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Equilibrium modeling of ion adsorption based on Poisson–Boltzmann equation

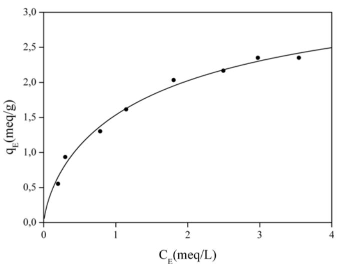
V. Steffen[a,*], L. Cardozo-Filho[a], E.A. Silva[b], L.R. Evangelista[c], R. Guirardello[d], M.R. Mafra[e]

[a] Departamento de Engenharia Química, Universidade Estadual de Maringá, Avenida Colombo, 5790, 87020-900 Maringá, Paraná, Brazil
[b] Centro de Engenharia e Ciências Exatas, Universidade Estadual do Oeste do Paraná, Rua da Faculdade, 645, 85903-000 Toledo, Paraná, Brazil
[c] Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo, 5790, 87020-900 Maringá, Paraná, Brazil
[d] School of Chemical Engineering, State University of Campinas, PO Box 6066, 13083-970 Campinas, SP, Brazil
[e] Departamento de Engenharia Química, Universidade Federal do Paraná, Centro Politécnico, Setor de Tecnologia, Jardim das Américas, 81531-990 Curitiba, Paraná, Brazil

HIGHLIGHTS

- A phenomenological model to represent the bulk adsorption of ions is proposed.
- The model proposed was based on a previous surface adsorption one.
- There was improvement and simplification in the previous model.
- The model was successful in accurately describe the investigated cases.
- It reduced the number of adjustable parameters with no lose in the fit quality.

GRAPHICAL ABSTRACT



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ABSTRACT

A phenomenological model representing ion adsorption equilibrium is proposed. It is an extension of the model used to represent surface adsorption, and it is intended to interpret bulk adsorption data. The fundamental equations of the model were established for fluid and solid phases mass balance and for the spatial distribution of ions across the sample. The electric field distribution in the system, modeled on Poisson's equation, and the chemical potential behavior were determined as a function of fluid phase equilibrium concentration. The concentration of ions as a function of electric potential is given by Boltzmann distribution. The proposed model was successfully tested to represent equilibrium adsorption of metallic ions in zeolite, showing results similar to conventional isotherms.

1. Introduction

The investigation of sorbent performance is basic for industrial application and for design of adsorption process equipment. The analysis is normally carried out through equilibrium studies on the system of interest [1]. There is a large number of available isotherms in the literature that may represent adsorption equilibrium data, among which may be mentioned the ones of Langmuir [2], Freundlich [3], Sips [4], Redlich–Peterson [5], Khan [6], Tóth [7], Radke–Prausnitz [8], Dubinin–Radushkevich [9], Frumkin [10], Flory–Huggins [11,12], and Fritz-Schluender [13]. The first two are the equilibrium adsorption isotherm models most widely accepted for single solute systems [14].

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* Corresponding author. Tel.: +55 44 3011 4749; fax: +55 44 3011 4792.
E-mail address: eq.vilmar@hotmail.com (V. Steffen).

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Nomenclature

A	adsorption energy
A_S	surface area, dm^2/g
$A_S{}^T$	total surface area, dm^2
C_0	initial concentration in the bulk fluid phase, mequiv. dm^{-3}
C_E	equilibrium concentration in the bulk fluid phase, mequiv. dm^{-3}
$C_\pm$	concentration of ± ions in the bulk fluid phase, mequiv. dm^{-3}
D	thickness of the interfacial region, dm
F_o	objective function
k_B	Boltzmann constant, J K^{-1}
L	intrinsic length, dm
m_S	adsorbent mass, g
n_S	density of ions in the surface, mequiv. dm^{-2}
N	number of sites per unit surface, mequiv. dm^{-2}
$N_\pm$	number of ± ions, mequiv.
q	electric charge of the ion, C mol^{-1}
q_E	concentration of ions on the adsorbent, mequiv. g^{-1}
T	temperature, K
V	volume, dm^3
ε	dielectric permittivity, C^2 N^{-1} m^{-2}
κ	number of elementary charges of the ion
μ	chemical potential
ψ	electrical potential
ψ_D	electrical potential at $z = D$
ψ_S	surface electrical potential

Due to the complexity of the adsorption mechanism it is rather difficult for researchers to choose isotherm models according to known mechanisms. The criterion for choosing an isotherm is, so far, mainly based on the use of statistical parameters of the model which best fit experimental data. However, a good curve, fitting in the sense of statistical evaluation, may not necessarily imply that the curve has true physical meaning, i.e., if a set of sorption data is analyzed by different isotherm equations, the best fit equation may not be the one reflecting the sorption mechanisms [15]. The importance of a model foregrounded on the physical phenomena involved in the process is thus evidenced.

