Molecular Dynamics Investigation of the Field-Effect at the Technologically Relevant Silica-Electrolyte Interface

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Abstract

The silica-electrolyte interface is an important component to many modern devices in bionanotechnology. In particular, many Field-Effect Transistor (FET) Sensors operate by detecting changes in the silica-electrolyte surface potential due to binding of analyte molecules. Addition of charged macromolecules to the electrical double layer at this interface results in a perturbation which cannot be accurately described using conventional mean-field models, which neglect the explicit contribution of water polarisation and the spatial arrangement of biomolecular charges. In this work, Molecular Dynamics simulations are performed to investigate the dominant factors controlling the surface potential for a system containing a highly charged biomolecular analyte. The results demonstrated the importance of water polarisation in generating the surface potential, and highlight the need for further investigation of the surface charging behavior of this interface.

1. Introduction

Silica and water represent some of the most abundant chemical systems on the planet, and their interface is relevant to a large range of fields from biosensing [1,2] to fundamental geochemical processes such as dissolution [3]. Despite over a century of extensive study, the precise structure and dynamics of this interfacial region, including the electrical double layer, remains elusive.

Silica is a popular choice of surface material for many chemical sensors. In the last three decades there has been significant interest in developing highly sensitive label-free nanoscale chemical sensors which offer the prospect of ultra-high sensitivity, low-cost production, portability and facile miniaturisation as part of a 'Lab-on-a-Chip'. A popular candidate technology is that of FET sensors. While FET-based pH sensors (often referred to as Ion-Sensitive or IS-FETs) were initially popularised several decades ago with the work of Bergveld [2], the extension of these devices to sensitive and reliable detection of biomolecular analytes ("BioFET" devices) has proved more difficult than initially expected, primarily due to the a limited understanding of the interfacial physics that drive their operation.

FET-sensor response is driven by changes in the electric field at the oxide sensor surface due to the presence of an aqueous solution containing an analyte (bio)molecule. This causes a change in concentration of charge carriers within the device, finally resulting in a measurable change in the device conductivity. Both IS-FETs and Bio-FET systems therefore provide a highly technologically relevant application for improving understanding of the structure and dynamics of the silica-water interface. The electrostatic potential difference from the surface to the bulk of the electrolyte determines the response of FET-sensors.

To investigate the surface potential behavior of this technologically relevant interface, explicit-solvent molecular dynamics (MD) simulation of the silica-electrolyte-DNA interface was performed.

2. Computational Methods

For the silica-electrolyte-DNA simulations, the COMPASS II 1.2 forcefield was used. This forcefield has been parameterised predominately using *ab initio* data for a wide range of condensed systems; both organic and inorganic systems and on a range of ionic liquids [4]. This forcefield can accurately describe water polarisation due to its explicit description of water O-H bond vibration. Simulations were performed under the NVT ensemble for 2 ns equilibration and 1 ns production.

Three different electrolyte systems considered: 0 M electrolyte (salt free, corresponding to deionised water); approximately 0.2 M ionic strength electrolyte; and approximately 1 M ionic strength electrolyte, each containing a 1:1 molar ratio of NaCl to $MgCl_2$. Systems with and without DNA were simulated.

In the model used, the silica surface and DNA each are assigned charges consistent with experimental data, and the net negative charge of both silica and DNA initially results in a negatively charged simulation cell. Then, in all simulations, Na^+ was introduced to compensate net charge and maintain charge neutrality in the system. Charge neutrality is expected within the length scale of the simulation cell based on calculations performed with the Poisson-Nernst-Planck equation for 200 mM or greater ionic strength mixed $NaCl:MgCl_2$.

