On the Interactions of Ions with the Air/Water Interface

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On the Interactions of Ions with the Air/Water Interface

Marian Manciu*

Department of Physics, University of Texas at El Paso, El Paso, Texas 79968

Eli Ruckenstein*

Department of Chemical and Biological Engineering, State University of New York at Buffalo, Buffalo, New York 14260

In the vicinity of a charged interface, the Poisson−Boltzmann approach considers that the ions obey Boltzmann distributions in a mean electrical field that satisfies the Poisson equation. However, the boundary between two dielectrics generates additional interactions between ions and the interface. The traditional models of ion hydration interactions, that assume that water is a homogeneous dielectric, predict that these interactions are repulsive for all kinds of ions, since all ions should prefer the medium with a larger dielectric constant, where they are better hydrated. In reality, the interactions between the ions and the neighboring water molecules can generate additional short-range ion-hydration interactions, which are either repulsive (for structure-making ions) or attractive (for structure-breaking ions). In the present paper, various models for the ion-hydration forces are examined and compared with the results of molecular dynamics simulations. At large ionic strengths, the latter results could be reproduced qualitatively only when short-ranged attractions between the structure-breaking ions and the interface were taken into account.

1. Introduction

It has long been known that the addition of a salt increases the surface tension of the air/water interface, an experimental result that indicates, via the Gibbs adsorption equation, that the ions are repelled by the air/water interface. The latter result can be intuitively understood in terms of simple electrostatics; the ions, being charged, prefer the medium with larger dielectric constant, in which their electrostatic energy is lower. When a charge approaches the interface between two dielectrics, the field generated by the charge induces a net charging of the interface. Because the interaction between the charge and the induced surface charge is mathematically equivalent to that between the charge and an imaginary charge placed on the other side of the interface (the image charge), the corresponding electrostatic force is commonly named the "image force".

Because of the long-range nature of Coulomb forces, the repelling of ions from the air/water interface due to the "image forces", calculated as free of ion screening, is so large that the Gibbs adsorption equation predicts a divergently large surface tension. This difficulty has been solved by Wagner, who noted that the image force acting on an ion is screened by the cloud formed by the other ions.[1] By assuming that the Debye−Hückel screening length λ_{DH} of the electrolyte solution does not depend on the distance from the interface, Onsager and Samaras obtained an analytical expression for the surface tension of dilute electrolyte solutions.[2]

At high salt concentrations, the surface tension of aqueous electrolyte solutions increases almost linearly with the salt concentration,[3] and the Onsager-Samaras law, which is valid only for low electrolyte concentrations, is not applicable. The qualitative behavior of the surface tension at high ionic strengths can be, however, understood by using a simple model suggested by Langmuir, who noted that it could be explained by the complete depletion of ions from the first water layer of the interface, of a thickness of about 4 Å.[4] Langmuir suggested that the specific ion effects (different slopes of the surface tension of salt aqueous solutions as functions of ionic strength) might be explained by different dissociation constants of the salts.[4] By selecting suitable "depletion lengths" for all kinds of salts, the behavior of surface tension at large electrolyte concentrations could be explained even quantitatively.[5]

Since then, the depletion of ions from the air/water interface became the commonly accepted representation of the surface tension of electrolyte solutions. However, this common picture is not always true; near a charged interface, there is an accumulation of counterions, predicted by the Poisson−Boltzmann treatment, which at very low electrolyte concentrations (less than 10^{-3} M) can dominate the interfacial depletion of ions due to ion hydration forces,[6] and consequently, the surface tension of aqueous electrolytes can decrease with increasing ionic strength (The Jones-Ray effect).[7] Even more significant, the surface tension of acids decreases with increasing

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*　Corresponding authors. Phone: (915) 747 7531. Fax: (915) 747 5447. E-mail: mmanciu@utep.edu. (Marian Manciu); Phone: (716) 645 2911/2214. Fax: (716) 645 3822. E-mail: feaeliru@acsu.buffalo.edu (Eli Ruckenstein).

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(4) Langmuir, I *J. Am. Chem. Soc.* **1917,** *39*, 1848.
(5) Aveyard, R.; Saleem, S. N. *J. Chem Soc. Faraday I* **1976,** *72,* 1609.
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electrolyte concentration,[3] which clearly points to an overall accumulation of ions at the water/air interface.

The possible accumulation of negative ions at the air/water interface was first predicted by Perera and Berkowitz,[8] who found out from molecular dynamics simulations, surprisingly, that the large anions (Cl^-, Br^-, and I^-) are expelled from water clusters to their interface. Their predictions are supported by the recent large-scale molecular dynamics simulations for the air/water interface of various electrolyte solutions, which reveal that, when the polarization of ions and water molecules is explicitly taken into account, the large anions are accumulated near the interface.[9]

The traditional models, such as the Wagner-Onsager-Samaras "screened image force" or the Langmuir "interfacial depletion length" imply that the ions prefer the medium with a higher dielectric constant, where they are better hydrated (surrounded by water molecules that screen their electric field). It is clear that these models cannot explain the accumulation of ions at the air interface of aqueous acid solutions, and the main question is what kind of ion interactions might be responsible for this effect. It was suggested that the ion-dispersion forces might explain the interfacial distribution of ions.[10] However, they predict that the cations are attracted by the interface and that the anions are repelled by the interface,[6] in disagreement with experiment[11] and simulations.[8,9]

