Supplementary Information for "Dynamic Behaviour of the Silica-Water-Bio Electrical Double Layer in the Presence of a Divalent Electrolyte"

B. M. Lowe, Y. Maekawa, Y. Shibuta, T. Sakata, C-K. Skylaris, and N. G. Green,

5th October 2016

In the interest of reproducibility, the molecular dynamics trajectories (.xyz files), videos of the trajectories, analysis code and analysis data are openly available from the University of Southampton repository at:

http://dx.doi.org/10.5258/SOTON/401018

1 Surface Charge Density

The surface charge density used in these simulations of $0.2 \,\mathrm{Cm}^{-2}$ corresponds to pH 5.5 according to the XPS experiments of Duval et al. on Quartz¹. However, accurate quantification of silica surface charge is complicated by the strong ionic strength dependency and variability depending on silica surface preparation. For example, some studies correlate this surface charge density to pH 8.5-9.5 based on 0.1 M ionic strength^{2,3}. Emami et al.⁴ estimates at 0.1-0.3 M this surface charge density would correspond to silica at pH >9 or quartz at pH between 7 and 9. This work utilised a (100) alpha-quartz (SiO₂) surface.

2 Electric Field Calculation Methodology

For electric field calculations within the main text, post-processing of the trajectory was performed to calculate the electric field at the position of a test charge. Two methods were utilised, each with advantages and disadvantages.

2.1 Coulomb Summation

In the Coulomb Summation method (e.g. Figure 12, main text) a non-periodic super-cell was extracted containing the unit cell and its 9 closest neighbors in the x-y plane. A finite-coulomb sum over all atoms to a -1e test charge was used to obtain the electrostatic force and thereby the electric field at the test charge coordinates. This method allows neglect of the field introduced by periodic images in the z-axis and is computationally cheap for calculating the electric field across a plane.

Figure 1 shows the electric field on a test charge centered 1 Å below the silica slab using the Coulomb Summation method.



Figure 1 Electric Field of mixed valency systems from this work, calculated via finite-coulomb summation for a test charge centered 1 Å below the slab, included in the calculation are the 9 adjecent periodic xy images.

2.2 Ewald Summation

The other method utilised was an Ewald sum (e.g. Figure 11, main text), which provides accurate treatment of periodic electrostatic interactions, but suffers from high computational expense and error introduced by the non-uniform compensating background charge introduced with the test charge for orthorhombic systems⁵. A test charge near the base of the cell will experience electrostatic forces dominated by the periodic image in the z-direction, therefore, for these calculations, an extra unit cell of vacuum padding was introduced to reduce this contribution. The Ewald sum was implemented using the open source software Pysic 0.6 (https://github.com/thynnine/pysic/) and the following parameters:

real_cutoff=10 k_cutoff=0.8999999999999999 sigma=3.333333333333333 epsilon=0.00552635

Where epsilon is in units of $\frac{e^2}{eVA}$.

Figure 2 shows the electric field on a test charge centered 1 Å below the silica slab using the Ewald Summation method.



Figure 2 Electric Field of mixed valency systems from this work, calculated via Ewald summation for a test charge centered 1 Å below the periodic slab.

3 Silanolate coordination numbers



Figure 3 Silanolate-[atom] Radial Distribution function (RDF) as a function of 0 mM, 200 mM and 1000 mM ionic strength for silica-water systems. (a) Silanolate-Na⁺ RDF, each silanolate showed an average of 1.6-2.3 Å O·...Na ion-pair distance (b) Silanolate-Water(H) RDF, each silanolate showed an average of 1.25-2.0 Å O·...H hydrogen bond length. These figures were integrated and scaled appropriately to obtain the coordination numbers displayed in the main text Figure 5. Increasing ionic strength resulted in an increase in sodium ion coordination to silanolate ions and corresponding decrease in water coordination.

4 Residence Times of $Si-O^- \cdot ...H_2O$



Figure 4 Residence time of water to silanolate groups at the silica surface as a function of ionic strength. The colored region around each line represents the standard deviation of the mean based on three separate samplings 100 ps apart, starting at 2 ns. No significant effect on the residence time is observed due to changes in ionic strength, with a fixed residence time (1/e) of approximately 80 ps. The residence time of water molecules around a silanolate ion was calculated from the Time Correlation Function calculated as per the definition of Impey et al.⁶ with a t_{absence}=0 and the solvation sphere defined based on the second RDF peak shown in Figure 5 i.e. hydrogen atoms within 3.5 Å.

5 Diffusion Coefficient of Dissociating Na⁺



Figure 5 Plot of the Mean Squared Displacement (MSD) as a function of time for Na^+ in a simple interfacial system (0 mM system), shown as a dashed line, compared to bulk water shown as a solid line. Both systems show a roughly linear increase in MSD which is characteristic of a freely diffusing system. The diffusion coefficients were calculated (Equation 1, main text) from the MSD as $4.02 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ and $3.24 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ for the interfacial dissociating ion and bulk systems respectively. A 1 ps interval was used for the MSD calculation. Bulk water simulation performed using 20 Å cubed simulation cell.

