THEORY OF THE COMPACT DOUBLE LAYER

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We know that from the magnitude of compact layer capacity the ratio between the dielectric permittivity within the layer and the thickness of the layer can be estimated. Reasonable model estimates of layer thickness lead to the conclusion that the effective dielectric permittivity of this layer in aqueous solutions is smaller than ten (usually a value of about six is accepted, i.e., a value but little higher than the infrared permittivity). This lowering of the dielectric permittivity usually is explained as an effect of dielectric saturation in the strong electric field of the electrode. But if this were so, then we ought to expect a more than tenfold increase in the dielectric permittivity, and therefore, in compact-layer capacity, when approaching the point of zero charge where the field in the double layer becomes zero. We know that this does not occur. But, the low effective dielectric permittivity in the double layer can be explained in terms of the concept of spatial correlation of the dipoles. The importance of this effect was demonstrated in the work of Dogonadze and co-workers [1, 2] concerning the theory of ion solvation. The correlation means that the free orientation of the dipoles in an external field is prevented by nonelectrostatic intermolecular forces, which produce a certain correlation in their mutual spatial arrangement. The thickness of the compact part of the double layer (some 4 to 5 Å), i.e., the distance at which the field changes substantially, is of the order of magnitude of the dipole correlation radius, and hence orientation polarization cannot have an appreciable effect within this layer. This must lead to low values of the effective dielectric permittivity of this layer.

LITERATURE CITED

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