Recently, two new models have been proposed to explain the interactions between ions and the air−water interface, based on changes of the hydration energy of ions with the distance from the interfaces.[6,12] In the first one,[6] the discrete nature of water molecule has been taken explicitly into account; when a structure-making ion approaches the interface, it loses some of its hydrating water molecules. Because the energetic penalty is much larger than kT, the interfacial region is practically forbidden to the structure-making ions, and the "Langmuir depletion length" approach can describe well the ion distribution. Because each ion has its particular hydrated structure, there is a particular "Langmuir depletion length" that can be associated with each kind of ion. In contrast, the structure-breaking ions are expelled from the bulk water toward the interface, and this implies an attraction between them and the interface, an interaction that can be roughly approximated by a square well described by two parameters. The other model[12] suggests that, because there is a lower density of water in the interfacial region than in bulk water, the dielectric constant is lower than in the bulk, and this leads to repulsions between all kinds of ions and the air/water interface.

The purpose of this article is to examine the effect of the ion-hydration forces, suggested by these models, on the distribution of ions near an interface, and to compare their predictions with those obtained from molecular dynamics simulations.[9]

2. Modified Poisson−Boltzmann Approach

Under the assumption that the ions interact with a "mean field" ψ generated by all of the other charges of the system, the Boltzmann distribution of ions in the vicinity of an interface is provided by the expression

$$c_i(x) = c_E \exp\left(-\frac{q_i\psi(x) + \Delta W_i(x)}{kT}\right) \quad (1a)$$

where c_i is the concentration of ions of kind "i", x is the distance from the interface (assumed planar), c_E is the electrolyte concentration in a reservoir in contact with the system, q_i is the charge of ions of kind "i", k is the Boltzmann constant, T is the absolute temperature, and $\Delta W_i(x)$ is an additional free energy of interaction between the ion and surface, not included in the mean field ψ (note that $\Delta W_i(x) = W_i(x) - W_i(\infty)$ is calculated with respect to a reservoir far away from the surface[6]). The mean field "ψ" is assumed to obey the Poisson equation

$$\Delta\psi(x) = -\frac{\sum_i q_i c_i(x)}{\epsilon\epsilon_0} \quad (1b)$$

where ϵ is the dielectric constant and ϵ_0 the vacuum permittivity.

Once the additional interactions are known, the distribution of the concentration of ions near the interface can be obtained from eqs 1a and 1b (for the appropriate boundary conditions), and consequently, the surface tension of electrolytes can be easily calculated, via the Gibbs adsorption equation.

However, the additional interactions ΔW_i are not known, and there is no consensus about their microscopic origin. One natural candidate for this "additional interaction" is the screened image force (Wagner-Onsager-Samaras)[2]

$$\Delta W_{OS,i}(x) = \left(\frac{\epsilon - \epsilon'}{\epsilon + \epsilon'}\right)\frac{\exp\left(\dfrac{a_i}{\lambda_{DH}}\right)}{1 + \dfrac{a_i}{\lambda_{DH}}}\frac{q_i^2}{16\pi\epsilon_0\epsilon x}\exp\left(-\frac{2x}{\lambda_{DH}}\right)$$

$$(2)$$

where a_i is the radius of ion "i", ϵ is the bulk dielectric constant of water, $\epsilon' = 1$ is the dielectric constant of air and

$$\lambda_{DH} = \sqrt{\frac{\epsilon\epsilon_0 kT}{\sum_i c_E q_i^2}}$$

is the Debye−Hückel screening length. Although the screened image forces are important at low electrolyte concentrations, simple calculations show that they become too weak at large ionic strengths and therefore cannot explain the surface tension of electrolytes at those concentrations.[6]

A simple treatment, which circumvents this difficulty, uses an alternative approximate treatment of the image forces. Because the Born energy of ions in bulk water is given by

$$W_{Born,i}(x) = -\frac{q_i^2}{8\pi\epsilon_0 a_i}\frac{1}{\epsilon} \quad (3)$$

one can suggest a distance-dependent interaction, based

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on a local approximation of the Born energy[13]

$$\Delta W_{\text{Born},i}(x) = \frac{q_i^2}{8\pi\epsilon_0 a_i}\left(\frac{1}{\epsilon(x)} - \frac{1}{\epsilon}\right) \qquad (4)$$

where $\epsilon(x)$ is the variable dielectric constant near the interface.

In the vicinity of the air/water interface, the dielectric constant is expected to be lower that in the bulk, because the rotation of the water molecules is there somewhat obstructed. As a result, eq 4 indicates a repulsion between ions and the interface. This approximate treatment of electrostatic interactions has the advantages that it does not lead to a diverging surface tension, and that the dependence of the dielectric constant on distance can be selected "a posteriori", such as to match the results provided by the experiment. However, the local approximation of the Born energy has two shortcomings. First, it predicts that all ions are repelled by the interface, which is not true. Second, eq 4 is not an accurate approximation: the correct Born energy has to be calculated by integrating the energy of the electric field over the entire space, including both dielectrics (note that eq 3 implies only one infinite dielectric). Consequently, the derivative of the Born energy with respect to the distance between the charge and the interface should provide rigorously the "image force". It is clear that the derivative of the approximate expression, eq 4, does not lead to the image force. However, it should be noted that both the "screened image force" and the "local approximation of the Born energy" are approximations of the same physical process, namely the change in the electrostatic energy of the system when a charge approaches a boundary between two continuous dielectrics. Therefore, they do not represent different contributions to the free energy.

