 2 Å increments, and the average velocity of the molecules and ions in a given bin is then averaged over the number of the molecules or ions present in the bin and over time. The resulting velocity profiles for the water molecules, Na^+ and Cl^- ions in 0.5 M NaCl systems are shown for each of the pore diameters in Figures 5 and 6, respectively.

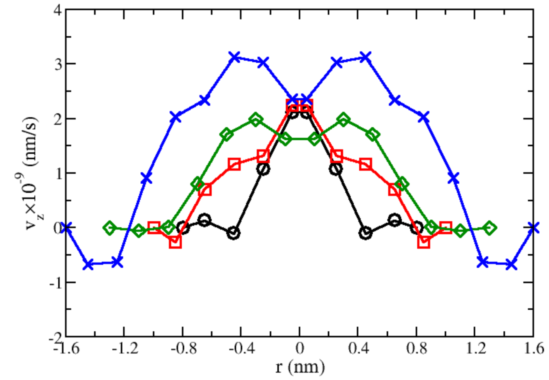

Fig. 5 Velocity profile of Na^+ ions across the pores, which have diameters of 1.5 nm (black circles), 2.0 nm (red squares), 2.5 nm (green diamonds) and 3.0 nm (blue X's). The center of the pore is represented by r = 0, and the velocity is the average velocity in the *z*-dimension.

.

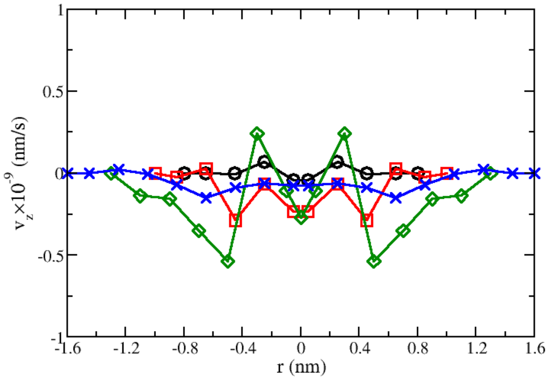

Fig. 6 Velocity profile of Cl^- ions across the pores, which have diameters of 1.5 nm (black circles), 2.0 nm (red squares), 2.5 nm (green diamonds) and 3.0 nm (blue X's). The center of the pore is represented by r = 0, and the velocity is the average velocity in the *z*-dimension.

.

In the case of the Cl^- ions, the velocity profiles show that the anions are moving in an opposite direction of the cations and water molecules in the system, in that they have negative velocities. Again, for the most part the magnitude of the peak velocity increases with pore size, although there is not a significant difference between the two largest pores ($d = 2.5$ and 3.0 nm). This trend agrees with the trend observed within the fluxes calculated for these systems. Like in the velocity profiles of the cations, the velocity profiles for all but the smallest pore demonstrate a plateau shaped velocity profile, which becomes more apparent as the magnitude of the peak velocity increases. This same plateau shape and relative directions was observed in the velocity profiles of water molecules, Na^+ and Cl^- ions from simulations of the electro-osmotic flow of 0.4 M NaCl solutions inside charged silica slit pores[?] .

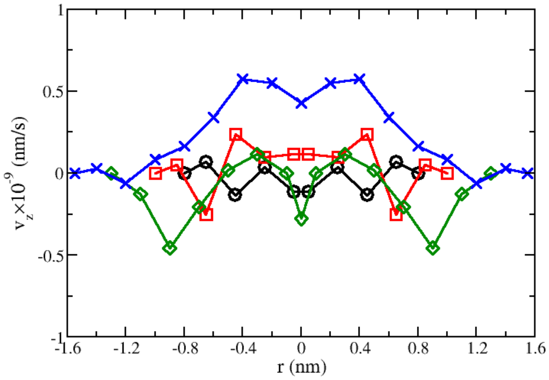

Fig. 7 Velocity profile of Ca^{2+} ions across the pores, which have diameters of 1.5 nm (black circles), 2.0 nm (red squares), 2.5 nm (green diamonds) and 3.0 nm (blue X's). The center of the pore is represented by r = 0, and the velocity is the average velocity in the *z*-dimension.

.

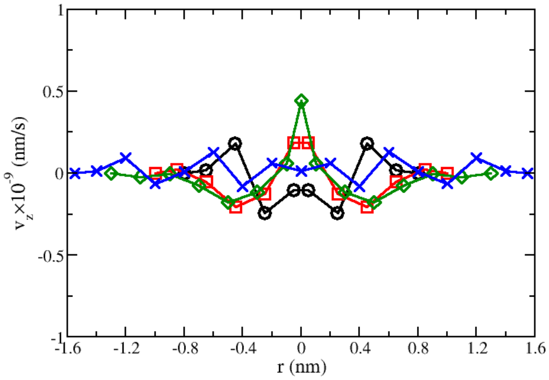

Fig. 8 Velocity profile of Cl^- ions across the pores, which have diameters of 1.5 nm (black circles), 2.0 nm (red squares), 2.5 nm (green diamonds) and 3.0 nm (blue X's). The center of the pore is represented by r = 0, and the velocity is the average velocity in the *z*-dimension.

.

Figures 7 and 8 show the velocity profiles of the Ca^{2+} and Cl^- ions, respectively, in the 0.5 M CaCl2 systems for the four different pores. The velocity profiles of the Ca^{2+} ions in the $CaCl_2$ systems (see Fig. 7) show that again as the pore size increases the peak velocity also increases. However, there is no such discernable trend observed in the velocity profiles of the Cl^- ions (Fig. 8). There is no significant velocity of either ion in the $d = 1.5$ nm pore. The velocity profiles of the Ca^{2+} then begin to adopt the same plateau shaped velocities as seen in the NaCl systems for the systems with the larger diameter pores.

The shape of the Cl^- velocity profiles is not as obvious due to the small magnitude of the velocities, but as the pore diameter increases a plateau in the velocity in the centre of the pore becomes more apparent. The magnitudes of the velocities of both the cations and anions in the $CaCl_2$ systems are smaller than those observed in the NaCl systems.