charged and neutral components of the solution are analysed.

Statistical Mechanical Theories of the Electric Double Layer

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A comparison is made of different recent developments in theories of the electric double layer in aqueous media, based on statistical mechanics. An important advance was made when Henderson, Blum and co-workers showed how the Ornstein–Zernike equations, which originally applied to bulk liquid mixtures, could be modified to yield the density and charge distributions in the diffuse layer next to a charged wall. The interface solution system was treated as a mixture in which the wall of the interface is a solute particle which is exceedingly large in size but small in concentration. In the case of electrolytes (systems with Coulombic forces) a correction was necessary to earlier formulations of the theory. Various approximations well-known in modern statistical mechanical theories of liquids were used by the above authors in the Ornstein–Zernike equations modified to apply at a plane interface. All these approximations make use of the primitive model of an electrolyte, in which ions are treated as charged hard spheres embedded in a continuous solvent medium with a uniform dielectric permittivity so that the ions (and their hydration shells) have the same permittivity as the bulk electrolyte. The hypernetted chain (HNC) approximation, which has been very successful for bulk electrolytes was shown to be equivalent to the non-linear Poisson–Boltzmann (P.B.) equation of Gouy and Chapman, when the effects of the ionic hard-sphere terms can be ignored. Another approach, the so-called mean spherical approximation (MSA), corresponds to the Gouy–Chapman–Stern (GCS) theory at small potentials (linearised P.B. or Debye–Huckel equation). In the GCS theory, the ions interact with the interfacial wall as hard-spheres but continue to interact with each other as point charges. In the MSA ion-size effects are taken into account in a consistent manner. Although the differential capacity of the charged interface is calculated by the MSA theory and compared with that derived from the Stern theory, there is an important difference. The inner region capacity is much too large in the MSA theory because the effective dielectric permittivity of the inner region is put equal to that of bulk electrolyte.

Monte Carlo calculations of the electric double layer, based on statistical mechanics, have been performed by Torrie and Valleau, who use the primitive model of the bulk electrolyte. Their concentration profiles in the diffuse layer are in good agreement even up to 1 *M* with the so-called modified Gouy–Chapman (MGC) theory, which introduces an inner region with the same permittivity as the bulk electrolyte. However the criticism mentioned above about the use of bulk permittivity applies also to these calculations.

An entirely different approach to electric double layer theory has been used by the authors and co-workers. This develops a modified Poisson–Boltzmann (MPB) equation for the electrostatic potential in the diffuse layer, which is based on the classical work of Kirkwood in strong electrolyte theory. The exclusion volume term and the fluctuation term are re-introduced, again with a primitive model of the bulk electrolyte. Making use of a 'closure' procedure originally due to Loeb for handling the fluctuation terms, the classical P.B. equation is replaced by a non-linear differential-difference equation which is solved numerically. At moderate electrolyte concentrations (>1 *M*) the mean electrostatic potential and the distribution of ions in the diffuse layer exhibit a damped oscillatory behaviour. The MSA shows similar oscillations which are attributed to ion-size effects, neglected in the P.B. equation. Physically the damped oscillatory behaviour means that there is a stratification of charge in the vicinity of the interface which depends primarily on the electrolyte concentration. At low surface charge and electrolyte concentration, the exclusion volume term has negligible effect compared to the fluctuation term but as the surface charge or electrolyte concentration is increased, the exclusion volume term becomes increasingly important. Comparison of the differential capacitance is made with preliminary calculations of Henderson, Blum and Smith, based on the HNC and identical behaviour is obtained at low surface charge. In both theories, the permittivity of the Stern inner region is equated to the bulk permittivity. Effects relating to solvent structure still remain to be incorporated. Solvent effects have been considered by Ninham and his school, using the Percus–Yevick and HNC equations, but these have been confined to non-coulombic solutes. Improvements in the model of the Stern layer can be incorporated into our theory based on the MPB equation. Also by adapting related work in the electrolyte bulk by one of the authors (C.W.) it is possible that some solvent effects can be incorporated into the MPB equation.