Structure of Electrified Interfaces

The picture of the metal/solution interface (Fig A) shows that it is consist of simple elements. The metal is made up of a lattice of positive ions and free electrons. when the metal is charged with an excess-charge density σ_m, it means that there is either an excess (σ_m is negative), or a deficit (σ_m, is positive) of free electrons at the surface of the metal.

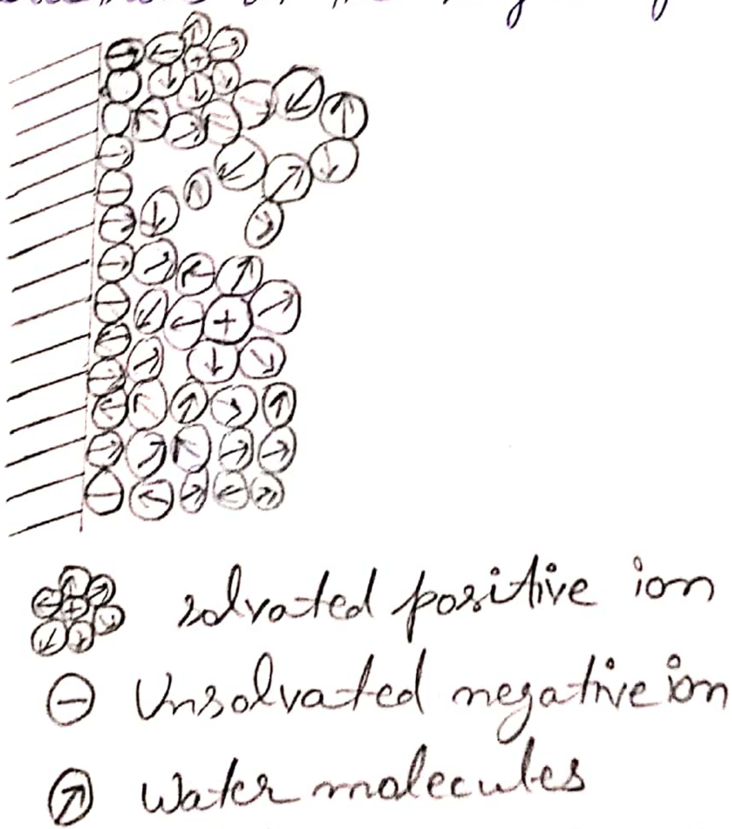

Fig-A Schematic representation of the structure of an electrified interface. The small, positive ions tend to be solvated, while the larger, negative ions are usually unsolvated.

The metal surface can be compared to a stage occupied by this excess-charge density σ_m. The particles of the solution constitute the audience that respond to the scene on the stage. The first row is largely occupied by water dipoles. The excess charge on the metal produces a preferential orientation of the water dipoles. This is the hydration sheath of the electrode. The net orientation of the dipoles changes with the charge on the metal, and the dipoles can even turn around and look away from the electrode. (Fig. B)

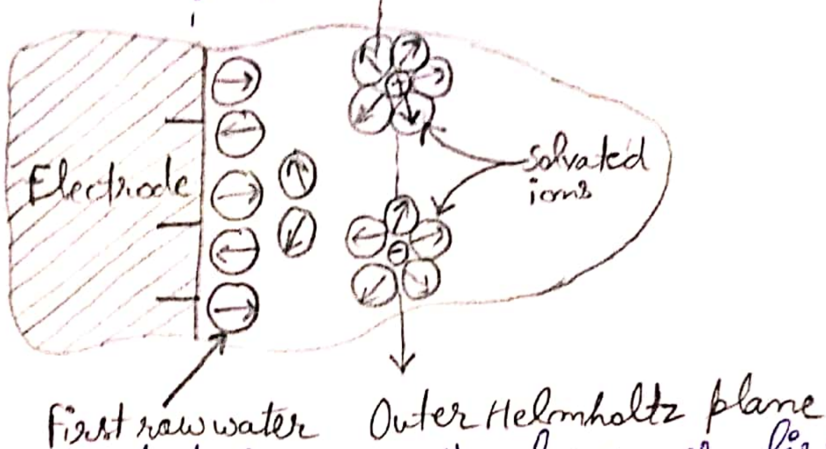

Fig B A layer of solvated ions on the layer of first-row water. The locus of the centres of these solvated ions defines the OHP.

The second row is largely reserved for solvated ions. The locus of centres of these solvated ions is called, for historical reasons, the outer Helmholtz plane, hereafter referred to as OHP (Fig B). On top of the first-row water (the primary water layer) and in between the solvated ions are other water molecules, a sort of secondary hydration sheath, weakly bound to the electrode.