Both the "image force" and the "local approximation for the Born energy" approaches account for the ion hydration, through the macroscopic dielectric constant of water, assumed a continuous dielectric. Because none of them could explain satisfactorily the distribution of ions near a water−air interface, it was suggested that another effect plays the main role, namely the van der Waals interactions between ions and the rest of the system. These ion-dispersion forces can be described by an equation of the type[10]

$$\Delta W_{\text{vdW},i} = \frac{B_i}{x^3} \qquad (5)$$

The theory based on ion-dispersion forces predicts, however, that the cations are attracted toward the interface and that the anions are repelled toward the bulk,[6] in contrast with the experimental[11] and computational[8,9] findings, which indicate the opposite. It was therefore suggested[6] that another short-range ion-hydration force, which involves changes in the hydration energy when an ion approaches the interface, due to interactions between the ion and the neighboring water molecules, should be employed to calculate the distribution of ions in the vicinity of the interfaces. In what follows, the predictions of the two models for the short-range ion-hydration force of refs 6 and 12 will be compared with the results of molecular dynamics simulations provided in ref 9 for various electrolyte solutions (NaCl, NaOH, HCl and HBr).

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3. Distribution of Simple Ions near the Water/Air Interface

3.1. Bostrom−Kunz−Ninham (BKN) Model for Ion-Solvation Forces. A new model for the short-ranged ion-solvation forces has been proposed recently.[12] It is based on the observation that the air/water interface is not sharp, the water density increasing gradually, over a distance of a few angstroms, from zero (in air) to the density of bulk water. The water density profile was obtained by fitting the results of the molecular dynamics simulations with the empirical expression[12]

$$p(x) = 1 - 1.0302 \exp(3.5 - x)/(1 + \exp(3.5 - x)) \qquad (6a)$$

where $p(x) = \rho(x)/\rho_0$, $\rho(x)$ being the density of water, ρ_0 the density of bulk water, and x is measured in angstroms.

In the region where the water density is lower than that of the bulk, the dielectric constant is expected to be smaller than in the bulk, and a Spaarnay-like local approximation of the Born energy of ions is given by[12]

$$\Delta W_{\text{solvation}}(x) = \Delta G_{\text{solvation}} \frac{\dfrac{1}{1 + p(x)(\epsilon - 1)} - \dfrac{1}{\epsilon}}{1 - \dfrac{1}{\epsilon}} \qquad (7)$$

where $\Delta G_{\text{solvation}}$ is the free energy of solvation in the bulk. The total additional interaction was considered to be the sum of the potentials of a screened image force (eq 2), an ion-dispersion force (eq 5), and an ion-solvation force (eq 7)[12]

$$\Delta W_i(x) = \Delta W_{\text{OS},i} + \Delta W_{\text{vdW},i} + \Delta W_{\text{solvation},i} \qquad (8)$$

In Figure 1a, the interaction potentials at $c_E = 1$ M are plotted for Cl⁻, using in calculations the values $\Delta G_{\text{solvation,Cl}} = 361.79$ kJ/mol and $B_{\text{Cl}} = 13.6 \times 10^{-50}$ Jm³, provided in ref 12. The ion-solvation contribution clearly dominates the interactions in the vicinity of the interface, for $x > 1$ Å. At lower distances ($x < 1$ Å), the total additional energy is larger than 20 kT, and practically no ions are allowed in that region; therefore, the fact that neither eqs 2 nor 5 are accurate for $x < 1$ Å is not relevant. It should also be noted that both the screened-image and ion-dispersion forces are longer-ranged than the ion-solvation force, and they dominate at large distances (see the inset of Figure 1a). However, at large distances and large ionic strengths, they are small compared to kT and hence negligible. In contrast, at low ionic strengths, the screened image force provides an important contribution at large distances, even when the short-range ion-solvation forces are strong: see the inset of Figure 1b, in which the additional interactions are calculated for Na⁺ at $c_E = 0.001$ M, using $\Delta G_{\text{solvation,Na}} = 407.65$ kJ/mol and $B_{\text{Na}} = 1.4 \times 10^{-50}$ Jm³.[12] From Figure 1b it is clear than the ion-dispersion forces are in this case negligible in the vicinity of the air/water interface. At large distances from the interface, they dominate the interactions (because of their $1/x^3$ dependence), but are too small compared to kT to affect the ion distribution.

In summary, the recent BKN model[12] supports the previous predictions[6] that the long-ranged screened image forces govern the interfacial distribution of ions at low ionic strengths, that the short-range ion-hydration forces govern their distribution at high ionic strengths, and that the ion-dispersion forces provides only minor corrections to the ion distributions.
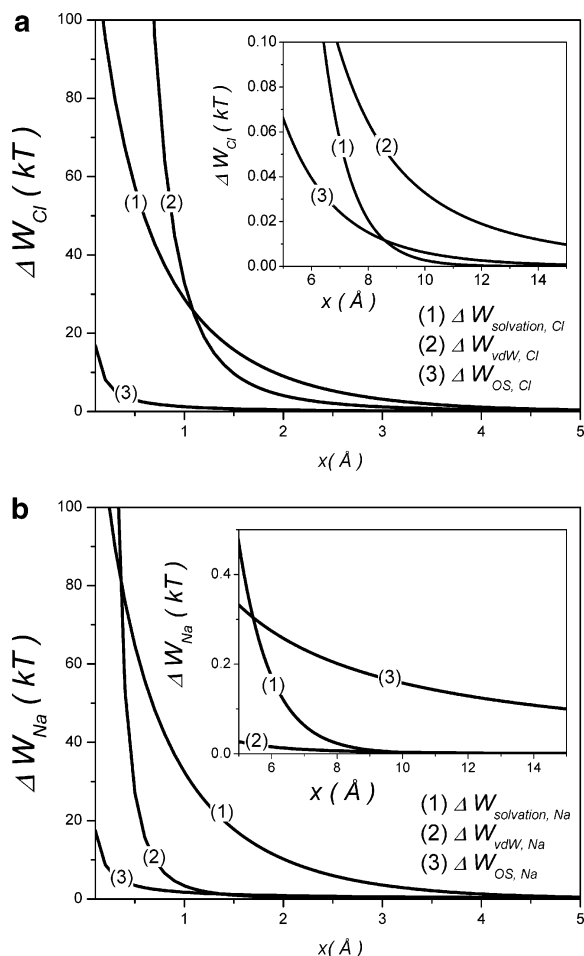
Figure 1. Contributions of the screened image, ion dispersion and ion-solvation to the additional energy $\Delta W_i(x)$ predicted by BKN model for (a) Cl$^-$, at $c_E = 1$ M and (b) Na$^+$ at $c_E = 0.001$ M. In the inset are represented the long-range behavior of the energetic contributions.

