Specific ion effects via ion hydration: I. Surface tension

Marian Manciu, Eli Ruckenstein*

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, NY 14260, USA

Abstract

A simple modality is suggested to include, in the framework of a modified Poisson–Boltzmann approach, specific ion effects via the change in the ion hydration between the bulk and the vicinity of the surface. This approach can account for both the depletion of the interfacial region of structure-making ions as well as for the accumulation of structure-breaking ions near the interface. Expressions for the change in interfacial tension as a function of electrolyte concentrations are derived. On the basis of this theory, one explains the dependence of the surface potential on pH and electrolyte concentration, the existence of a minimum in the surface tension at low electrolyte concentrations and the linear dependence, with a positive or sometimes negative slope, of the surface tension on the electrolyte concentration at sufficiently high ionic strengths.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Specific ion effect; Ion hydration; Structure-making ion; Structure-breaking ion

Contents

1. Introduction .......................................................... 64
2. The mean-field formalism (the Poisson–Boltzmann approach) ....................... 65
   2.1. The Poisson–Boltzmann equation ............................ 66
   2.2. The image forces (Wagner–Onsager–Samaras theory) ...................... 67
   2.3. Ion hydration effects via the dielectric constant ......................... 68
   2.4. Ion size effects ................................................. 69

*Corresponding author. Tel.: +1-716-645-2911/2214; fax: +1-716-645-3822.
E-mail address: feaeliru@acsu.buffalo.edu (E. Ruckenstein).
1. Introduction

The distribution of electrolyte ions around a charged surface was first calculated by Gouy [1] and Chapman [2]. Their theory assumed that the ions are point charges embedded in a continuum of constant dielectric constant, which are distributed according to Boltzmann statistics and interact with all the other charges via a mean field obeying the Poisson equation. The limitations of a theory with such drastic approximations was obvious from the beginning, and Stern pointed out [3] that this Poisson–Boltzmann approach can predict, in the vicinity of the surface, an ion concentration larger than that corresponding to close compaction. Since then, the theory was corrected in many ways to account for image forces [4], finite sizes of the hydrated ions [5], ion correlations [6,7], dependence of dielectric constant on the field [8] and electrolyte concentration [9] and many other effects.

The Poisson–Boltzmann approach [1,2] has the advantage of simplicity and is surprisingly accurate, at least for univalent ions in a certain range of electrolyte concentrations (1.0 × 10^{-3}–5 × 10^{-2} M) and not too close to the interface. It was later employed [10] to explain the repulsion due to the overlap of two double layers, and the stability of colloids thereafter [11,12].

It is instructive to compare the Poisson–Boltzmann approach as applied to colloid stability to a related example regarding the surface tension of electrolyte solutions. For most electrolytes, the surface tension of the water/air interface increases with increasing ionic strength. This increase is caused (via the Gibbs equation) by the negative adsorption of electrolyte ions on the surface [13]. The depletions of such ions near the interface were attributed for a long time to a more favorable free energy when the ion is fully hydrated [13], which occurs when the ion is sufficiently far from the interface. However, the Poisson–Boltzmann approach always predicts, for a charged interface and a symmetric electrolyte, an increase in the total number of ions in the vicinity of the interface, as compared to the bulk, because the counterions increase always exceeds the coions depletion. Hence, to calculate the distribution of ions in the vicinity of a surface and their surface adsorption, additional interactions have to be included in the Poisson–Boltzmann treatment. A
charge embedded in a dielectric is repelled by the charge density it induces on the
dielectric boundary (the ‘image force’). The use of the image force to calculate the
(negative) surface adsorption of ions led to a diverging increase in surface tension
[14]. However, Wagner [14], inspired by the then-recent Debye–Hückel theory of
electrolytes, realized that the other ions screen the image force. The screening length
around an ion depends on the local concentration of ions and is, therefore, a function
of the distance from the surface. Onsager and Samaras [15] simplified the
calculations of Wagner, by assuming a constant screening length through electrolyte,
and obtained an analytic ‘limiting law’ for the dependence of the surface tension
on electrolyte concentration. However, the theory failed at high electrolyte concen-
trations (above \( \approx 0.2 \) M), and the authors pointed out various sources of error and
suggested various modalities to account for them into a more complete theory.

