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On the surface tension and Zeta potential of electrolyte solutions

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ABSTRACT

The distribution of ions in the vicinity of the air/water interface is still a matter of strong debate, with numerous calculations and experiments providing contradictory results, even regarding the preference of simple ions (such as H^+ and OH^-) for interfacial or bulk water. When short range interactions between ions and the interface are assumed independent of bulk concentrations, if they are compatible with the surface tension data, they underpredict the experimental Zeta potentials by orders of magnitude. If they are compatible with Zeta potential data, they are in strong disagreement with surface tension experiments. It is suggested that these observations might be a result of the relatively low number of interfacial water molecules available to hydrate the ions and the competition between various ions for adsorption sites. Therefore, whereas at low bulk concentrations, the Structure-Breaking ions prefer the interface, at sufficiently large bulk concentrations the surface adsorptions of these ions become saturated, and their interfacial concentrations may become lower than in the bulk. Consequently, the total interactions of ions with the interface can be strongly attractive at low bulk concentrations, and less attractive (or even repulsive), at high concentrations. To model this effect, the interactions between ions and interface are taken into account via modified Langmuir adsorption expressions for OH^- and Cl^-, while the H^+ ions are considered to be attached to any interfacial water molecule, even if the latter participate in the hydration of anions. The simple model of adsorption employed here is in agreement with both experiments on Zeta potential and on surface tension, and might reveal the conditions under which a given ion exhibits propensity for either the air/water interface, or for bulk water.

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1. Introduction

The distribution of ions in the vicinity of a water/air interface is still a controversial topic, in spite of its relevance to many biological and environmental processes. There is no agreement, even on relatively simple issues, such as whether the interface is positively or negatively charged in a given range of pH values and salt concentrations. Even more importantly, for some ions it is not clear whether they are more abundant or less abundant on the interface than in the bulk water.

Computer simulations (Molecular Dynamics or ab initio calculations) are typically limited to high ionic strengths. For example, a 0.1 M concentration of an electrolyte requires that more than 500 water molecules be taken into account. However, even at high ionic strengths, the polarizable force field calculations [1,2] indicate a

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positively charged surface at an electrical potential of 600 mV, whereas the ab initio calculations indicate a propensity of anions for the interface, hence a negatively charged interface [3]. There are currently a large number of computations, supporting either of these hypotheses [1,2,3].

The preference of some important ions, such as H^+ and OH^-, for the interface or for the bulk is also a matter of debate. For example, Molecular Dynamics simulations indicate an excess of H^+ on the surface, but a depletion of OH^- [4], which led to the conclusion that the interface is more acidic than the bulk [5]. However, ab initio calculations indicate the propensity of both H^+ and OH^- for the interface, with a stronger effect for hydroxide than for hydrogen [6]. Yet other calculations show no significant preference for the bulk or the interface for either of these ions [7].

Experiments are also inconclusive; whereas it seems that the (large) negative Zeta potential of neat water is due to the preferred adsorption of OH^- as compared with H^+, many other experiments indicate that the surface adsorption of H^+ is larger than that of OH^- (Second Harmonic Generation [8], Vibrational Sum-Frequency Spectroscopy [9], Phase Sensitive Sum-Frequency Vibrational Spectroscopy [10], Photoelectron Spectroscopy [11]). However, other experiments indicate that the proton availability at the interface is much lower than in the bulk [12].

Even some very simple experimental results cannot be easily reconciled; for example, the positive Zeta potentials of acidic water solutions and negative Zeta potentials for the remaining pH range, of gas/water interfaces [13,14,15] indicate that both H^+ and OH^- are strongly adsorbed at the interface, with OH^- adsorption dominating that of H^+ (because the Zeta potential of neat water is negative). However, the slight decrease of the surface tension of acidic solutions at high HCl concentrations [16] indicates very weak overall adsorptions of all ions involved (H^+ and Cl^-). On the other hand, the increase in surface tension for both salts and bases indicates an overall surface depletion of ions, which can hardly be attributed only to the commonly accepted interfacial depletion of the structure making (SM) cation (Na^+). Moreover, the surface adsorptions of Cl^- and OH^- seem to be comparable in the surface tension experiments; if the surface strongly prefers H^+ to Cl^- for comparable H^+ and Cl^- bulk concentrations, it is not clear why it strongly prefers OH^- to H^+ for comparable H^+ and OH^- bulk concentrations (in neat water).