Because the solvation energy of any kind of ion in the BKN model is extremely large near the air/water interface, the interface is practically depleted of any kind of ions. Let us assume, for the sake of simplicity, that the mean field electrical potential is negligible (because of the large ionic strength considered); therefore, the distribution of ions in the vicinity of the air/water interface is well approximated by

$$c_i(x) \cong$$
$$c_E \exp\left(- \frac{\Delta W_{\text{solvation},i}(x) + \Delta W_{\text{OS},i} + \Delta W_{\text{vdW},i}(x)}{kT} \right) \quad (9)$$

The distributions of the ions Na$^+$, Cl$^-$, and I$^-$, for which both the solvation energies and the ion-dispersion constants B_i have been provided in ref 12 ($\Delta G_{\text{solvation},i} = 407.65$, 361.79, and 209.49 kJ/mol; $B_i = 1.4$, 13.6, and 15.1×10^{-50} J m^3, respectively), are plotted in Figure 2, together with the density profile of the air/water interface. The ion distributions are also compared in Figure 2 with those predicted by a simple model, in which "Langmuir depletion lengths" (e.g., $\Delta W_i = \infty$ for $x < d_{\text{cut-off}}$ and $\Delta W_i = 0$, $x > d_{\text{cut-off}}$), with $d_{\text{cut-off}} = 1$ and 2 Å, have been arbitrarily selected, and all of the other interactions have been ignored. The calculations for the latter distributions take into account the interfacial profile of the water using a statistical distribution of sharp interfaces, a procedure which is detailed in the next section.
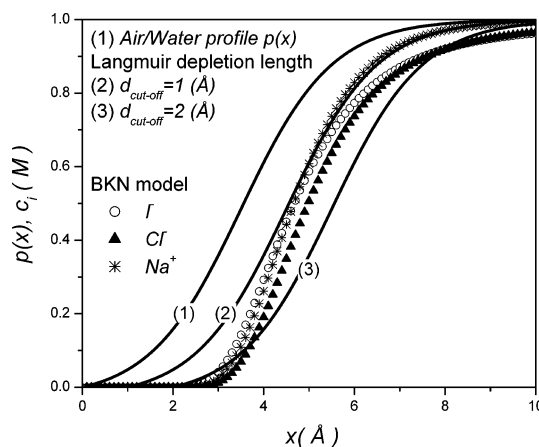
Figure 2. Distribution of ions predicted by BKN ion-hydration model, for $\psi(x) \cong 0$. The first curve is the water profile obtained from fitting MD simulations. The circles, triangles and stars represent the distribution of I$^-$, Cl$^-$, and Na$^+$, respectively. Note that the interfacial region is depleted of all kind of ions, and therefore, the distribution of ions can be well approximated by a simple model using suitable chosen Langmuir depletion lengths (the distributions corresponding to $d_{\text{cut-off}} = 1$ Å and $d_{\text{cut-off}} = 2$ Å are represented in the figure).

Although providing comparable results with the simple model based on "Langmuir depletion lengths", the main advantage of the BKN model is that it allows the direct calculation of the ion distributions without any fitting parameters, once the profile of the interface eq 6, the van der Waals parameters B_i in eq 5, and the solvation energies in eq 7 are known. There are, however, some difficulties associated with the model. The most important is that it predicts that all of the ions are repelled from the interface, in contrast with the experimental data[11] and simulations,[8,9] which indicate that some anions (e.g., Cl$^-$, Br$^-$, I$^-$, but not F$^-$) are attracted by the interface.

The second difficulty is that it predicts very small changes in the interfacial forces for different ions and, therefore, can hardly account for ion specific effects (Figure 2 shows only a minute difference between the distributions of Na$^+$ and I$^-$ ions). In Figure 3a, the predictions of the BKN model for $c_E \cong 1.2$ M are compared with the distributions of Na$^+$ and Cl$^-$ ions near the air/water interface, obtained via molecular dynamics simulations in ref 9; note that in the molecular dynamics simulations the water molecules occupy the region from $x = 0$ to the water/air interface, located at $x_0 = 13.9$ Å; therefore, the expression

$$p(x) = 1 - 1.0302 \exp(x - 13.9)/(1 + \exp(x - 13.9)) \quad (6b)$$

has been employed instead of eq 6a.

