

A Grand Canonical Ensemble Model for Electrolytes Confined in Mesoporous Domains

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Electrodes with highly porous morphologies are of great technological interest, as their exceptionally high specific surface areas make them ideal for use in capacitors, battery electrodes and electrochemical sensors. There is a large body of research focusing on the structure of confined electrolytes in these systems, but the majority of these studies focus on cases where the length scale of the porous domain is equal to or less than the Debye screening length of the electrolyte. We discuss a recently published thermodynamic model of the structure of electrolytes in mesoscale domains, where the pore dimensions are significantly larger than the Debye screening length. In this limit, the interface is screened by the electrochemical double layer and the enclosed volume primarily consists of an electroneutral 'bulk liquid' domain. Despite the absence of direct interactions between ions in the bulk domain and the charged interface, we show that minimization of the free energy of the system leads to a reduction in the ionic strength of the electrolyte within the bulk liquid domain of the pore. Based on our model studies, we anticipate that this depletion will apply for porous domains with widths of the order of hundreds of nanometers even under mild experimental conditions. The results imply relationships between electrolyte strength, surface morphology and applied voltage that may be important in device design.