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Review

Ions and water molecules in an electrolyte solution in contact with charged and dipolar surfaces

Ekaterina Gongadze[a], Aljaž Velikonja[b,c], Šarka Perutkova[a], Peter Kramar[b], Alenka Maček-Lebar[b], Veronika Kralj-Iglič[d], Aleš Iglič[a,*]

[a] Laboratory of Biophysics, Faculty of Electrical Engineering, University of Ljubljana, Tržaška 25, SI-1000 Ljubljana, Slovenia
[b] Laboratory of Biocybernetics, Faculty of Electrical Engineering, University of Ljubljana, Tržaška 25, SI-1000 Ljubljana, Slovenia
[c] SMARTEH Research and Development of Electronic Controlling and Regulating Systems, Trg tigrovcev 1, SI-5220 Tolmin, Slovenia
[d] Laboratory of Clinical Biophysics, Faculty of Health Studies, University of Ljubljana, Zdravstvena 5, SI-1000 Ljubljana, Slovenia

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ABSTRACT

The electrolyte-charged surface interface is described within the Langevin–Poisson–Boltzmann (LPB) and Langevin–Bikerman models. It is shown that in the saturation regime close to the charged surface, water dipole ordering and depletion of water molecules may result in a strong local decrease of permittivity. Analytical expressions for the space dependence of relative permittivity are derived for both models. The differential capacitance as a function of the surface potential is calculated within the modified Langevin–Bikerman model and compared to the prediction of the classical Gouy–Chapman theory. As an example of the application of the models described, a zwitterionic lipid surface with non-zero dipole moments in contact with an electrolyte solution of monovalent salt ions and water dipoles is studied within the LPB model. An analytical expression for the osmotic pressure of the electrolyte solution between the zwitterionic lipid surface and a charged particle (macroion) is derived. Some of the predictions of the described electric double layer mean-field theoretical considerations are evaluated using the results of a molecular dynamics simulation. At the end a theoretical description of the possible origin of the attractive interactions between like-charged surfaces mediated by charged macroions with distinctive internal charge distribution is given.

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[*] Corresponding author. Tel.: +386 1 4768 825; fax: +386 1 4768 850.
E-mail address: ales.iglic@fe.uni-lj.si (A. Iglič).

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1. Introduction

In the complex interface between a charged surface and a surrounding electrolyte (Fig. 1), the electric double layer (EDL) plays a crucial role [1–11]. It causes the ions and water molecules to rearrange near the charged surface and thus to screen the electric potential [12–16]. Due to electrostatic forces between the charged surface and the ions in the electrolyte solution, the counterions (ions with a charge of the sign opposite to the charged surface) are accumulated close to the surface and the co-ions (ions with a charge of the same sign as the surface) are depleted from the surface.

Study of the EDL was begun in 1879 by Hermann von Helmholtz who treated the double layer as a simple capacitor, assuming that the surface charge density is neutralized by the counterions located at a distance equal to their hydrated radius. Gouy [17] and Chapman [18] considered the thermal motion of ions and pictured a diffuse double layer composed of counterions and co-ions. Within the so-called Poisson–Boltzmann (PB) theory [6,12,13,17–20], the ions in electrolyte solution are treated as dimensionless, the surfaces are considered as uniformly charged and uniform permittivity of the electrolyte solution is assumed. The Stern model [21] was the first attempt to incorporate the finite size of ions in EDL theory by combining the Helmholtz [22] and Gouy–Chapman [17,18] models [12,23,24]. Later Bikerman introduced the first complete modified Poisson–Boltzmann (MPB) model which took into consideration the finite size of molecules in the electrolyte solution [25]. This approach was continued by Grimley and Mott [26,27], Freise [28] and Wicke and Eigen [29–31]. Also more recently, the finite size of the molecules was incorporated into EDL theory using lattice statistics models [3,32,33], by functional density approaches [34–36] and by a modified PB theory where the ions and solvent molecules were treated as hard spheres [14,15,37].

