THE LIMIT OF APPLICABILITY OF THE IDEAL SOLUTION MODEL FOR DESCRIBING A DOUBLE ELECTRIC LAYER

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Surface effects always occur at the interface between two substances, determining the chemical and physical properties of the medium on either side of the boundary. A key characteristic of this interface is the formation of a electrical double layer (EDL). The simplest system to study EDL is the interface between two aqueous solutions of electrolytes with differing concentrations. The Gouy-Chapman model [1], based on the assumption of an ideal solution, is widely used to describe the electrokinetic properties of these solutions. However, in the region of high electrolyte concentrations, where free ions become strongly correlated, models based on mean field theory break down. At present, there are no analytical theories available to describe EDL in this concentration area.

The study focused on a EDL at the interface between two aqueous solutions of LiCl ions with different Li^+ concentrations. The interface was modeled as a wall that is impermeable to Li^+ ions, but permeable to other atoms and ions. Molecular dynamics (MD) simulations were performed using the LAMMPS software package.

In the course of our research, We developed a program to construct electrostatic potential profiles along MD trajectories based on the solution of the Poisson equation. We obtained the exponential asymptotics of the electrostatic potential in the region of high electrolyte concentrations. At $N_D > 0.1$ ($n < 0.4$ M), the ideal solution model provides a satisfactory description of the dielectric surface (r_D). We compared our results with data from electrocapillary experiments [2]. Above $N_D < 0.07$ ($n > 0.7$ M), we observed a deviation towards increased shielding of the electrode in MD and experimental results compared to the ideal solution model. This deviation may be attributed to an increase in ion-ion interactions due to the overlapping of hydration shells in the LiCl solution.

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