Fluid Phase Equilibria 296 (2010) 99–105

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Ion-specific thermodynamic properties of colloids and proteins

Frederico W. Tavares[a,b,*], Mathias Boström[a], Eduardo R.A. Lima[b,c], Evaristo C. Biscaia Jr.[b]

[a] *Escola de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, CEP 21949-900, Rio de Janeiro, RJ, Brazil*
[b] *Programa de Engenharia Química, COPPE, Universidade Federal do Rio de Janeiro, 21945-970, Rio de Janeiro, RJ, Brazil*
[c] *Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, USA*

ARTICLE INFO

Article history:
Received 7 December 2009
Received in revised form 18 February 2010
Accepted 19 February 2010
Available online 25 February 2010

Keywords:
Hofmeister series
Specific ion effects
Modified Poisson–Boltzmann equation
Density functional theory
Non-electrostatic
Potential of mean force

ABSTRACT

Franz Hofmeister established in 1888 that different salt solutions with the same ionic charges have different efficiencies in precipitating proteins from whole egg white. We will discuss how this can be understood from the modified Poisson–Boltzmann equation that accounts for ion specificity via the ion-surface non-electrostatic potential of mean force (NE-PMF) from molecular dynamics simulations. Using this approach, it is at least in principle possible to capture the important physics of the system due to the inclusion of ion-surface van der Waals forces, short range hydration, image potential and different solvent-mediated forces. The method has been proved to be efficient and suitable for describing phenomena where the water structure close to the interface plays an essential role. As an illustrative example, we demonstrate why the double layer force between two gold electrodes coated with hydrophobic self-assembled monolayers in different electrolytes can be highly ion specific. Important thermodynamic properties related to protein aggregation, essential in biotechnology and pharmaceutical industries, can be obtained from the method shown here.

1. Introduction

Ion-specific effects in biological and biochemical systems [1] have been known since 1888 when Franz Hofmeister [2] established an efficiency series in precipitating proteins from whole egg white when the species of anions were changed and the choice of cation kept constant. Similarly for fixed anion and varying cation, and the series can sometimes even be reversed [3–7]. Hofmeister (specific ion) effects have been found everywhere: in studies of protein stability and unfolding, enzymatic activity, membrane permeability to anions, growth of bacteria, uptake of water by wool and leather, in molecular forces in colloid science, pH measurements, electrolyte activities and viscosities, ion binding to micelles, ionic microemulsions, vesicle formation, cloud points of non-ionic surfactants. The list appears to be endless [8–14].

The overall aim of this paper is to discuss how one can put an understanding of systematic Hofmeister effects to work in solution chemistry, biophysical chemistry, and in chemical engineering. The proposed program for such an ambitious goal is to show how a modified Poisson–Boltzmann equation that accounts for short range ion-surface non-electrostatic potentials of mean force (NE-PMF) from molecular dynamics simulations can be exploited to provide long range PMF between colloidal particles. With PMF between colloidal or protein surfaces one can calculate thermodynamic properties of colloid and protein solutions. The number of areas that depend on a better theoretical understanding of specific ion effects is so large that insights into even one would have significant long-term economic and scientific benefits. A better foundation could also provide optimal directions for experiment [14].

The shared property of these ion-specific phenomena is that none are accommodated by classical theory! So what to do? One way of testing specific ion effects in colloid science is to consider the air–solution interface of simple aqueous salt solutions. In a pioneering work Jungwirth and Tobias [15] could show that it is probably crucial to take into account the polarizability of the ions, much as Ninham and Yaminsky [1] proposed in their landmark paper several years earlier. But in contrast to Ninham and Yaminsky, Jungwirth and Tobias used molecular dynamic simulations in order to predict surface tensions. They found out that it is probably necessary to consider the influence of the ion polarizability on the solvent structure in order to get the right ordering of the surface tension. However, although MD simulations roughly predicted the right Hofmeister series of surface tensions, such simulation techniques are computer heavy to carry out, give rather bad results for surface tension of pure water, and are too complicated to be used in many practical applications.

In any case, MD simulations are not appropriate for rapid calculations of surface properties. In this respect the approach by Ninham and Yaminsky [1] is much easier to use. In principle the

---

* Corresponding author at: Escola de Química, Departamento de Eng. Quimica, Universidade Federal do Rio de Janeiro, Cidade Universitária, Ilha do Fundão, CEP 21949-900, Rio de Janeiro, RJ, Brazil. Tel.: +55 21 25627650; fax: +55 21 25627567.
E-mail address: tavares@eq.ufrj.br (F.W. Tavares).

0378-3812/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2010.02.031

influence on the ion-surface potential from some solvent effects can be taken into account within the DLVO model by using a convenient Lifshitz-like ansatz [3–7]. There, the relevant non-electrostatic (NES) interactions are taken into account via frequency summations over all electromagnetic interactions that take place in the solutions. If done rigorously, the result will be quite accurate. As a proof of principle, Boström et al. made a first attempt in this direction [16,17]. The classical DLVO ansatz was replaced by a modified Poisson–Boltzmann equation (MPBE), in which a dispersion term was added to the electrostatic interaction [16,17]. In this way ion specificity came in natural via the polarizability and the ionization potential of the ions. However, it turned out that this approximation of the non-electrostatic interactions was not sufficient to predict the Hofmeister series of surface tension [17]. The problem apparently comes at least partly from the neglect of ion–water interactions and their changes near the surface. To introduce such interactions in primitive model calculations Boström et al. [18] used Jungwirth and Tobias [15] water profile perpendicular to the surface as a basis to model a distance dependent electrostatic function, instead of a spatially constant dielectric constant.

