



Modeling of Electric Double-Layers Including Chemical Reaction Effects



J.M. Paz-García^{a,b,c,*}, B. Johannesson^c, L.M. Ottosen^c, A.B. Ribeiro^d,
J.M. Rodriguez-Maroto^e

^a Division of Solid Mechanics, Lund University, Lund, Sweden

^b Wetsus, centre of excellence for sustainable water technology, Leeuwarden, The Netherlands

^c Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark.

^d CENSE-Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal.

^e Departamento de Ingeniería Química, Facultad de Ciencias, Universidad de Málaga, Málaga, Spain.

ARTICLE INFO

Article history:

Received 14 July 2014

Received in revised form

26 September 2014

Accepted 12 October 2014

Available online 29 October 2014

Keywords:

Electric double-layer

Gouy-Chapman

Surface complexation

Reactive-transport modeling

Nernst-Planck-Poisson

Finite element analysis

ABSTRACT

A physicochemical and numerical model for the transient formation of an electric double-layer between an electrolyte and a chemically-active flat surface is presented, based on a finite elements integration of the nonlinear Nernst-Planck-Poisson model including chemical reactions. The model works for symmetric and asymmetric multi-species electrolytes and is not limited to a range of surface potentials. Numerical simulations are presented, for the case of a CaCO₃ electrolyte solution in contact with a surface with rate-controlled protonation/deprotonation reactions. The surface charge and potential are determined by the surface reactions, and therefore they depend on the bulk solution composition and concentration.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The term electric double-layer (EDL) refers to the interface between an electrolyte solution and a solid surface [1]. Most solid materials in contact with an electrolyte develop a surface electrical charge due to, for example, adsorption/desorption processes, dissociation of surface groups, presence of potential determining ions in solution or the application of an external electric field. As a result, a nonelectroneutral region (a region with an excess of either cationic or anionic charge) appears in the electrolyte near the solid surface. Both the charged surface and the layer of liquid containing the balancing charges form the so-called EDL.

Several models for the EDL have been proposed [1,2]. Helmholtz (1879) treated the EDL as a simple capacitor, assuming a single and immobile layer of strongly attached ions immediately next to the charged solid surface. Gouy (1910) and Chapman (1913) (GC) proposed a diffuse layer model in which the electric potential decreases exponentially from the surface to the electrically neutral bulk

liquid. The Gouy-Chapman-Stern (GCS) model is a combination of the Helmholtz and the GC diffuse model. In the latter, the ion size was not taken into account. Stern (1924) stated that modeling chemical species as dimensionless points was not valid at the immediate vicinities of the charged surface, and he suggested a compact layer between the surface and the diffuse layer, with a thickness approximately equal to the radius of one hydrated ion (~0.5 nm). In the Stern (or compact) layer, it is assumed that there is no free charge and that the electric potential distribution approaches linearly to the surface. In the GCS model, the boundary between the compact layer and the diffuse layer is usually referred to as the Helmholtz plane, characterized by the potential ϕ_d . The Helmholtz plane was subdivided into the inner and the outer Helmholtz layers by Grahame (1947) who considered free of charge up to the inner layer, and the existence of specific adsorption between the inner and the outer layers [3].

Beside the Helmholtz plane, there is the so-called shear (or slipping) plane, from where a mobile portion of the EDL can flow under electric fields, leading to the different electrokinetic phenomena [3]. The electric potential at the shear plane is known as the zeta (or ζ) potential, which can be measured, for example, using the Helmholtz-Smoluchowski model in electroosmotic flow systems

* Corresponding author.

E-mail address: juanma.paz@me.com (J.M. Paz-García).

[4–6]. As the compact layer is thin compared to the diffuse layer, the surface potential, ϕ_0 , is approximated by the ζ potential in many cases.

The GC diffuse model is probably the most commonly used model for the EDL. The widely known analytical solution of the GC model derives from the Nernst-Planck-Poisson (NPP) system of equations, which mathematically describes the reactive-transport phenomena of chemical species in multi-species electrolytes [7–11]. In the GC model, the Boltzmann distribution and the Poisson-Boltzmann equations are used to describe respectively the ionic concentration and the electric potential in the diffuse layer, and they derive from the NPP system for the steady-state case. Using the Debye-Hückel approximation (valid for surface potentials lower than 25 mV in absolute value), and for the case of simple electrolytes, the Poisson-Boltzmann equation can be linearized and an analytical solution can be obtained (for details see OSM). In other cases, the system of equations is strongly nonlinear and numerical methods are needed, as pointed out by Lim et al. [2] who presented a comprehensive review of numerical solutions for EDL models.

In addition to the previously mentioned limitations, the classical definition of the diffuse layer model is based on the following Gouy-Chapman premises [12,1], that are: (1) The diffuse layer is in dynamic equilibrium (steady-state), (2) the only significant interactions in the diffuse layer are due to electrostatic forces (no chemical reaction), and (3), the surface potential is constant.

