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MOLECULAR DYNAMICS MODELING OF ELECTRIC DOUBLE LAYERS WITH SPECTROSCOPIC APPLICATIONS

by

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Molecular dynamics is used to model the structure and dynamics of electric double layers at a charged metal surface and to ask questions of spectroscopic interest. In particular: What is the molecular basis for changing the position of the outer Helmholtz plane (OHP) thereby tuning the electric field across the inner layer? Another topic is the microscopic basis of modulation spectroscopies like SNIFTIRS Our MD simulations of an immersed electrode show features corresponding to: compact layer, diffuse layer, highly oriented water layer next to the metal when the electrode is charged and ions are present, penetration of nominally diffuse layer species into inner layer, ion pair formation between contact adsorbed ion and diffuse layer ion when the electrode is uncharged, poorly oriented surface water when the electrode is uncharged. All these properties arise from the model with the restriction that charge on the metal and aqueous phase sums to zero, ie., $q_M + q_{ions} = 0$.

Molecular Dynamics Modeling of Electric Double Layers with Spectroscopic Applications

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Introduction and Model

We use molecular dynamics (MD) to model the structure and dynamics of electric double layers at a charged metal surface and to ask questions of spectroscopic interest. In particular: What is the molecular basis for changing the position of the outer Helmholtz plane (OHP) thereby tuning the electric field [1, 2] across the inner layer? Another topic is the microscopic basis of modulation spectroscopies like SNIFTIRS [3]. Our MD simulations of an immersed electrode show features corresponding to: compact layer, diffuse layer, highly oriented water layer next to the metal when the electrode is charged and ions are present, penetration of nominally diffuse layer species into inner layer, ion pair formation between contact adsorbed ion and diffuse layer ion when the electrode is uncharged, poorly oriented surface water when the electrode is uncharged. All these properties arise from the model with the restriction that charge on the metal and aqueous phase sums to zero, ie., $q_M + q_{ions} = 0$.

Interaction with the metal was represented by a 9-3 potental for Pauli repulsion and attractive dispersive interactions, and an image potential for interaction with the conduction electrons. On the side opposite the metal the electrolyte was constrained by the 9-3 potential of a 'dielectric-like' bounding surface. This boundary limited the extent of the fluid phase, and kept the calculations tractable. System composition was $mM^{+} + nX^{-} + (N-m-n)H_2O$

where N is the number of water molecules in the absence of ions, and (m,n) = (0,0),(1, 0),(0, 1),(1, 1),(2, 1),... . Heinzinger parameters [4] for st2 water model and alkali halides MX were used. Electrostatic fields were calculated exactly (no cut offs) by the fast multipole method.

Double Layer on Charged Electrode

We display a sample result here (see Figure 1) for a system composed of one Li^+, two I^- and 155 waters in a cubic simulation cell with edge length 1.862 nm and periodically replicated in the (x,y) plane. The metal surface at $z = 0.932$ nm has $q_M = +|e|$ (anodic). Figure 1 shows the density profiles averaged over the xy plane as a function of z for all components of the system. The iodide distribution is sharply peaked near 0.7 nm just inside the repulsive portion (dash line) of the 9-3 potential. The iodide distribution is compact and the Li^+ distribution is diffuse. At negative z the Li density has the gradual fall off expected for an electrostatically bound species. The main component of the Li density ends at 0.05 nm which we interpret as the position of the OHP, being approximately two water diameters from the repulsive wall at $z = 0.682$ nm. In the region between 0.05 and 0.3 nm the cation has finite probability of penetrating the inner layer. This process is not part of usual Stern-Gouy-Chapman theory. The structure near the metal surface in the densities for water, H, and PC (point charge of the st2 model) arises from an oriented layer of water with a PC pointing at the metal. This an important result of our model with implications for modulation spectroscopy.

