

# STRUCTURE OF THE ELECTRIC DOUBLE LAYER IN HYDROTHERMAL SYSTEMS. MOLECULAR SIMULATION APPROACH AND INTERPRETATION OF EXPERIMENTAL RESULTS

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## INTRODUCTION

When an aqueous electrolyte solution is put in contact with a solid surface the solid-liquid interface develops a net electric polarization resulting from the formation of an electric double layer. While this phenomenon has been known for more than a century, giving rise to a variety of theories including the first one by Helmholtz followed by Gouy-Chapman (Israelachvili 1992), and Bockris-Devanathan-Müller (Bockris, Devanathan et al. 1963). The existence of the electric double layer has a strong impact on many chemical (electrochemical metal deposition, corrosion, catalysis), biochemical (ion channels), and geological (mineral dissolution/deposition and reactivity, crystallization) processes due to charge-shielding resulting from the movement of ions toward the interface to balance the charged surface.

Typically, the theoretical investigation of the microscopic structure of the medium near the (charged or uncharged) interface has been done with simplified models, involving a structureless surface in contact with point (or hard-sphere) ions immersed in a dielectric continuum (Schmickler and Henderson 1986). Obviously, these models neglect important physicochemical aspects of the system, such as the solvent structure around the species in solution (solvation effects), as well as the reactive interaction between the solvent and the solid surface. In order to interpret the actual electrochemical behavior of ionic species in solution, their interaction with the solid surface and their mobility we

need to develop molecular-based tools. These tools must take explicitly into account the discrete nature of all species in solution and the essential features to describe the solid surface and its interactions with the contact solution (ultimately, it will include the discrete nature of the surface).

The main goal of our research is the analysis of the microscopic behavior of high-temperature aqueous electrolyte solutions in contact with metal oxide surfaces, to gain an improved understanding of the configurational behavior of the electric double layer. For that purpose we develop molecular dynamics protocols to characterize formation of the electric double layer through the determination of the profiles of species' concentrations, electric field, species diffusivity, and solvent polarization normal to the oxide surface.

## METHOD

Our study involves rather simple intermolecular potential models, most of which have been previously used in the study of high temperature aqueous electrolyte solutions (Chialvo and Cummings 1999). That is, we will initially describe the water-water interactions with the SPC/E model (Berendsen, Grigera et al. 1987), and ion-ion interactions based on the corresponding parameterization of Dang and collaborators (Smith and Dang 1994), complemented by water-interface and solute-interface interactions according to the choice of solid surface. Our system is defined as the "immersed electrode" configuration, where the electrolyte solution is sandwiched between a metal oxide and an uncharged non-metallic "restraining" wall (Glosli and Philpott 1996). We start with a structureless flat surface interacting with all species according to a restraining '9-3' type potential located at  $\pm z_{\text{wall}}$ . In addition, if there is an uncompensated surface charge on the wall located at  $z_{\text{wall}}$  the corresponding axial uniform electric field will interact with the electrolyte solution. In a second stage we explicitly include the surface structure of the metal oxide (titanium oxide) to match the X-ray standing waves (Fenter, Cheng et al. 2000) and potentiometric studies (Ridley, Machesky et al. 1999). To ensure system (surface plus electrolyte) electro-neutrality, the ionic composition is adjusted accordingly.

## RESULTS AND DISCUSSION

Our preliminary results for hydrothermal electrolyte solutions of  $\text{Sr}^{+2}$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$  in contact with a charged flat surface (within the range of experimentally-determined surface-charge density (Ridley, Machesky et al. 1999)) lend support to a long-standing belief that anions can be adsorbed on a negatively charged interface. This adsorption appears to be facilitated by the formation of anion-cation pairs, in addition to the cation's partial hydration, and does not require any specific surface site interaction. The most probable locations for the cations from the negatively charged surface are 1.6-1.8Å ( $\text{Sr}^{+2}$ ) and 1.85-2.0Å ( $\text{Na}^+$ ), in remarkably good agreement with the values obtained in the latest X-ray standing waves experiments (Fenter, Cheng et al. 2000).

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