6 Residence time of $Na^+ \cdot ... H_2O$



Figure 6 The residence time of water molecules around sodium ions as a function of ionic strength for the interfacial systems. The system is divided into two regions, the surface being z < 22 Å, i.e. within ~5 Å of the surface, and the bulk being the rest of the system. Calculated from the Time Correlation Function calculated as per the definition of Impey et al. ⁶ with a t_{absence}=0 and thesolvation sphere defined based on the second RDF peak shown in Figure 5 (main text) i.e. hydrogen atoms within 3.5 Å. The time correlation function represents the average number of water molecules which haven't been exchanged with the bulk solvent, i.e. 1 represents the initial state and 0 represents all ions completely exchanging their initial solvation sphere. The colored region around each line shows the standard deviation of the mean based on three separate samplings 100 ps apart, starting at 2 ns. The residence time (1/e) can be seen to be approximately 20 ps at the surface and approximately 11 ps in the bulk, with a slight dependence on ionic strength. The demonstrated increase in residence time at the surface suggests a more kinetically stable solvation sphere for surface coordinated ions, and is likely a result of the structuring of water and ions found at the interface.

7 Poisson-Nernst-Planck Theory

The PNP model utilised in this work is an extension of the 1D model provided by COMSOL Multiphysics[®] for diffuse double layers, modified to incorporate Mg^{2+} mixed electrolyte⁷. The fluxes (N_i) of the ions are obtained by solving the Nernst-Plank equation:

$$\mathbf{N}_i = -D_i \nabla c_i - u_m i z_i F c_i \nabla \phi,$$

where the concentrations c_i where i = Na, Cl, Mg with respective charges z_i of +1, -1 and +2. D_i is the diffusion coefficient, $u_{m,i}$ the mobility (s.mol/kg), F the Faraday constant and ϕ the electric potential in the electrolyte phase.

From conservation of mass:

$$\nabla \cdot \mathbf{N_i} = 0.$$

For the potential, Poisson equation states:

$$\nabla \cdot (-\varepsilon \nabla \phi) = \rho,$$

where ε is the permittivity, which is the vacuum permittivity multiplied by the relative permittivity of the medium ($\varepsilon_0 \varepsilon_r$) and ρ is the charge density, which depends upon the ion concentration according to:

$$\rho = F(z_{Na}c_{Na} + z_{Mg}c_{Mg} - z_{Cl}c_{Cl}).$$

With regard to boundary conditions, the bulk is grounded ($\phi(bulk) = 0$) and at the bulk position, the ion concentrations are set to their bulk values, whereby the positive and negative ions have equal concentration. At the surface, a Stern layer is incorporated, which extends to λ_s . The numerical simulation 1D domain spans from λ_s to x = bulk, therefore x = 0 represents the outer Helmholtz plane (OHP), for which the following boundary condition is satisfied:

$$\mathbf{n} \cdot (-\varepsilon \nabla \phi) = - \frac{\varepsilon(\phi_M - \phi)}{\lambda_S}$$

Where ϕ_M is the electrode/surface potential, ϕ is the electrolyte potential at x = 0 and **n** is the vector normal to the surface (i.e. x-direction in this 1D model).

Therefore surface charge density σ is obtained over the Stern layer as (simple capacitor):

$$\sigma = rac{arepsilon(\phi_M-\phi)}{\lambda_S}$$

The parameters used in these simulations can be found in Table 1.

The effect of ionic strength at 190 mV surface potential can be found in Figure 7, independent of ionic strength, the bulk concentration is reached within \sim 1 nm.



Figure 7 GCS model, calculated concentration profile of ions relative to bulk concentration $(C - C_0)$, as a function of distance from the surface at a surface potential of 190 mV. Bulk ionic strengths of 0.1 M, 1 M and 10 M are shown. Calculated using parameters in Table 1. Independent of ionic strength, the bulk concentration is reached within ~1 nm.