In contrast, the bare-bone Poisson–Boltzmann approach has had an unusual
success in explaining quantitatively the double layer repulsion and the colloid
stability. A few reasons for this success might be the partial cancellation of some
effects decorating the bare-bone equations [5], or the fact that the corrections are
important particularly within a few molecular diameters from the interface. The
model inaccuracies could be reasonably well accounted for by a simple theoretical
construction (the Stern layer) or by using the surface charge, surface potential or
the dissociation constant of surface groups as a fitting parameter. The series of
decorations of the Poisson–Boltzmann equation is long, and in spite of the rich
literature available in the field, the calculations of the interactions are still mostly
performed in the traditional DLVO manner (the bare-bone Poisson–Boltzmann
approach).

It was recently shown that such a decoration of the theory with van der Waals
interactions between individual ions and the interface might account in a simple
manner for the inaccuracies of the Poisson–Boltzmann approach regarding the ion
specific effects [16] and also for those of the Wagner–Onsager–Samaras theory
[17,18]. In this article, we will first review the general framework of the Poisson–
Boltzmann approach and will discuss the various kinds of approximations it involves.
Some of the decorations will be briefly reviewed. The emphasis will be, however,
on the recent van der Waals correction and arguments will be brought that the
specific ion effects can be explained through ion hydration. A simple manner to
account quantitatively for ion hydration and its relevance to ion specific effects will
be suggested, and a comparison with the approach involving the van der Waals
interactions made.

2. The mean-field formalism (the Poisson–Boltzmann approach)

A fundamental hypothesis of the Gouy–Chapman theory is that the interaction of
an ion with all the other charges can be described by a ‘mean potential’ \( \psi(x) \),
where \( x \) is the distance from the surface. The chemical potential of an ion of species
‘\( i \)’ with charge \( q_i \) in the liquid is then given by:

\[
\mu_i(x) = \mu_{i_0} + kT \ln(c_i(x)) + q_i \psi(x) + W_i(x),
\]

(1)
where \( \mu_{0i} \) represents the standard chemical potential of the ion of species ‘\( i \)’, of concentration \( c_i(x) \) and charge \( q_i \). The interaction free energy \( W_i(x) \) includes all the other interactions of the ion with the medium (not accounted for by the mean field). Some examples are examined below.

The distribution of ions of species ‘\( i \)’, \( c_i(x) \), is related to the bulk concentrations \( c_{0i} \) of ions by the Boltzmann equation:

\[
c_i = c_{0i} \exp \left( - \frac{q_i \psi(x) + \Delta W_i(x)}{kT} \right),
\]

where \( \Delta W_i(x) \) is calculated with respect to the bulk and can depend also on \( \psi_i \) and other parameters, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature.

The mean field is assumed to satisfy the Poisson equation:

\[
\nabla^2 \psi(x) = - \frac{\sum_i c_i(x)q_i}{\varepsilon_0} + \frac{\partial P(x)}{\varepsilon_0 \partial x},
\]

where the polarization \( P(x) \) is typically assumed proportional to the macroscopic electric field:

\[
P(x) = - \varepsilon_0 (\varepsilon - 1) \nabla \psi(x),
\]

\( \varepsilon_0 \) being the vacuum permittivity and \( \varepsilon \) the dielectric constant of the medium.

**2.1. The Poisson–Boltzmann equation**

The most simple approximation is \( \Delta W_i(x) = 0 \); for an uni-univalent electrolyte of concentration \( c_{0E} \) the potential in the vicinity of a planar surface can be calculated from Eqs. (2)–(4), which lead to,

\[
\frac{d^2 \psi(x)}{dx^2} = \frac{2e c_{0E}}{\varepsilon \varepsilon_0} \sinh \left( \frac{e \psi(x)}{kT} \right)
\]

the well-known Poisson–Boltzmann equation, where \( e \) is the proton charge. It can be solved for suitable boundary conditions, such as constant surface charge density, constant surface potential, dissociation or adsorption equilibrium at the surface. Once the ion distribution is known, the other characteristics of the system, such as the free energy, can be calculated.