The distributions of Na$^+$ and Cl$^-$ predicted by the BKN model are very close to each other, both kinds of ions being repelled from the air/water interface. Furthermore, the Na$^+$ cations more closely approach the interface than the Cl$^-$ anions, in qualitative disagreement with the simulations.

Whereas the average interfacial depletion of ions might be close to the value required to explain the behavior of the surface tension of NaCl solution, the distributions of ions does not reproduce even qualitatively the Molecular Dynamics simulations. The situation is particularly dramatic for acids: the hydrogen ion has a Gibbs free
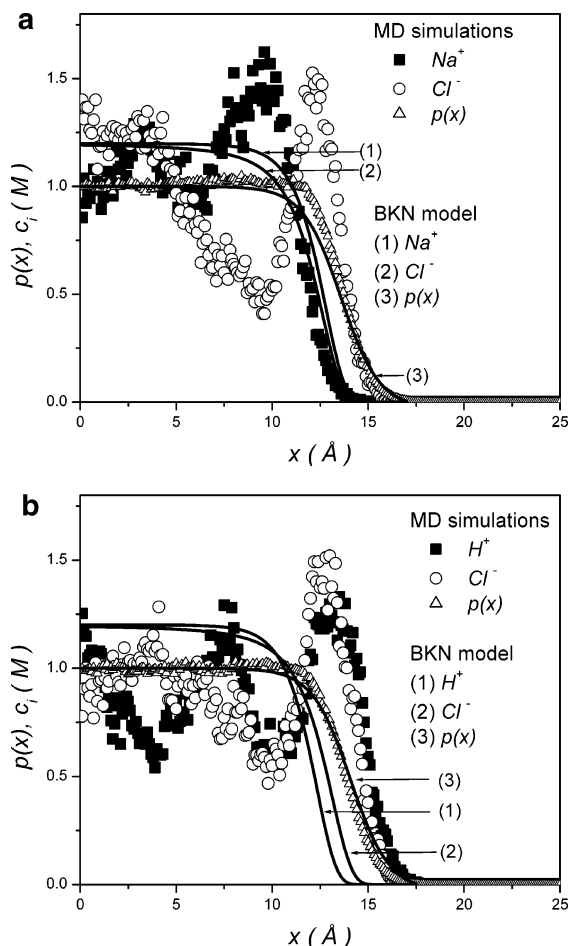
a

b

Figure 3. (a) Distributions of Na$^+$ and Cl$^-$ ions near the air/water interface of a NaCl solution, predicted by the BKN model (note that the Na$^+$ ions approaches the interface closer than the Cl$^-$ ions), are compared with the molecular dynamics simulations of ref 9. (b) The distributions of H$^+$ and Cl$^-$ ions near the air/water interface of a HCl solution, predicted by the BKN model (note that the interface is depleted of both H$^+$ and Cl$^-$ ions), are compared with the molecular dynamics simulations of ref 9, that show an accumulation of both H$^+$ and Cl$^-$ ions at the interface.

energy of hydration of about $\Delta G_{\text{solvation,H}} \cong 1100$ kJ/mol[14] and consequently should be repelled from the interface by ion-solvation forces much stronger than the simple cations (Na$^+$, K$^+$, and Li$^+$). Assuming a negligible ion-dispersion interaction for H$^+$, the ions distributions in the vicinity of the air/water interface of the HCl solution at $c_E = 1.2$ M, predicted by the BKN model, are compared to molecular dynamics simulations[9] in Figure 3b. In this case, the BKN model leads to an average interfacial depletion of ions larger than that predicted for the NaCl solution (Figure 3a), which implies that the surface tension of the HCl solution should increase with ionic strength stronger than the surface tension of the NaCl solution. This is not true; in reality, the surface tension of acid solutions is not even increasing but decreases with the ionic strength.[3] The reason for this behavior can be clearly seen from the results of the molecular dynamics simulations[9] reproduced in Figure 3b: both H$^+$ and Cl$^-$ prefer the air/water interface, where they accumulate.

3.2. Structure Making/Structure Breaking (SM/SB) Model for the Short-Range Ion-Hydration

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Forces. A simple model has been suggested recently for the ion-hydration forces,[6] based on the old common intuition that some ions are able to structure the water (the structure making ions), and for this reason they prefer the bulk, while other ions generate disorder in water (the structure-breaking ions), and for this reason, they are expelled toward the interface. When a structure making ion approaches an interface, it loses some of its hydration molecules, a process which is thermodynamically unfavorable. The hydration energies are of the order of 10^2 kT, and even a change of a few percents of this energy affects drastically the ion distribution; an increase in the total free energy by 5 kT implies (via the Boltzmann distribution) a decrease in concentration by more than 2 orders of magnitude. For this reason, one can assume that this region is practically depleted of structure-making ions, in agreement with the Langmuir suggestion.[4]

The main difference between the traditional ion-hydration models and the SM/SB model is that the previous ones assumed that water is a continuous dielectric, characterized by a macroscopic dielectric constant, whereas the latter takes into account that, microscopically, water is constituted of discrete molecules. The change in hydration occurs when the hydrated ion loses some of its hydrating water molecules, a process that starts from a certain distance $d_{\text{cut-off}}$ from the interface. Therefore, for $x > d_{\text{cut-off}}$, there are no "ion-hydration" interactions, whereas the region with $x < d_{\text{cut-off}}$ can be considered completely depleted of ions. Furthermore, because different structure-making ions have different cutoff thicknesses in which they lose hydrating water molecules, $d_{\text{cut-off}}$ is a parameter that describes the specificity of the structure-making ions (in contrast to the suggestion of Aveyard and Saleem, who suggested that a $d_{\text{cut-off}}$ should be associated with the specificity of salts, not of the corresponding ions).[5]