3. Results and Discussion

MD simulations of the silica-electrolyte interface were first performed in absence of DNA. The orientation of water molecules was calculated as a function of their z-position

within the simulation cell as shown in Figure 1. Water molecules close to the negatively charged silanolate groups water reoriented with hydrogens pointing towards the silica surface ($\cos(\theta) < 1$). Na^+ and Mg^{2+} ions condensed at the interface, and water molecules solvating these ions reoriented in the opposite direction, resulting in a layer of inversed water molecules ($\cos(\theta) > 0$). Waters in the bulk were isotropic ($\cos(\theta) = 0$). Orientation water polarisation around the condensed cations at the silica-water interface was found to strongly determine the surface potential of the system.
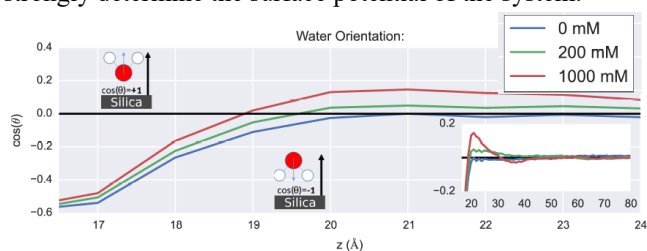

Fig. 1 Water orientation as a function of distance from silanol groups at the silica surface (z=16.5 Å). The inset shows the same plot across a larger scale.

MD simulations of the silica-electrolyte-DNA interface were also performed. Ions were found to condense on the DNA phosphate groups with proportions in agreement with experimental and theoretical predictions [5]. The surface potential was calculated before and after DNA addition and no statistical difference was found for the electrolyte containing systems. This counterintuitive result was a consequence of combined electrostatic screening by condensed ions and a polarized layer of water surrounding the highly charged DNA.

Given that the detection of highly charged polyelectrolytes by FET sensors has been experimentally demonstrated, this result suggests that DNA generates a response by a mechanism not described within this simulation such as (a) modifying the surface charge or (b) disrupting the electrical double layer over much longer timescales.

To address these mechanisms and extend upon our previous *ab initio* simulations of surface charging [6] we are currently performing MD simulations. To investigate mechanism (a), the simulated surface charge is modified in accordance with experimental surface charge measurements. The simulated potential can be directly validated against experimental surface potential data, shown in Figure 2. Experimental data shows that thermally grown silica surfaces have a characteristic change in surface potential of ~33 mV/pH. In order to investigate (b), MD simulations are currently being performed for investigating an order of magnitude longer time-scales over a range of initial ion configurations.

4. Conclusions

The surface potential at the silica-water interface is important for understanding FET-sensor response, but remains poorly understood. MD simulations of the silica-electrolyte-DNA interface were performed to investigate the surface potential behavior. Water polarisation was found to dominate

the electrostatic potential. The results suggest that the mechanism of FET-sensor response due to DNA could be via disruption of surface charge or the layer of condensed ions at the surface, rather than the simple net charge considerations often made in current mean-field models of the interfacial layer. This result is currently being investigated via a systematic MD study of surface charging of silica; for which reliable experimental data is widely available for model validation.
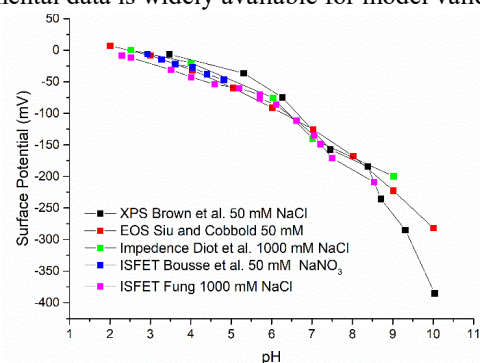

Fig. 2 Surface potential measurements of the silica-water interface extracted from the literature. In the pH range most relevant to biosensing (~pH 6-8), silica typically demonstrates 33 ± 3 mV/pH. The legend shows the measurement technique, first author and electrolyte composition. XPS=X-ray Photoelectron Spectroscopy [7], EOS (Electrolyte-Oxide-Semiconductor) [8], Impedance measurement on EOS system [9], IS-FET (Ion-Sensitive Field-Effect Transistor) of Bousse et al. [2], Fung et al. [10].

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