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Ion-specific effects on surface potential and surface tension of water solutions explained via volume exclusion effects

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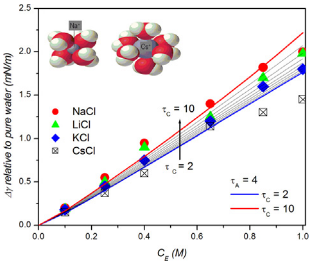
HIGHLIGHTS

- A modified Poisson–Boltzmann model, including volume exclusion effects, was proposed.
- It was shown that the effects are negligible at low ionic strengths.
- However, above about 0.1 M they become important.
- Different hydration numbers can explain ion-specific effects in surface tension.

GRAPHICAL ABSTRACT



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ABSTRACT

The competition of ions for available neighboring hydrating water molecules (the exclusion volume effect) is important at high ionic strengths. Because of the differences in the hydration numbers of various ions, the volume exclusion effects might be responsible for the observed specific ion effects (the Hofmeister series) at large electrolyte concentrations. The exclusion volume is taken into account in the framework of the Structure Making/Structure Breaking (SM/SB) model, in which the interface with a thickness of a few Ångstroms is assumed to be depleted of SM ions (typically, the cations, such as Na^+, K^+ or Li^+), while the SB ions (such as H^+, OH^-, Cl^-, Br^-, I^-) are adsorbed on the air/water interface via the Langmuir adsorption equations. Whereas at low electrolyte concentrations, the volume exclusion has negligible effect on both Zeta potential and surface tension, for ionic strengths above 0.1 M it leads to ion specificity for both of them, and this can explain the Hofmeister series in the behavior of surface tension at large electrolyte concentrations. Whereas the surface tension of salt solutions depends on the hydration number of SB anions, their equilibrium constants might be partially responsible for the ion specificity.

1. Introduction

The distribution of ions in water, in the vicinity of a surface, is typically explained in terms of the Boltzmann distribution of ions, considered as point charges, in a mean field potential provided by the Poisson–Boltzmann equation. However, this model represents only a rough approximation. Indeed, Stern pointed out long ago, that it could predict that the concentrations of ions at the surface exceed the available volume [1]. The Stern layer was the first in the long series of approaches, which took into account other interactions of ions, not included in the mean field. For example, the presence of a dielectric discontinuity at the interface leads to the image force [2], the polarizability of ions leads to the ion dispersion force [3] and the Structure Making/Structure Breaking force leads to short-range interactions between ions and surface [4]. Recently, Levin suggested that the interactions between ions

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and interfaces can be described in terms of polarization, hydrophobic cavitation, dispersion and image forces [5]. The later model was extended recently to a “continuum solvent model” that can explain the ion specificity[6]; however the calculated interaction free energy between OH^- and the air/water interface is much smaller than that required (about 20 kT) [7] to predict the Zeta potential of neat water, which is around −0.06 V [8].

Langmuir was the first to suggest that the increase in the surface tension of water upon addition of salts can be explained simply by assuming that the first water layer, with a thickness of about 4 Å, is completely depleted of ions [9]. However, the decrease of the surface tension of water upon addition of an acid implies that some ions (such as the anions ions, and H^+) have a positive surface excess. This behavior is in agreement with the large and negative Zeta potential of neat water. Additional evidence has been found recently, that the density of water at the hydrophobic air/water interface is much smaller than in the bulk, suggesting that a “Langmuir” layer with very different properties from the bulk water might exist [10,11].

It has been recently shown that a model that considers a bulk Poisson–Boltzmann distribution of ions, combined with an interfacial layer of about 4 Å, free of cations, on which the Structure Breaking ions (the anions and H^+) can adsorb, is compatible with the Zeta potential and the surface tension measurements for NaCl [12]. However, this model does not consider the ion-ion excluded volume interactions, which become important at large electrolyte concentrations [13–17]. The goal of the present paper is to show that excluded volume interactions can account for the ion specificity at least for cations, as has been determined by surface tension experiments. Although the anions exhibit also volume exclusion effects, in their case the value of the equilibrium constant might play an important role for specificity.