For structure-breaking ions, it was suggested that their attraction toward the interface is governed by a simple surface potential well, described by two adjustable parameters (the width and the depth of the surface potential well).[6] When this simple model was employed for the air/water interface, it could explain the dependence of the surface potential on the electrolyte concentration and on pH, the behavior of surface tension of salt and acids at high ionic strengths and the Jones-Ray effect (the existence of a minimum in the surface tension of salts at a small electrolyte concentration).[7]

To compare the results with the existing simulations,[9] one should note that the simulations were performed at a fixed number of ions, and not for a system in contact with a reservoir. Therefore, instead of eq 1 one should use

$$c_i(x) = c_{0,i} \exp\left(-\frac{q_i\psi(x) + \Delta W_i(x)}{kT}\right) \quad (10a)$$

with the constant $c_{0,i}$ provided by the normalization condition

$$\iint_A dydz \int_0^{x_{\max}} c_i(x)\, dx = \frac{N}{N_A} \quad (10b)$$

where the integral in the interface plane yz is on an area 30×30 Å^2, the integral along the distance x, perpendicular to the interface, is up to $x_{\max} = 25$ Å, $N = 18$ represents the number of ions (either cations or anions) from the box and N_A is the Avogadro number.

The total additional interaction ΔW_i is the sum of contributions from a short-range ion-hydration force, a long-range ion-hydration force (the screened image force)

and a ion-dispersion force. The long-range ion hydration forces are due to the behavior of water as a homogeneous dielectric, characterized by a macroscopic dielectric constant, whereas the short-range ion-hydration forces are due to the local, discrete structure of water. At low electrolyte concentrations, the screened image forces are dominant (leading to the Onsager−Samaras law),[2] whereas at large ionic strengths, they are negligible and the behavior of ions near interfaces is determined by the short-ranged ion-hydration forces.[6] As noted earlier, the inclusion of the ion-dispersion interactions is equivalent to a slight modification of the parameters of the short-range ion-hydration forces.[6]

Explicit expressions for the additional interactions between ions and interfaces, $\Delta W_i(x)$, allow us to calculate the distribution of ions $c_i(x)$ (for a sharp water/air interface) eqs 10a and 10b, for the appropriate boundary conditions

$$\frac{d\psi}{dx}\Big|_{x=0} = -\frac{\sigma_s}{\epsilon\epsilon_0} \tag{11a}$$

and

$$\psi(x)|_{x=x_{max}} \cong 0 \tag{11b}$$

where σ_s is the surface charge density (assumed $\sigma_s = 0$ in what follows) and with the last approximation holding because x_{max} of the numerical simulations is at about 5 Debye-Hückel lengths from the air/water interface.

The traditional Modified Poisson−Boltzmann (MPB) approach (eqs 1a and 1b) assumes a sharp air/water interface. It is more reasonable to consider that our system is constituted from a statistical ensemble of sharp interfaces, with a statistical distribution

$$\varphi(\xi) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(\xi - x_0)^2}{2\sigma^2}\right) \tag{12a}$$

around the average position $x=x_0$ of the interface, the variable ξ denoting the position of the sharp air/water interface in one component of the statistical ensemble.

Once the ion distributions for sharp air/water interfaces, $c'_i(x)$, are calculated, the concentrations of ions for the statistical ensemble, $c_i(x)$, are obtained by summing up the corresponding contributions to concentrations provided by each element of the ensemble. For an element with a sharp interface located at ξ, the concentration of ions at the distance $(x - \xi)$ from the sharp interface represents the contribution to the concentration of ions at location x in the statistical ensemble (because $\xi + (x - \xi) = x$). Adding up all of these contributions (from the sharp interfaces located at all possible ξ values) multiplied with the probability of a sharp interface at the distance ξ in the statistical ensemble (eq 12a), one obtains the convolution

$$c_i(x) = \int_{\xi = -\infty}^{\infty} \varphi(\xi)c'_i(x - \xi)\,d\xi \tag{12b}$$

where the prime denotes the concentration calculated for a sharp air/water interface. The water density profile for a sharp interface located at ξ is described by the Heaviside function $\Theta(x - \xi) = 0$ for $x - \xi < 0$, $\Theta(x - \xi) = 1$ for $x - \xi > 0$; therefore, the water profile for the statistical ensemble is given by

$$p(x) = \int_{\xi = -\infty}^{\infty} \varphi(\xi)\Theta(x - \xi)\,d\xi = \frac{1 + erf\left(\dfrac{x - x_0}{\sigma}\right)}{2} \tag{12c}$$

The distributions of ions and the water density profile for a water/air interface (water molecules located in the region $x < x_0$), as considered in the molecular dynamics simulations[9] (instead of an air/water interface) are simply obtained by the transformation $(x - \xi) \rightarrow (\xi - x)$ for $c_i'(x - \xi)$ in eq 12b and $\Theta(x - \xi)$ in eq 12c.

This treatment does not generate large repelling forces between ions and interfaces, as the BKN model does, because the structure-breaking ions expelled at the interface are still hydrated in each subsystem of the statistical ensemble. Intuitively, this means that the structure-breaking ions arrive at the interface surrounded by their hydration water molecules. Whereas, on average, the water density is lower near the air/water interface, so there are sufficient water molecules locally to hydrate each interfacial ion. In contrast, the BKN model suggests that the (average) low density of water leads to a low dielectric constant near the air/water interface, and consequently, no ion will approach the interface.

