Journal of Colloid and Interface Science 488 (2017) 180–189

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

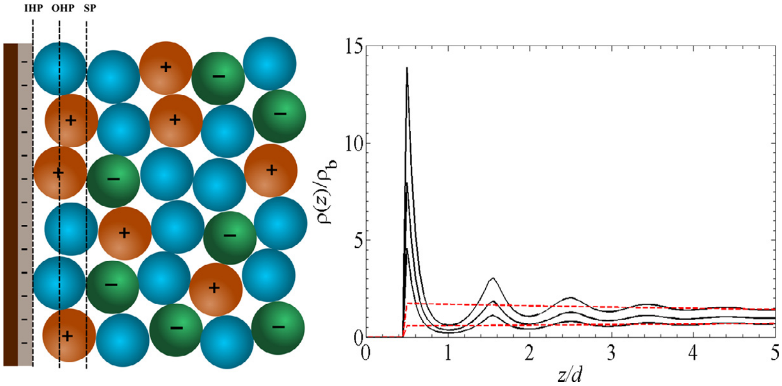
journal homepage: www.elsevier.com/locate/jcis

Electrolyte solution structure and its effect on the properties of electric double layers with surface charge regulation

R. Vangara, D.C.R. Brown, F. van Swol, D.N. Petsev *

Department of Chemical and Biological Engineering, and Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM 87131, United States

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 September 2016
Revised 26 October 2016
Accepted 27 October 2016
Available online 29 October 2016

Keywords:
Electric double layer
Charged interfaces
Electrolyte solutions

ABSTRACT

The physical origin of charged interfaces involving electrolyte solutions is in the thermodynamic equilibrium between the surface reactive groups and certain dissolved ionic species in the bulk. This equilibrium is very strongly dependent on the precise local density of these species, also known as potential determining ions in the solution. The latter, however, is determined by the overall solution structure, which is dominated by the large number of solvent molecules relative to all solutes. Hence, the solvent contribution to the molecular structure is a crucial factor that determines the properties of electric double layers. Models that explicitly account for the solvent structure are often referred to as "civilized" as opposed to the "primitive" ones that consider the solvent as a structureless continuum. In the present paper, we demonstrate that for a physically correct description of charged interfaces that involve electrolyte solutions (electric double layers), the full solution structure needs to be taken into account in conjunction with the precise surface chemistry governed by the thermodynamic equilibrium. The analysis shows how the surface charge depends on various experimentally relevant parameters, many of which are outside the realm of simple electrostatics. We present results on the effects of solvent molecular dimensions, ionic solvation, surface chemistry, solvophilicity and solvophobicity.

1. Introduction

Interfaces involving electrolyte solutions are common in nature as well as in various fields of fundamental and applied research. The contact surface between the electrolyte solution and the sec-

---

* Corresponding author.

E-mail addresses: vanswol@unm.edu (F. van Swol), dimiter@unm.edu (D.N. Petsev).

http://dx.doi.org/10.1016/j.jcis.2016.10.084

ond phase is usually charged, leading to a spatial redistribution of ions historically known as an electric double layer (EDL). The surface charge is due to an externally applied potential in the case of metal electrode or to specific surface chemistry in the case of dielectric materials. The EDL is a key concept pertinent to important areas such as colloid and interface science, electrochemistry, corrosion and material science. Therefore it is not surprising that EDLs have been extensively studied for more than a century and the efforts to obtain deeper insights continue at the present time. The first attempt to provide a physical interpretation of the EDL was offered by Helmholtz [1], who considered the charge redistribution at the interface as a simple capacitor. Later it was realized that this is not an accurate representation because of the diffuse distribution of ions in the vicinity due to the thermal motion. A better model, proposed independently by Gouy [2] and Chapman [3], described the ionic distribution using a continuum approximation known as the Poisson-Boltzmann (PB) equation [4]

$$\nabla^2\Psi = -\frac{1}{\varepsilon\varepsilon_0}\sum_i \rho_i^0 q_i \exp\left(\frac{-q_i\Psi}{k_B T}\right) \qquad (1)$$

where Ψ is the electrostatic potential, q_i is the charge of ion species "i" (in units of the elementary charge e), k_BT is the thermal energy, ρ_i^0 is the bulk number density of charged species i, ε and ε_0 are the medium dielectric permittivity, and the dielectric constant of vacuum. The Gouy-Chapman approach does not explicitly account for the ionic size and associated correlations in the EDL, which is problematic near the charged interface. This issue was first addressed by Stern [5] and Graham [6] who suggested the presence of a finite sized layer of ions and solvent molecules adjacent to the surface. This layer acts as a capacitor in addition to the diffuse potential determined by the PB Eq. (1). The idea was further developed by other authors [7–11] who offered various modifications of the PB equation in an attempt to improve the description of the EDL.