Parameter	Value	Units
Cl _{bulk} ⁻ (Bulk Cl ⁻ concentration)	0.745251724	mol/dm ³
Mg_{hulk}^{2+} (Bulk Mg^{2+} Cation concentration)	0.248417241	mol/dm ³
Na _{bulk} ⁺ (Bulk Na ⁺ concentration)	0.248417241	mol/dm ³
<i>I</i> _{bulk} (Ionic Strength of Bulk)	$0.5(4Mg_{hulk}^2 + Na_{hulk}^+ + Cl_{hulk}^-)$	-
D_{Cl} (Diffusion Coefficient)	2×10^{-9}	m^2/s
D_{Mg} (Diffusion Coefficient)	$0.71 imes10^{-9}$	m^2/s
D_{Na} (Diffusion Coefficient)	1.3×10^{-9}	m^2/s
Relative permittivity of water ($\varepsilon_{\rm r}$)	78.5	1
Maximum mesh element size: bulk	(Cell length)/20	m
Maximum mesh element size: electrode	(Debye Length)/100	m
Cell length	(Debye Length)*10	m
$\phi_{ m M}$	-0.19	V
T_0 (Temperature)	298.15	K
<i>V_{therm}</i> (Thermal voltage)	RT_0/F	V
Debye length	$\operatorname{sqrt}(\varepsilon_0 \varepsilon_{h_2o} V_{therm}/(2F I_{bulk}))$	-
Stern layer thickness	$0.5 imes 10^{-9}$	m

Table 1 Parameters used in GCS calculations. The mobility constants were calculated via the Einstein relation.

8 Average Charge Distribution and Electric field

In this paper, the average charge distribution as a function of distance from the silica surface was calculated, as shown Figure 8. The cumulative sum of this curve is plotted in the main paper Figure 9. In order to calculate the potential, the 1D Poisson Equation was solved using the average charge distribution, and the electric field was calculated as the gradient of this curve, both of which can also be found in Figure 8.



Figure 8 The mean charge density as a function of distance normal to the silica surface, note that Figure 9 (main text) is the cumulative sum of this curve. Potential calculated by solving the Poisson equation using the charge density in the top figure. The Gauss–Seidel method was used with Neumann boundary conditions at the base of the silica ($z_{base}=0$ Å) and at $z_{bulk}=80$ Å, which was considered the bulk, thereby providing a relative potential within the system. The solution was converged such that successive iterations of the surface potential ($\psi(z_{bulk})-\psi(z=16.86\text{\AA})$) were within a tolerance of 1e-6 V. An additional constraint required convergence of the each point with its previous iteration to be within 1e-5 V for the entire system and remain so for over 5000 iterations. The potential shown was then reference d to the minimum potential in the system due to a layer of atoms in the fixed silica substrate, which offers a consistent reference potential between all the simulations. The electric field is calculated as a the gradient of the potential. Calculated based on the mean charges in 0.01 Å thick slabs parallel to the xy plane.

9 Effect of DNA on Water Orientation

The negative charge on the DNA phosphate groups is expected to orientate the water in its environment, much like the silica surface charge. A plot of the water orientation with respect to the silica surface is shown in Figure 9, the DNA significantly affects the water orientation at the surface. For the 200 mM/1000 mM systems, the DNA linker was more extended and the perturbation due to the DNA can therefore be seen at a greater distance from the surface than for the 0 mM system.



Figure 9 The mean orientation of water dipoles $(cos(\theta))$ relative to the silica surface normal, as a function of the z-distance from the surface, using 1 Å bins. Increased ionic strength led to a layer of water at 20 Å which oriented towards the chloride ions, as discussed in Figure 9(C) (main text) and the work of Maekawa et al.⁸. Dashed lines show the corresponding system incorporating DNA; it can seen that DNA is disrupting the orientation of water across the system, particularly in the case of low ionic strength. The standard error of the mean was negligible near the surface due to the strongly oriented water but 0.05 ± 0.01 for all $cos(\theta)$ past 20 Å.

10 Electric Field in NaCl



Figure 10 Electric Field of monovalent interfacial silica-water systems from Maekawa et al. as a function of ionic strength⁸. Calculated via Ewald summation for a test charge 1 Å below the periodic slab. Error bars show the standard error of the mean.

References

- [1] Y. Duval, J. A. Mielczarski, O. S. Pokrovsky, E. Mielczarski and J. J. Ehrhardt, J. Phys. Chem. B, 2002, 106, 2937–2945.
- [2] M. Löbbus, W. Vogelsberger, J. Sonnefeld and A. Seidel, *Langmuir*, 1998, 14, 4386–4396.
- [3] M. Kosmulski, Journal of Colloid and Interface Science, 1993, 156, 305–310.
- [4] F. S. Emami, V. Puddu, R. J. Berry, V. Varshney, S. V. Patwardhan, C. C. Perry and H. Heinz, Chem. Mater., 2014, 26, 2647–2658.
- [5] E. Wasserman, J. R. Rustad and A. R. Felmy, Surf. Sci., 1999, 424, 19–27.
- [6] R. W. Impey, P. A. Madden and I. R. McDonald, J. Phys. Chem., 1983, 87, 5071–5083.
- [7] COMSOL Multiphysics®v. 5.2, Diffuse Double Layer Application ID: 21981, Comsol ab technical report, 2016.
- [8] Y. Maekawa, Y. Shibuta and T. Sakata, ChemElectroChem, 2014, 1, 1516–1524.