2. The model

The interface is considered to have a thickness δ of the order of 4 Å, which is completely depleted of Structure Making ions, and on which the adsorption of the Structure Breaking ions obeys Langmuir equation. The adsorption parameters have been determined by fitting the existing Zeta potential data [18]. Since the ions require in bulk τ_j hydrating molecules, the number of water molecules available for them becomes [13,16,17]:

$$n_{\text{available}} = n\left(1-\frac{\sum_j c_j\tau_j}{n}\right) \tag{1}$$

where n is the number of water molecules per unit volume, c_j are the ion concentrations, with the subscript j running over all the ions. Thus, the probability of finding τ_i molecules available (assuming that they are independent of each other) is:

$$p_i = \left(1-\frac{\sum_j c_j\tau_j}{n}\right)^{\tau_i} \tag{2}$$

This probability provides an additional entropic term for each ion, $-kT\ln(p_i)$, where k is the Boltzmann constant and T the absolute temperature. The thermodynamic equilibrium between the ions from the vicinity of the surface and the bulk becomes [17]:

$$\mu_i^0 + kT\ln c_{i,o} - kT\ln\left(1-\frac{\sum_j c_{0,j}\tau_j}{n}\right)^{\tau_i} = \mu_i^0 + q_i\psi(x) + \Delta W_i(x) + kT\ln c_i - kT\ln\left(1-\frac{\sum_j c_j\tau_j}{n}\right)^{\tau_i} \tag{3}$$

where $c_{0,i}$ are the ion concentrations in the bulk, q_i is the charge, x is the distance from the air/water interface (the dielectric boundary), ψ is the electrical potential, and ΔW_i is a free energy change due to additional interactions, which are not included in the mean field potential, such as the image force [2]:

$$\Delta W_i(x) = \left(\frac{\varepsilon-\varepsilon'}{\varepsilon+\varepsilon'}\right)\frac{\exp\left(\frac{a_i}{\lambda}\right)}{1+\frac{a_i}{\lambda}}\frac{q_i^2}{16\pi\varepsilon_0\varepsilon x}\exp\left(-\frac{2x}{\lambda}\right) \tag{4}$$

where a_i is the radius of ion “i”, ε_0 is the vacuum permittivity, ε is the dielectric constant of water, $\varepsilon' = 1$ is the dielectric constant of air and $\lambda = \sqrt{\varepsilon\varepsilon_0 kT/\sum_i c_{0i}q_i^2}$ is the Debye–Hückel length. Since $\exp(a_i/\lambda) = 1 + a_i/\lambda + 1/2(a_i/\lambda)^2\ldots$, the ion specificity effect in Eq. (4) is negligible until very large electrolyte concentrations (about ~1 M), when λ becomes comparable to a_i. At intermediate concentrations, the volume exclusion effects (i.e. the competition for hydrating water molecules) provide the ion- specificity.

Eq. (3) can be rewritten as:

$$c_i(x) = c_{0,i}\exp\left(-\frac{q_i\psi(x)+\Delta W_i(x)}{kT}\right)\frac{\left(1-\sum_j c_j\tau_j/n\right)^{\tau_i}}{\left(1-\sum_j c_0\tau_j/n\right)^{\tau_i}} \tag{5}$$

Assuming that the added acid, base and salt are completely dissociated, the bulk concentrations of ions are provided by:

$$c_{0,\mathrm{H}} = 10^{-\mathrm{pH}};\ c_{0,\mathrm{OH}} = 10^{\mathrm{pH}-14};\ c_{0,\mathrm{A}} = c_{\mathrm{HA}} + c_{\mathrm{E}};\ c_{0,\mathrm{C}} = c_{\mathrm{E}} + c_{\mathrm{COH}} \tag{6}$$

where C is an univalent cation (such as Na^+, Li^+, K^+), A is an univalent anion (such as Cl^-, Br^-, or I^-), and c_E is the salt concentration. The available data for zeta potential at various pH are only for added NaCl [18], hence in what follows the equilibrium constants will be determined for H^+, OH^- and Cl^-.

The mean field potential ψ is considered to obey the Poisson equation for distances larger than δ:

$$\nabla^2\psi(x) = -\frac{\sum_i q_i c_i}{\varepsilon_0\varepsilon}\quad x > \delta \tag{7}$$

with the boundary conditions:

$$\psi(x)|_{x\to\infty} = 0 \text{ and } \sigma = -\varepsilon\varepsilon_0\frac{d\psi}{dx}\Big|_{x=\delta} \tag{8}$$

where the surface charge density, σ, is provided by the number of ions adsorbed per unit area, N_k:

$$\sigma = q(\mathrm{N_H} - \mathrm{N_{OH}} - \mathrm{N_{Cl}}) \tag{9}$$

q being the proton charge and $k = H^+$, OH^- or Cl^-.

We will assume that the water molecules at the interface provide the adsorption sites for H^+ and OH^-, and that Cl^- is located in