In this paper, a numerical method is used for the integration of the strongly coupled NPP system for modeling the transient formation of an EDL at the vicinity of a charged flat surface assuming chemical equilibrium in the electrolyte in contact with the surface and rate-controlled protonation/deprotonation reactions at the surface. We compute the concentration and electric potential profiles for an asymmetric multi-species electrolyte consisting of a solution of $\text{CaCO}_3(\text{aq})$ in equilibrium with $\text{CO}_2(\text{g})$ at 400 ppm (atmospheric CO_2 pressure).

The literature about theory and numerical models for electric double-layers is extensive. The key novelty of this work, with respect to research being performed up to now, is the consideration of the simultaneous electrostatic and chemical equilibrium in the diffuse layer near a flat charged surface. Additionally, in the specific case studied here, the surface chemistry is also taken into account and the time of formation of an electric double-layer is related to the kinetics of that surface reaction. Furthermore, the numerical model presented here is generalized in such a way that it can be used for different chemical systems and it can be applied to other fields such as electro-diffusive transport through charged membranes.

The work presented here allows progress in this well established field. The specific goals in this paper are: (1) to compute the transient formation of a chemically and electrostatically equilibrated EDL and (2) to estimate the time required to reach the steady-state including chemical reaction effects and for variable surface potentials not limited to the Debye-Hückel range.

2. Materials and methods

2.1. The physicochemical model

The modeled system, depicted in Fig. 1, consists of a chemically-active flat surface placed into contact with an aqueous solution. Protonation/deprotonation reactions take place at the interface between the solid and the electrolyte, in a layer of 0.5 nm thickness. Due to these protonation/deprotonation reactions, the solid develops a surface charge (negative in the given example). The property $\kappa^{-1/2}$ (m) is the Debye length, which is a characteristic value for the thickness of the diffuse layer (see OSM). In the model presented

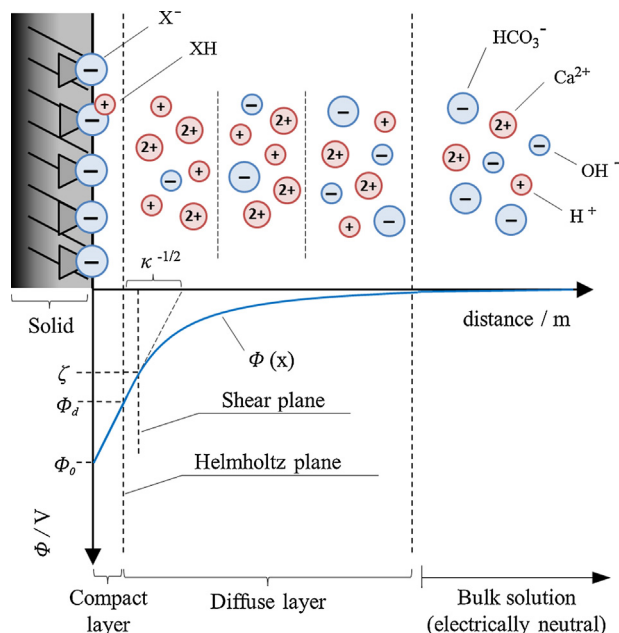


Fig. 1. Schematic representation of the modeled system.

here, we focus on modeling the diffuse layer. In the compact layer, we assume that only surface species exist, and $\phi_0 \approx \phi_d$.

The electrolyte is an unsaturated solution of CaCO_3 in equilibrium with atmospheric CO_2 (g) at 400 ppm. We assume CO_2 (g) as a simple gas and we use the Henry's law to describe the equilibrium between vapor and liquid, as

$$\frac{p_{\text{CO}_2(\text{g})}}{[\text{CO}_2(\text{aq})]} = K_H \quad (1)$$

where $K_H = 29.76 \text{ atm L mol}^{-1}$ at 25°C . From Eq. 1, the concentration of CO_2 (aq) of an electrolyte at equilibrium atmospheric CO_2 (g) at 400 ppm will be constant and equal to $0.0135 \text{ mol m}^{-3}$.

The CaCO_3 electrolyte is used to demonstrate that the model presented here is able to compute the EDL distribution in complex systems. This electrolyte solution is a multi-species and charge asymmetric mixture, meaning that the most abundant ions in the electrolyte, Ca^{2+} and HCO_3^- , have ionic charge in a proportion 2:1. The solution resulted from the dissolution of CaCO_3 is also chemically active. The concentration of CO_3^{2-} , HCO_3^- and CO_2 depends on the pH of the solution, which in the bulk electrolyte, is determined by the equilibrium with the atmospheric CO_2 .

The equilibrium reactions describing the chemical system in the diffuse layer and the bulk solution are [13,14]:



In aqueous solution, carbonic acid exists in equilibrium with non-hydrated carbon dioxide, and the concentration of H_2CO_3 is much lower than the concentration of $\text{CO}_2(\text{aq})$, as $[\text{H}_2\text{CO}_3]/[\text{CO}_2(\text{aq})] = 1.7 \times 10^{-3}$ at 298 K [15]. Based on this, in the chemical system used here we include only the species $\text{CO}_2(\text{aq})$, neglecting the hydrated form of carbonic acid.

Download English Version:

<https://daneshyari.com/en/article/6612709>

Download Persian Version:

<https://daneshyari.com/article/6612709>

[Daneshyari.com](https://daneshyari.com)