MODELING OF ELECTRIC DOUBLE LAYER ON A METAL-ELECTROLYTE INTERFACE IN THE FRAMEWORK OF SELF-CONSISTENT FIELD THEORY

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In this work, we present a unified self-consistent field theory that incorporates key physical components often neglected in classical models: short-range specific interactions, ion hydration, dielectric saturation of the solvent, and excluded volume effects. By solving a modified Poisson-Boltzmann equation derived from the grand thermodynamic potential and employing parameters informed by quantum chemistry calculations, we accurately reproduce the differential capacitance of aqueous electrolytes at silver electrodes. We first validated our approach on the Ag(100) face, successfully modeling systems without significant specific adsorption, such as KPF_6 and $NaClO_4$ [1].We then extended the theory to account for specific ion adsorption and partial charge transfer, applying it to the Ag(100)/NaF system where fluoride ions exhibit weak specific adsorption [2]. The introduction of a Morse potential to describe the adsorption energy and the explicit inclusion of the charge transfer process yielded fitted parameters that compared favorably with independent estimates from quantum chemical calculations. Building on this foundation, we apply the model to the Ag(111) and Ag(110) faces in contact with NaF electrolyte. By fitting the model within a consistent theoretical framework, we obtain face dependent parameters, including adsorption energies, potential range parameters, and partial charge transfer coefficients, that reveal how ion-surface and water-surface interactions vary with atomic scale surface structure. These results provide new insights into the experimentally observed ordering of fluoride adsorption strength across the three low index silver surfaces. This work establishes a pathway for incorporating electrode crystal face specificity into continuum scale EDL modeling, offering a molecularly informed framework which may potentially be used in the development of supercapacitors and electrochemical energy storage devices.

1. Mazur DA, Brandyshev PE, Doronin SV, Budkov YA. Understanding the Electric Double Layer at the Electrode-Electrolyte Interface: Part I - No Ion Specific Adsorption. Chemphyschem.

2. Daria A. Mazur, Petr E. Brandyshev, Doronin S., Yury A. Budkov Understanding the electric double layer at the electrode–electrolyte interface: Part II - specific adsorption and partial charge transfer *// Electrochimica Acta. 2026.* Vol. 545. Article 147660