Several kinds of approximations are involved in the derivation of Eq. (5). First, it implies that the interactions between charges can be described by an ‘average’ potential, which is a mean field type of approximation. A theory devoid of this assumption can be developed in the general framework of statistical mechanics, using pair correlation functions. One of the successful approaches, based on the
inhomogeneous hypernetted chain approximation, was presented by Kjellander and Marcelja [7]. However, the results provided by this method depend strongly on the ion pair potentials employed and it was shown [19] that minor changes in the ion-pair potentials can lead to qualitatively different results. It is not yet clear if the ion-correlation effects can be described to a good approximation by a suitable-chosen function $\Delta W_i(x)$.

Another limitation of the Poisson–Boltzmann approach is that the interaction between two surfaces immersed in water might not be exclusively due to the electrolyte ions. For instance, water has a different structure in the vicinity of the surface than in the bulk and the overlapping of such structures generates a repulsion even in the absence of electrolyte [20]. In this traditional picture, the ‘hydration’ repulsion is not related to ion hydration; actually it is not related at all to electrolyte ions. However, as recently suggested [21], this ‘hydration’ interaction can still be accounted for within the Poisson–Boltzmann framework, assuming that the polarization is not proportional to the macroscopic electric field, but depends also on the field generated by the neighboring water dipoles and by the surface dipoles.

There are also other effects, which cannot be incorporated easily in the Poisson–Boltzmann formalism, such as the non-planarity of the interface, its thermal fluctuations, the charge fluctuations and so on.

The other kinds of approximations are due to the oversimplification $\Delta W_i = 0$. Many effects can be accounted for by decorating the Poisson–Boltzmann equation with more suitable expressions for $\Delta W_i(x)$. The rest of the article is devoted to the examination of a few possible choices.

### 2.2. The image forces (Wagner–Onsager–Samaras theory)

As already noted, the Poisson–Boltzmann equation fails to describe the ion depletion in the vicinity of the surface, which is basically due to the preference of the ions for the bulk liquid, where they can be fully hydrated.

One of the first corrections to the formalism was the addition of the interaction between the ions of charge $q_i$ and the surface via the (screened) ‘image force’ [14]:

$$\Delta W_{w,i}(x) = \left(\frac{\varepsilon - \varepsilon'}{\varepsilon + \varepsilon'}\right) \frac{q_i^2}{16\pi\varepsilon_0\varepsilon x} \exp\left(-\frac{2x}{\lambda(x)}\right),$$

where $\varepsilon'$ is the dielectric constant of the medium which has an interface with water and $\lambda(x)$ is the screening length. This interaction is the same for both kinds of ions of a symmetric electrolyte, hence the ion depletions are in this case the same for both ions and, in the absence of surface charges or other interactions, the electric potential is vanishing everywhere. To account for different ion sizes (and hence to obtain, to some extent, ion-specific effects), Onsager and Samaras [15] proposed an
interaction potential modified in a Debye–Hückel spirit:

\[
\Delta W_{\text{OS},i}(x) = \left( \frac{\varepsilon - \varepsilon'}{\varepsilon + \varepsilon'} \right) \frac{\exp \left( \frac{2a_i}{\lambda} \right)}{1 + \frac{2a_i}{\lambda} \frac{q_i^2}{16\pi \varepsilon_0 \varepsilon x}} \exp \left( - \frac{2x}{\lambda} \right),
\]

(6b)

where \(a_i\) are the ion radii and \(\lambda = \sqrt{\varepsilon \varepsilon_0 kT \sum q_i^2} / \Sigma q_i\) is the Debye–Hückel screening length.

The Onsager–Samaras theory fails at electrolyte concentrations above approximately 0.2 M. One of the reasons is the assumption that the screening length \(\lambda\) does not depend on the distance to the interface. In reality, the screening in the ion-depleted region near the surface is smaller than in the bulk. Only when \(\lambda\) is large compared to the thickness of the depleted layer, the above approximation is accurate. Other reasons for the inaccuracy (additional interactions and surface charge) will be examined later in the paper.