The results of the numerical calculations for the distributions of ions for NaCl are presented in Figure 4a, in which we employed the following values for $\Delta W_i(x)$

$$\Delta W_{Na} = \infty \quad \text{for } 0 < x < 3 \text{ Å} \tag{13a}$$

and

$$\Delta W_{Na} = 0 \quad \text{for x} > 3 \text{ Å} \tag{13b}$$

which involves a total depletion of ions in the first $d_{cut-off} = 3$ Å of water and

$$\Delta W_{Cl} = -1.7kT \quad \text{for } 0 < x < 2.5 \text{ Å} \tag{14a}$$

and

$$\Delta W_{Cl} = 0 \quad \text{for x} > 2.5 \text{ Å} \tag{14b}$$

which involves a simple square potential near the interface, with a width of 2.5 Å and a depth of 1.7 kT (the parameters selected in eqs 13 and 14 are assumed to include also the ion-dispersion interactions). The parameters of statistical distribution of the sharp air/water interfaces have been selected $\sigma = 1.4$ Å and $x_0 = 13.9$ Å, in order to fit the profile of the interface provided by the molecular dynamics simulations.[9]

The simple SM/SB model clearly cannot explain the behavior of ions at distances larger than 10 Å from the interface, but it is not yet clear whether longer-ranged forces are involved or whether the strong variation of the ions distributions in that region are artifacts of the limited size of the system employed in simulations.

To reproduce the simulations for the ion distributions in the aqueous solution of HCl (see Figure 1b), ΔW_{Cl} has been selected as above (eqs 14a and 14b) and an attractive interaction between hydrogen ions and the air/water interface has been employed

$$\Delta W_H = -1kT \quad \text{for } 0 < x < 1 \text{ Å} \tag{15a}$$

and

$$\Delta W_H = 0 \quad \text{for } x > 1 \text{ Å} \tag{15b}$$

Such an interaction has been suggested by experiment regarding the surface tension of aqueous acid solutions.[3] The accumulation of H⁺ at the interface has been recently
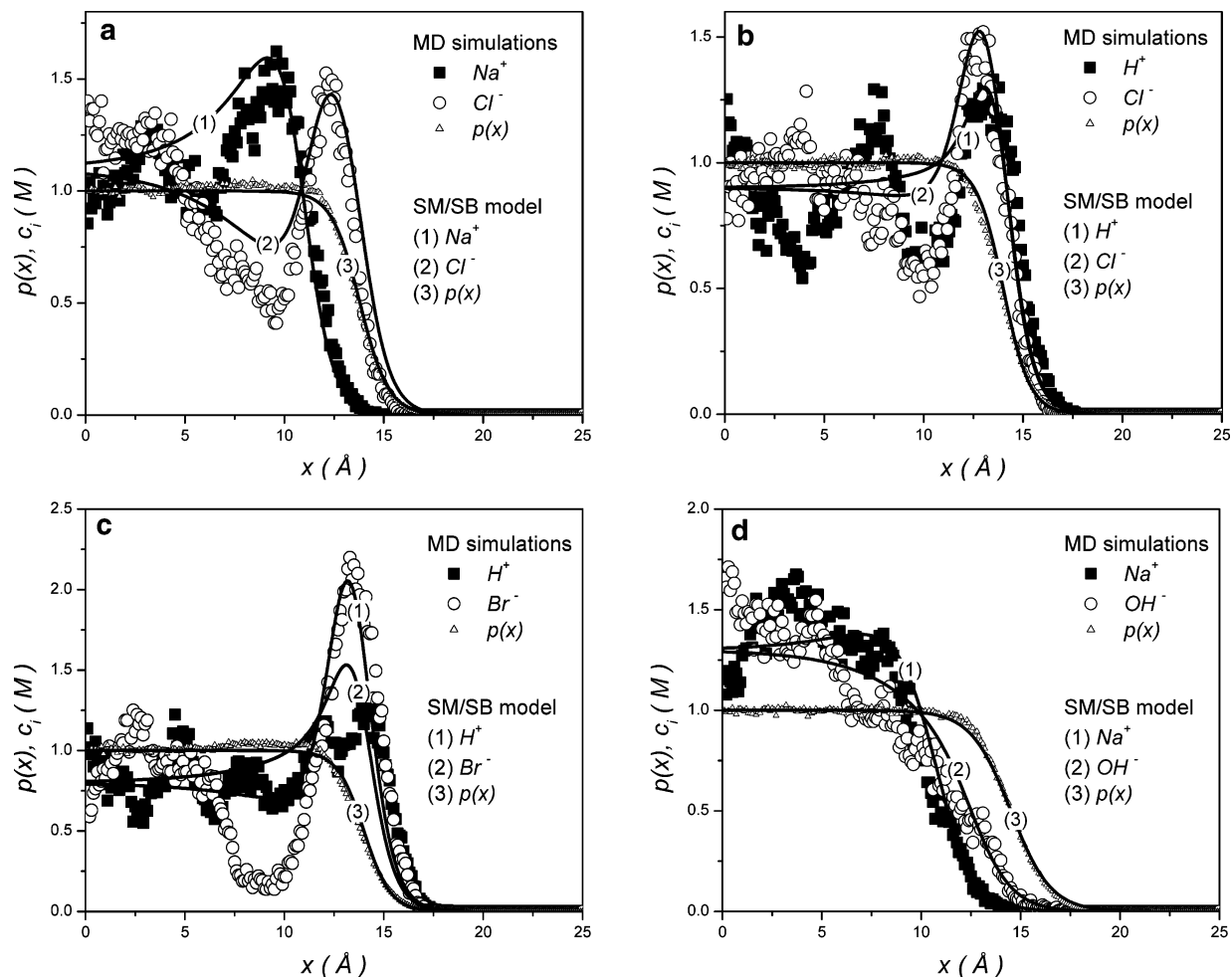
Figure 4. (a−d) Distribution of cations (1), anions (2), and water (3) at the air/water interface. The continuous curves are calculations based on the SM/SB model for short-range ion-hydration forces. The squares (cations), circles (anions) and triangles (water) are the molecular dynamics results of ref 9. (a) NaCl; (b) HCl; (c) HBr; (d) NaOH.