Here, we propose a model for selective adsorption phenomenon in an isotropic liquid that takes into consideration localized adsorption energies. The model basically consists of a set of equations that determine the profile of the electric field and the chemical potential. It is intended to use Poisson–Boltzmann equation, a model well known in the representation of surface adsorption, for treating bulk adsorption data, but due to the complexity of the model, it is necessary to approximate the adsorbent (composed by little porous particles) as a plane surface.

The adsorption of ions in the liquid phase involves the interaction between a solvent (usually water) containing a dissolved species, the adsorbate (metallic ions), and an adsorbent solid which must have high affinity to the adsorbate. Sorption reactions inside the pores and on the surface of the adsorbent depend on the type of dissolved ions in the aqueous medium, on the chemical nature of the adsorbate, and the nature of the adsorbent surface. Thus, electrolyte ions in the aqueous medium migrate to the electrically charged sorbent surface. The cations in the sorbent solid surface are substituted by the metallic ions in the solution.

Another approach for the representation of metallic ions adsorption equilibrium data has been forwarded by Mafra et al. [16], whose mathematical model is based on the Poisson–Boltzmann equation [17–19]. The model, used to represent surface adsorption, describes the electric field distribution of a sample limited by two adsorbent surfaces. However, the equations of the model [16] are valid only for the representation of batch equilibrium data since there are variables, such as adsorbent mass, system volume and initial concentration of metallic ions, in the formulation. Moreover, the model has four adjustable parameters.

The model we are proposing here applies the Poisson–Boltzmann equation to ion adsorption and presents a mathematical formulation in terms only of adsorbate equilibrium concentrations in the fluid phase and on the adsorbent. It also evaluates strategies to reduce the number of parameters in the model when compared with the formulation developed by Mafra et al. [16]. The proposed model consists of a set of algebraic/differential equations that determine the profiles of electric and chemical potentials (differential equations) and the concentration on the adsorbent (algebraic equation).

The model will be applied to the analysis of adsorption experimental data of Fe (III) and Zn (II) on zeolite NaY, provided by Ostroski et al. [20] to illustrate the usefulness of the proposed model.

2. Basic theory

The Poisson equation is a partial differential equation of fundamental importance and wide usefulness in several research areas. It connects the electric potential (V) with the charge density (ρ) in the form:

$$\vec{\nabla}^2 V = -\frac{\rho}{\varepsilon} \tag{1}$$

where ε is the dielectric permittivity of the medium.

The liquid charge density is given by

$$\rho = q(C_+ - C_-) \tag{2}$$

where q is the charge of the ion and $C_\pm$ is the concentration of ±ions.

By inserting Eq. (2) into Eq. (1), we obtain

$$\vec{\nabla}^2 V = -\frac{q}{\varepsilon}(C_+ - C_-) \tag{3}$$

One may observe that in Equation (3) the ions densities have to be related with the electric potential. One of the most used tools to establish this relation is the Boltzmann distribution, which holds true for low concentrations and high temperatures. It may be written here as

$$\frac{N}{N_0} = e^{-(E-E_0)/(k_B T)} = e^{-\Delta E/(k_B T)} \tag{4}$$

where N is the number of systems in the energy state E, N_0 is the number of systems in the reference energy state E_0, k_B is the Boltzmann constant, and T is the absolute temperature.

Since the modeled system involves ion adsorption, the more appropriate reference state for Boltzmann distribution is the ion equilibrium concentration in the bulk fluid phase (C_E):

$$C_\pm = C_E e^{(\mu \mp qV)/(k_B T)} \tag{5}$$

where μ is the chemical potential. For convenience, the energies entering Eq. (5) will be measured in $k_B T$, i.e., $\mu/k_B T \to \mu$, and $qV/k_B T \to \psi$.

Substitution of Eq. (5) into Eq. (3) yields

$$\vec{\nabla}^2 \psi = -\frac{q^2 C_E e^{\mu}}{\varepsilon k_B T}(e^{-\psi} - e^{+\psi}) \tag{6}$$

When the Poisson–Boltzmann equation is written in one dimension, we have

$$\frac{d^2\psi}{dz^2} = \frac{e^{\mu}}{L^2} \sinh(\psi), \quad \text{with} \quad L^2 = \frac{\varepsilon k_B T}{2q^2 C_E} \tag{7}$$

defining an intrinsic length of the problem.