The image force formalism was intended primarily to relate, via the Gibbs adsorption equation, the increase of the surface tension of water to the negative adsorption of the electrolyte ions. Its effect on the double layer interactions was examined by Jönsson and Wennerström [4].

2.3. Ion hydration effects via the dielectric constant

Another modality to include the ion hydration effects in the Poisson–Boltzmann formalism is via the dielectric constant. If the surface charge is sufficiently large, then there is a large electric field and a high concentration of counterions near the surface. Both of these factors lead to a decrease of the dielectric constant. The main contribution to the polarizability of a water molecule is a result of the alignment of its dipole by the electric field, the polarization being proportional with the field when the latter is sufficiently low, but becoming saturated at high fields. In addition, the presence of an electrolyte hinders the polarizability of the water molecules, thus decreasing the dielectric constant. To account for these effects, one should first account for the dependence of the dielectric constant on the magnitude of the field [9] and on the counterions concentration [8] in Eq. (4). Second, one should account, via the Born energy, for the change of the ion hydration free energy due to the change in the dielectric constant of the medium in Eq. (2).

The Born hydration energy is the electrostatic energy of an ion in a dielectric and depends on the field generated by the ion in the entire space. When there is a boundary between two media with different dielectric constants, the change in the electrostatic energy when the ion approaches the boundary generates an image force, which induces a diverging negative surface adsorption. One can avoid this behavior by accounting for the screening of the interaction by the electrolyte [14]. This treatment does not include the non-uniformity of the dielectric constant.
Another possible treatment [9] is to define the Born energy in term of a local dielectric constant \( \varepsilon(x) \):

\[
\Delta W_{B,J}(x) = \frac{q_i^2}{8\pi \varepsilon_0 a_i} \left( \frac{1}{\varepsilon(x)} - \frac{1}{\varepsilon} \right),
\]

where \( \varepsilon = \varepsilon(\infty) \) is the bulk dielectric constant. In this case, the ions are repelled by the interface only because the dielectric constant of water in its vicinity, \( \varepsilon(x) \), is lower than in the bulk. If the dielectric constant would be larger near the interface, the ions would be attracted there.

When the interface is charged, the Poisson–Boltzmann equation predicts stronger fields and higher ionic concentrations in the vicinity of the surface, therefore a dielectric constant smaller than in the bulk, and the ‘local’ Born energy indicates that the ions are repelled by the interface. However, a neutral surface depleted of ions should have a dielectric constant larger than the bulk and the ions should be attracted, not repelled by such an interface. Therefore, other interactions should be included to explain the ion depletion near a neutral surface.

2.4. Ion size effects

It has been long accepted that the Poisson–Boltzmann equation can lead to ion concentrations that exceed the volume available in the vicinity of a surface. Stern included the effect of the ion size on its distribution around a charged surface by assuming the existence of a layer in the vicinity of the surface containing only condensed counterions [3]. The effect of the ion size on the double layer interaction was later incorporated in the modified Poisson–Boltzmann formalism in a manner similar to that described here [22]. The difference in the free energy of ions between bulk and interface can be written as a function of ion concentrations, either in a lattice model [22], in terms of the occupation probabilities or in a continuum treatment [23], by assuming that the hydrated ions behave as rigid spheres and employing the excess chemical potential with respect to an ideal gas.