confirmed directly by experiment.[15] One should note that there is a minimum in the concentrations of both anions and cations around 10 Å. This minimum cannot be explained either by the simple potentials selected for the ion-hydration forces or by the traditional electrostatic mean field interactions (for which the depletion of one kind of ions is associated with the accumulation of ions of the other kind). Furthermore, the Poisson−Boltzmann treatment predicts a monotonic variation of charge, whereas in Figure 4b successive inversions of charges with the distance are apparent. One possible reason for this behavior might be another interaction between ion and the surface, perhaps due to the structuring of the water near the interface.

The behavior of ions is similar for other aqueous acid solutions (HBr, Figure 4c) for which an attractive potential has been selected for the interaction between Br⁻ and the interface, whereas for H⁺ the same potential as above (eqs 15a,b) was employed

$$\Delta W_{Br} = -2.0kT \quad \text{for } 0 < x < 1.5 \text{ Å} \quad (16a)$$

and

$$\Delta W_{Br} = 0 \quad \text{for } x > 1 \text{ Å} \quad (16b)$$

It is of interest to note that, for a basic solution (NaOH,

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Figure 4d), both the cations and the anions are repelled by the interface (in contrast with the simple acids, for which both H⁺ and Cl⁻ or Br⁻ are accumulated on the interface). To obtain a reasonable agreement with experiment, we used a repulsive potential for OH⁻ with a cut off $d_{OH} = 2.0$ Å, whereas for Na⁺, we had to use $d_{cut-off} = 3.5$ Å, which is slightly different from the value selected in eqs 13.

The agreement between the numerical results and those obtained via the simple SM/SB model for the short-range ion-hydration forces is satisfactory, if one takes into account that the interactions between ions and interfaces have been assumed to have a very simplified form, and the possible charging of the air/water interface by other mechanisms, other than the accumulation/depletion of ions, was ignored.

4. Conclusions

The distributions of ions in the vicinity of an air/water interface are due not only to the electrostatic interactions among ions, but also to the additional interactions between ions and the interface. Whereas it is plausible to consider that the ions prefer the medium with a larger dielectric constant and hence that the corresponding interactions should repel the ions from the interface, the traditional treatments of the hydration of ions via screened image forces[1,2] or local approximations of the Born energy,[12,13] which consider water as a continuous dielectric, failed to reproduce the experiment at high ionic strengths. This

failure led to a search for additional forces, such as the ion-dispersion forces, due to van der Waals interactions between ions and the rest of the system.[10] Such interactions predicted, however, qualitatively wrong ions distributions (an accumulation of cations and a depletion of anions at the air/water interface, instead of the opposite).

We proposed recently a simple model (SM/SB) for the short-range interactions between ions and interface, based on the fact that the water surrounding the ion is formed of discrete molecules.[6] Consequently, the repelling ion-hydration forces, acting on structure-making ions could be described by one parameter (a cutoff length), whereas the attractive ion-hydration forces, acting on structure-breaking ions, could be described by two parameters (a simple potential well at the interface). It is clear that the ion-hydration forces are more complex, but there is no theory yet that can provide an "ab initio" prediction of these interactions. The reason for this failure consists of the large number of molecules involved in these interactions. A natural way to calculate the interactions would be to simulate the air/water interface of an aqueous solution and to calculate "a posteriori" the potential that matches the distribution of ions. However, only systems with a limited number of molecules (for the time being, about 1000) could be treated in a reasonable time.[9] It is apparent that in these cases, boundary effects are influencing the distribution of ions in all figures (Figure 4a–d), because the systems investigated were limited only to a slab of water of a thickness of about 15 Å from the air/water interface.

We showed previously that a simple model for the ion-hydration interactions, which separates the ion-hydration forces in a long-range term due to the behavior of water as a continuous dielectric (the screened image force) and a short-range term due to the discreteness of the water molecules (SM/SB), can explain almost quantitatively a number of phenomena related to the electrolyte interfaces.[6] In this article, we examined the limitations of the model in predicting the distributions of ions near the air/water interface, by comparison with molecular dynamics simulations. It is clear that the real ion-hydration forces are more complicated than the simple model employed here; however, the interfacial phenomena (including specific ionic effects) can be understood, at least qualitatively, in terms of this simple approach.

The situation is similar to the success of the traditional Poisson–Boltzmann approach: its ability in describing, at least qualitatively, and many times even quantitatively, the behavior of most colloidal systems probably resides in the use of at least one adjustable parameter (surface charge, surface potential, recombination constant and so on) in the fitting of the experimental results. If that parameter could be accurately measured, one would have to address the inaccuracies generated by the mean field treatment itself.