Application to Surface Spectroscopy

The idea of altering the position of the outer plane to change the field across the inner layer has been proposed many times [1, 2]. This effect can be modeled with the primative system used here. Based on the total charge distribution given in Figure 1 we see that the iodide and oriented surface waters determine the charge density near the metal. Note the positive charge peak at 0.65 nm. It and weaker positive peaks near 0.4 and 0.2 nm make it difficult for positive ions to approach the interface even though the latter carries net negative charge because of two adsorbed anions. Two opposing effects operate as cation size is increased, and their balance determines the field effect. First the OHP will move to more negative z due to larger radius and electrostatic repulsion from the positive charge peaks. Second at larger radii the cation hydration shell is softer making it easier for the ion to penetrate the inner layer. In Figure 1 the tail between 0.0 and 0.3 nm indicates how difficult this is for Li ion with its strongly bound solvation shell. More calculations exploring this effect are in progress and will be presented at the meeting.

Conclusion and Acknowledgement

Molecular dynamics calculations show that a simple model based on sound chemical ideas reproduces phenomena familiar from experiments on the electrochemical interface. Important new insights arise concerning the time averaged electric fields across the inner layer which in turn deepen our understanding of spectroscopic probes.

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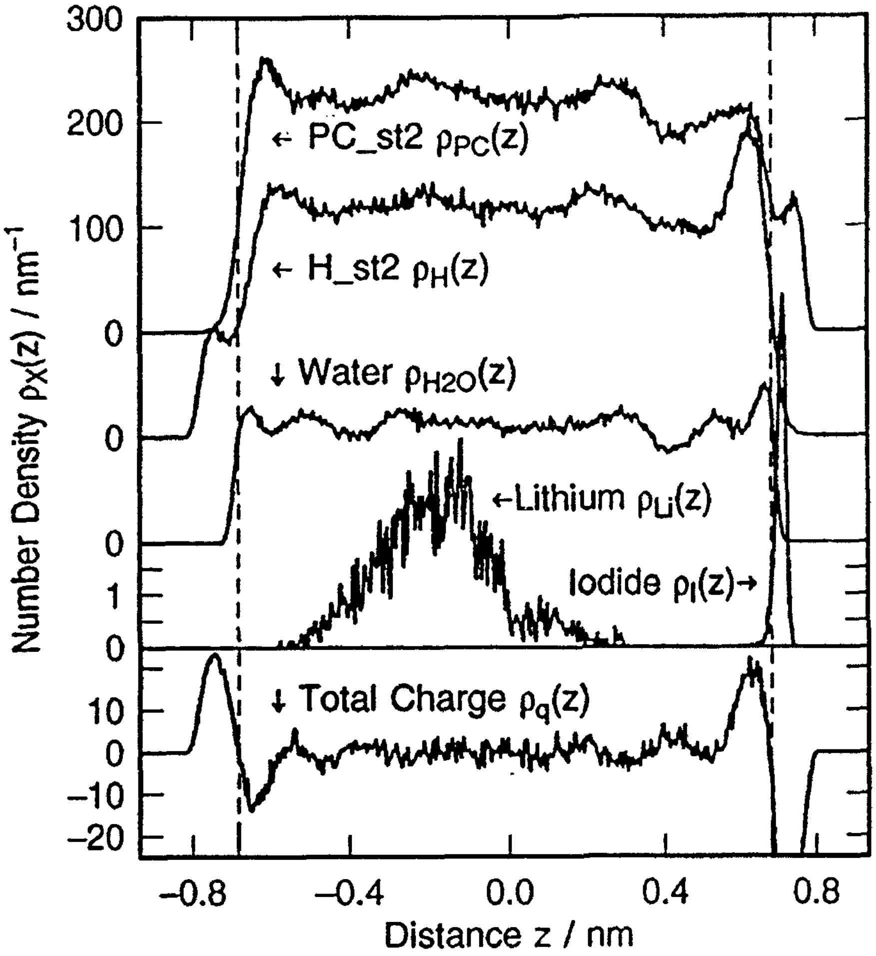

Figure 1. Density profiles for two I^-, one Li^+ and 155 st2 water molecules next to immersed electrode. Anodically charged electrode $q_M = +|e|$. Iodide distribution is compact and Li^+ diffuse. Metal on rhs, dielectric constraining boundary on lhs. Distance across the cell 1.892 nm. Repulsive portion of wall, dashed line, at $|z| = 0.682$ nm. Temperature 290K.