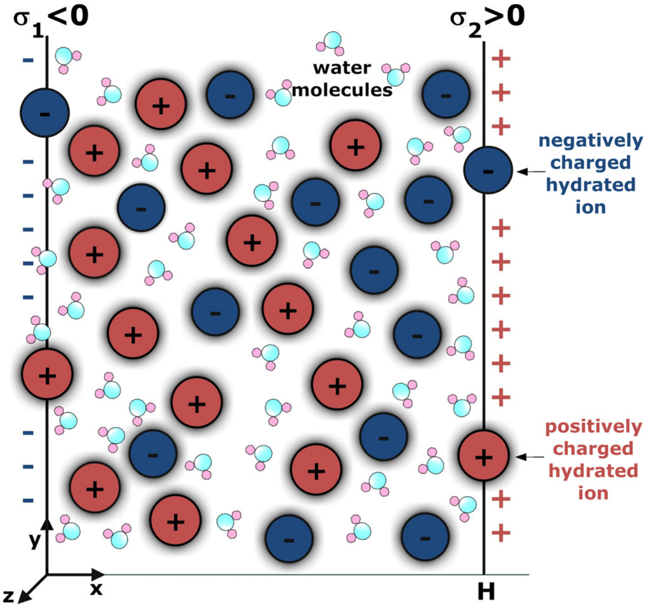

Fig. 1. Schematic figure of an electrolyte solution confined between negatively and positively charged surfaces characterized by surface charge densities σ_1 at $x = 0$ and σ_2 at $x = H$. The water dipoles in the vicinity of both charged surfaces are partially oriented towards the surfaces.

Most of the EDL models published to date are based on the concept that the relative permittivity is constant throughout the whole system [2,12,17,18,38,39]. The dipole moment vectors of water molecules at the charged metal surface are predominantly oriented in an orthogonal direction with respect to the charged surface. This results in a strong local decrease of permittivity [4,5,7,9,14–16,37,40–43], whereas all orientations of water dipoles further away from the charged surface are equally probable.

Considering simultaneously the orientational ordering of water and the finite size of molecules, Outhwaite and co-workers developed a modified PB (MPB) theory of the electrical double layer composed of a mixture of hard spheres with point dipoles and finite sized ions [14,15,37]. Later, Szalai et al. [44] published a mean spherical approximation-based theory [45] that can reproduce simulation results for the electric field dependence of the dielectric permittivity of a dipolar fluid in the saturation regime. The problem was also considered within lattice statistics [16,42,46]. It was shown that due to accumulation of counterions near the charged metal surface, the permittivity in this region is additionally reduced [46].

The Gouy–Chapman (GC) mean-field theory and its Poisson–Boltzmann (PB) equation may be used to estimate the interactions between like-charged surfaces in an electrolyte solution [12,13,47]. For a monovalent salt, it predicts repulsion between like-charged surfaces [58] in agreement with the experimental results and computer simulations. Therefore at first glance, an attractive interaction between two like-charged surfaces would seem impossible. However, the presence of ions with internal charge distribution (mediators) in the intermediate solution between the like-charged surfaces may change the repulsive interaction into an attractive one – not predicted by the mean-field GC approach. The mediators can be charged particles with a quadrupolar internal charge distribution [49–51]. This attraction is currently the subject of much interest because it is observed in a number of biologically relevant processes such as condensation of DNA [52], or the interactions between like-charged lipid membranes that occur during membrane adhesion [53] and fusion [54,55]. Electrostatic attraction between like-charged surfaces is also possible due to direct ion–ion correlations [56,57] in the limit of a high surface charge density and high ion charges [58].

In this review we present a lattice statistics approach to the theory of the EDL. First, we upgrade the description of GC theory and its PB equation by considering the orientational ordering of water molecules near a highly charged surface, the electronic polarizability and the cavity field of water molecules within the Langevin–Poisson–Boltzmann (LPB) model for point-like molecules in electrolyte solution. It is shown that the dielectric permittivity of an electrolyte close to a charged surface is decreased due to the increased orientational ordering of water dipoles. An expression for the osmotic pressure difference between the charged surfaces (Fig. 1) is also derived. The next section is devoted to the effects of ion size of the EDL within the Langevin–Bikerman