

Surfaces, double layers, and adsorption I: some historical and scientific context

The interface between a mineral and the solution in which it resides is complicated by the effect of the solid mineral's surface charge on the solvent molecules and solvent ions. Most commonly, earth scientists are concerned with an aqueous solution where the solvent molecules are H₂O and the solutes are hydrated ions. On the solid side, we can also commonly assume that the mineral surface has a negative charge, because mineral cations have been removed from that surface by hydration and dissolution. The resulting configuration of charge and solutes is commonly called a "double layer" or "electrical double layer" because of the layers of charge at this interface.

Explanations of the mineral-solution interface commonly focus on the historical development of the treatment of double layers. That history begins with Hermann von Helmholtz's (1879) simple notion of a row of adsorbed ions and was advanced by Louis Charles Gouy's and David Leonard Chapman's (~1910) models of a more dynamic and diffuse zone of ions defined by the balance of electrostatic attraction to the solid surface and diffusion away from that surface. These models assumed that the ions in solution were point charges with zero diameter, an obviously unreasonable assumption. (One must remember that von Helmholtz worked in an era when the atomic theory of matter was still hotly debated.) Only later would Otto Stern (1924) propose a more reasonable model involving ions of finite size spaced at a finite distance from a solid surface. David C. Grahame's (1947) model further included variation in hydration, and the model of Bockris, Devanathan, and Muller (1963) further dealt with water

molecules adsorbed on the solid surface. The works of Graham and of Bockris et al. is part of a tradition in electrochemistry that has used mercury as its "surface" on which adsorption takes place. From the standpoint of an experimental chemist, mercury is a convenient substance because it can carry a charge and does not develop the structural defects common in the solids used as electrodes. However, an earth scientist must wonder how applicable the results of this tradition are to earth materials.

Because of the implausibility of the early models and the tendency of electrochemists to study mercury and/or electrode surfaces, this series of pages does not take the usual historical approach but instead presents models of the mineral-solution interface that progress from the least level of interaction to more involved interaction. It builds on the model presented by Paul Schindler and Werner Stumm (1987) wherein the surface of a mineral consisting of cations and O²⁻ interacts with a solution.

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