More rigorous analyses of EDLs are based on modern statistical mechanics [12–14]. These approaches are usually based on the Ornstein–Zernike (OZ) integral equation or classical density functional theory (DFT) [15–20]. Often their implementation is limited to explicitly accounting only for the charged ionic species while the solvent is considered as a structureless continuum. Such models are referred to as "primitive", while a full inclusion of all species including the solvent defines a "civilized" model (this terminology is attributed to R.H. Stokes [21]). Both the primitive [22–28] and civilized [20,29–36] models are applied to study charged interfaces. Clearly, the civilized models are superior because they account for all species in the electrolyte solution. In fact, it was demonstrated that the primitive statistical mechanical models yield results that are identical to those obtained from solving the modified PBandelman equation [37]. Hence a truly realistic description of charged interfaces that involve electrolytes requires a civilized model that explicitly acknowledges the explicit presence of the solvent molecules alongside all ionic species.

Another important aspect of EDLs is associated with the mechanism of surface charge formation. It usually originates from dissociation of surface groups, ionic adsorption from the solution bulk or both [38]. These details are lost when Eq. (1) is solved as Dirichlet or a Neumann boundary value problem where either the surface potential Ψ_s or the surface charge $\sigma = -\varepsilon\varepsilon_0(\nabla\Psi)_s$ are fixed at a constant value. This is not physically correct as pointed out by Ninham and Parsegian [39] who insisted that the boundary condition at the interface should reflect the thermodynamic equilibrium between the surface reactive groups and certain ionic species in the bulk referred to as potential determining ions (PDIs). This boundary condition is known as surface charge regulation (CR) and it presents a significant improvement in analyzing a variety of physical problems involving EDLs [40–49].

Until recently, the CR condition was not applied in conjunction with more elaborate statistical mechanical analysis of EDLs as those discussed above. An important step in that direction was taken by Heinen et al. [28], who applied the CR concept to a charged colloidal dispersion analyzed using the primitive (solvent excluded) OZ integral equation approach. The solvent effect in combination with CR boundary condition was first analyzed in our recent publication [36]. The analysis revealed that the surface CR condition strongly couples to the detailed solution structure in the immediate vicinity of the charged interface. This structure is dominated by the solvent because of its enormous concentration in comparison to that of the dissolved ions. The solvent molecules provide a structural matrix which determines the local ionic distribution. We have demonstrated that due the solvent effect the density distribution for the ionic species is liquid-like despite the fact that their actual concentration is gas-like [36].

In the present work, we perform an extensive analysis of the solvent impact on the properties of EDLs with surface charge regulation. Our particular focus is mostly on effects that have a *non-electrostatic* origin. These effects are largely responsible for experimental observations as the Hofmeister series [50,51], the well-known electrokinetic measurements of Tadros and Lyklema [52], or the more recent results on the interactions between surfaces [53–55].

The paper is organized as follows: the next section outlines the DFT model for a double layer with CR condition at the charged interface. Section 3 present the results and discussion and Section 4 summarizes the conclusion.

2. Theory

2.1. Density functional theory for charged interfaces

The focus of our study is on charged interfaces that involve electrolyte solutions (see Fig. 1). Our model is civilized as it explicitly includes all solution components including the solvent. The charge and potential are dependent on the local distribution of all ionic species and the solvent clearly has an impact on it. Following the historical tradition we will refer to the physical interface between the charged interface and the electrolyte solution as the inner Helmholtz plane (IHP), the layer of ions and solvent molecules in the immediate vicinity to the charged interface as Stern layer, [5]. The midplane of the Stern layer defines the outer Helmholtz plane (OHP). There is another plane of interest that is located between the first layer of ions (and solvent molecules) in the immediate vicinity of the interface and the bulk solution. It is often assumed that this is the shear plane (SP) known from the theory of electrokinetic phenomena [38,56–58]. Detailed molecular dynamics simulations have shown that indeed the stagnant layer thickness is usually of the order of ions or solvent molecular diameter [59–63]. Hence, an electrokinetic measurement [57] is relevant to the charge and potential at the SP, after the first layer of ions and solvent molecules near the wall.

The theoretical analysis is performed in the framework of a classical DFT [15,16,18,20,33,36]. DFT is very well-suited to be applied to inhomogeneous fluid in an external field, and hence accurately describes an EDL. The electrolyte solution is represented by PDIs, non-PDIs and counterions to both. All are dissolved in a Lennard-Jones [14] type of solvent. The functional has the form

$$\Omega[\{\rho_i(z)\}] = k_BT\sum_{i=1}^{N}\int dz\,\rho_i(z)\{\ln\left[\lambda_i^3\rho_i(z)\right] - 1\} + F_{HS}^{ex}[\{\rho_i(z)\}]$$
$$+ F_{long}^{ex}[\{\rho_i(z)\}] + \sum_{i=1}^{N}\int dz\,\rho_i(z)\left[V_i^{ext}(z) - \mu_i\right], \qquad (2)$$