We will argue that an important ingredient in the understanding of the distribution of ions at the water air interface is the availability of hydrating water molecules on the surface. Even if OH^- (or Cl^-) is strongly adsorbed on the interface at low bulk concentrations, at large concentrations the surface becomes saturated, and the density of ions in the interfacial region might become lower than in the bulk. Since the number of hydrating water molecules is different for each type of ion, the saturation of the surface is consequently different for different kinds of ions. For example, the experiments regarding the surface tensions of NaOH and NaCl solutions are compatible with a slightly larger number of hydrating water molecules for Cl^- than for OH^-. Moreover, H^+ being a small ion requiring fewer hydrating molecules, the surface saturation of H may occur at much larger bulk concentrations; therefore experiments at high ionic strengths should indicate more H^+ and less OH^- on the interface than in the bulk, whereas those at low ionic strengths (below saturation) indicate the opposite.

Such collective effects in ion distribution, for which the ion adsorption on the surface depends strongly on the ions previously adsorbed, cannot be described by individual interaction potentials associated with each ion (e.g., potentials independent of bulk ion concentrations), as argued in the second section of this paper. In the third section, a simple model involving the competitive adsorption of ions will be proposed and it will be shown that it is in qualitative agreement with both surface tension and Zeta potential experiments. Some reasons for not obtaining a better agreement (e.g., the neglect of the volume-exclusion effect for ions in the vicinity of the surface) will also be discussed.

2. Description of the surface tension and Zeta potential via short range interaction potentials

In this section, it will be shown that a simple model that takes into account only individual interactions between ions and the interface has to employ weak attraction (or even repulsion) between SB ions and the interface at large bulk ion concentrations, but very strong attraction at low bulk concentrations.

The distribution, $c_i(x)$, of ions in water as a function of the distance x from the charged interface is well understood, in terms of a Boltzmann distribution of ions:

$$c_i(x) = c_{0,i}\exp\left(-\frac{q_i\psi(x)}{kT}\right) \tag{1}$$

where the "mean field" potential $\psi(x)$ obeys the Poisson equation [17,18]:

$$\nabla^2\psi(x) = -\frac{\sum_i q_i c_{0,i}\exp\left(-\frac{q_i\psi(x)}{kT}\right)}{\varepsilon\varepsilon_0} \tag{2}$$

and $c_{0,i}$ is the concentration of ions of kind "i" in the bulk (considered monovalent), q_i is their charge, k the Boltzmann constant, T the absolute temperature, ε_0 the vacuum permittivity and ε the dielectric constant of water, assumed as a homogeneous medium. Whereas the "double layer" theory was successful in qualitatively predicting the ion distribution, it quickly became obvious that additional interactions between the ions and the rest of the system should also be taken into account.

These additional interactions can be roughly considered as long-range (such as the image force and the volume-exclusion force, due to the sizes of the hydrated ions), and short range interactions, that govern the distribution of ions in the vicinity of a surface (ion hydration force, ion dispersion force, cavitation, polarization, Born energies and so on).

The short range interactions are responsible for the charging of the interface and consequently affect the whole distribution of ions, as shown by the Jones–Ray effect [19], which predicts a positive surface excess of ions for all electrolytes at low ionic strengths, due to the double layer. In spite of the major theoretical, experimental and computational efforts devoted to the understanding of these interactions, there is still no agreement regarding their origin. As a matter of fact, for some ions (such as OH^-), there is no common agreement even as to whether they are attracted or repelled by the air/water interface.

From a qualitative point of view, all of these short range interactions can be approximated as short, attractive or repulsive potential wells. For simplicity, in the analysis that follows, we will assume that the interaction potentials can be described by a constant interaction potential ΔW_i (positive or negative) acting along the distance δ from the surface (the thickness of the interfacial layer). The Poisson–Boltzmann equation then becomes:

$$\nabla^2\psi(x) = -\frac{\sum_i q_i c_{0,i}\exp\left(-\frac{q_i\psi(x)+\Delta W_i}{kT}\right)}{\varepsilon_0\varepsilon} \quad \text{for} \quad x<\delta \tag{3a}$$

$$\nabla^2\psi(x) = -\frac{\sum_i q_i c_{0,i}\exp\left(-\frac{q_i\psi(x)}{kT}\right)}{\varepsilon_0\varepsilon} \quad \text{for} \quad x>\delta \tag{3b}$$

Using the boundary conditions:

$$\left.\frac{\partial\psi(x)}{\partial x}\right|_{x=0} = 0 \quad \text{and} \quad \psi(x)|_{x\to\infty} = 0 \tag{3c}$$

and the continuity of the potential and its derivative at $x = \delta$, Eqs. (3a)–(3c) can be solved if the values of δ and ΔW_i are known for

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