With such a modification the description of ion profiles on surfaces became more physical within this modified DLVO approach. However, not all profiles were satisfactory, partly because of the still too crude approximation when hydration effects [5–7] and the effects from the anisotropy of the water surface layer near the interface on the dispersion potential were not included.

In a very interesting paper Luo et al. [19] used molecular simulations that included a finite size ion and explicit water molecules to calculate NE-PMF acting on an ion near an interface. As shown by Luo et al. this NE-PMF approximate reasonably well the ion-specific short range potential acting between an ion and a liquid–liquid surface. Similar simulations were recently performed for an ion near a self-assembled monolayer (SAM) [20] and for an ion near an air–water interface [21]. In parallel with this work Parsons et al. recently calculated non-electrostatic potentials that accounted for hydration effects through the use of both ion and water polarizabilities [5]. The hydration model assigns an explicit hydration shell to kosmotropic (strong hydrated) ions only. The different Hofmeister series appears to be coming out correct from a combination of ion-surface dispersion interactions and hydrated ion size. These two complementary approaches are very promising. The modified Poisson–Boltzmann equation with a proper ion-specific potential provides reasonable result for interactions across salt solutions between two surfaces that are not too close together. For interactions when the colloids come closer together it should be preferable to use simulations that include ion-specific potentials [19–26].

One question that could be raised is if ion size correlation and electrostatic correlation not accounted for in MPBE may influence the result. Solvent averaged Monte Carlo (MC) simulations were performed by Boström et al. [25] for ion distributions outside a single globular macroion in different salt solutions. The model used included both electrostatic, hard-sphere finite ion size, and NES interactions between ions and between ions and macroions. Simulation results were then compared with the predictions of the Ornstein–Zernike equation (OZ) with the hypernetted-chain (HNC) closure approximation and the non-linear Poisson–Boltzmann equation in spherical coordinates, both extended to include NES potentials. We show in Fig. 1 that there is good agreement between modified Poisson–Boltzmann theory, MC simulations, and OZ-HNC calculations when the counterions and co-ions are monovalent. This suggest that short range ionic dispersion potentials, or as an alternative the ion-surface NE-PMF from simulations that include solvation effects, can be used in solvent averaged mean-field theories such as the modified Poisson–Boltzmann equation. We present in Section 2 some discussions about how density functional theory can be used to verify under what conditions Poisson–Boltzmann is a valid theory.

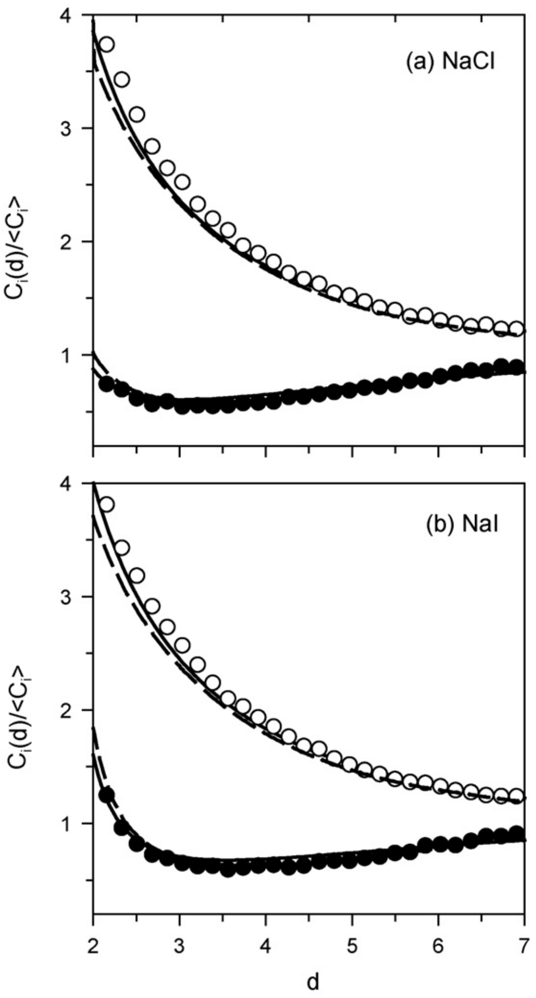

Fig. 1. Concentration profiles near a macroion ($\sigma_M = 30$ Å and $-20e^0$) in a monovalent electrolyte solution of ionic strength 1.0 M for NaCl (a) and NaI (b). Open circles represent counterion concentrations and dark circles the co-ions. Solid lines are numerical solutions of the non-linear Poisson–Boltzmann equation and dashed lines are for the OZ-HNC integral equation [13].

We have in a series of papers reported that inclusion of short range ion-surface potentials obtained from simulation [27–30], or from extended Lifshitz theory that accounts for hydration [5], probably is essential to obtain correct results. It may also be important to account for the spatial variation of the local dielectric constant near the interface [27].

The outline of this article is as follow. In Section 2, we present a discussion on how Poisson–Boltzmann theory comes out as a limiting form of the density functional theory (DFT). We also compare ion distributions obtained from DFT and PB. The conclusion is that Poisson–Boltzmann theory works well for monovalent ions, at least when the salt concentrations or surface charge densities are not too high. In Section 3 we recapitulate briefly the story of ion-surface NE-PMF from molecular dynamics simulations. Then in Section 4 we describe how the non-linear modified Poisson–Boltzmann (MPB) equation that account for such short range ion-surface NE-PMF can be exploited to obtain the long range potential of mean force between colloidal particles or proteins. This interaction between colloidal particles can then be used to calculate thermodynamic properties (e.g., phase diagrams or second virial coefficients). In Section 4 we show that the experimentally observed reversal of the Hofmeister series when pH passes the isoelectric point comes