By accounting for the size of the ions one can explain the depletion of ions in the vicinity of the surface and obtain in most cases an increase in the double layer repulsion as compared to the Poisson–Boltzmann equation (in some special cases, it might lead to a decrease of the repulsion [24]). It also can account, at least partially, for some specific ion effects. However, the differences in hydrated radii between various ions are small and the specific effects become important in this treatment only at high ionic strengths and high surface potentials. While the hydrated ion radius hinders the ions to approach to close the interface, the ‘depletion region’, which will be estimated later in this paper from the change in the interfacial tension, might either exceed or be much smaller (sometimes, even negative) than the hydrated radius of the ions.
2.5. The van der Waals interactions between ions and media

Onsager and Samaras were interested in a qualitative explanation of the experimentally determined increase in surface tension with increasing electrolyte concentrations. The screened image force provided a good agreement with experiment, up to approximately 0.2 M. They suggested that better agreement could be obtained if higher multipolar correction would be included in the treatment. Onsager and Samaras also remarked that these interactions should be important only in the close vicinity of the surface, since they should decrease with at least the third power of the distance.

It was later conjectured by Sienko [25] that the multipolar corrections to the Onsager–Samaras theory might account for specific ion effects, because of different ion polarizabilities. A quantitative attempt to investigate this conjecture was made recently by Stairs [25], by including the interaction between a dipole and its image, using the (screened) Onsager–Samaras potential. However, because of screening, the effect is small at high ionic strengths.

Ninham and Yaminisky [26], and Karraker and Radke [18] realized that the van der Waals interactions between the ions and interface are not screened by the electrolyte and hence might become more important than the image force, at large electrolyte concentrations. Recognizing that the hydration of ions might also play a role, Boström et al. [16,17] showed that the van der Waals interactions alone (with suitable values selected for the interaction parameters) might account for the ion specific effects.

The van der Waals interaction between an ion and the interface between two dielectric media, calculated in the Lifshitz approach, has as leading term [26]:

$$\Delta W_{NY}(x) = \frac{B}{x^3}. \quad (8)$$

Let us first address some quantitative issues, using the more simple Hamaker approach. If one assumes pairwise additivity, the interaction between a sphere of kind (1) immersed in a fluid of kind (3) and a planar half-space of kind (2) is given by [27]:

$$\Delta W_{H}(x) = -\frac{A_{132}a}{6(x-a)} \left[ 1 + \frac{x-a}{x+a} + \frac{x-a}{a} \ln \left(\frac{x-a}{x+a}\right) \right] = -\frac{2A_{132}a^3}{9x^3} - \frac{4A_{132}a^5}{15x^5} - \ldots \quad (9)$$

where $x$ is the distance from the interface to the center of the ion of radius $a$ and $A_{132}$ is the effective Hamaker constant between ion (1) embedded in a fluid (3) and a medium (2) on the other side of the interface, given by [27]:

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad (10)$$
where $A_{ij}$ are the Hamaker constants of the interactions between the media ‘$i$’ and ‘$j$’ in vacuum. Eq. (8), with $B = -(2A_{123}a^3)/9$, is a good approximation of Eq. (9) for $a \ll x$ (the difference is less than 10% for $x > 4a$).

Since three media are involved in these van der Waals interactions, the effective Hamaker constant can become negative. For the water/air interface, $A_{12} = A_{23} = 0$, and hence:

$$A_{132} = +A_{33} - A_{13}. \quad (11)$$

If the Hamaker constant between ion and water $A_{13}$ (in vacuum) is larger than that between water and water $A_{33}$, the effective Hamaker constant is negative and the ions are repelled by the interface. On the other hand, if $A_{13} < A_{33}$, the ions are attracted by the interface.

Boström et al. [16,17] showed that the positive ions are less polarizable and the negative ions more polarizable than water. Therefore, the former should be attracted to and the latter repelled by the interface. The values of $B_i$ have been, however, obtained by fitting the experimental interfacial tensions.

Karraker and Radke [18], accounting only for the interactions between the individual ions and the water and air continua (thus ignoring the term $A_{33}$ in Eq. (11)), concluded that the dispersion interactions always repel the ions from the water/air interface, with the exception of the non-polarizable $H^+$, for which $B_{11} = 0$.

By assuming a radius $a = 1.8 \text{ Å}$ for the $\text{Cl}^-$ ion embedded in a water continuum, one obtains the value $B_{\text{Cl}} = 31 \times 10^{-50} \text{ J m}^3$ employed by Boström et al. [16,17] if $A_{132} = 23 \times 10^{-20} \text{ J}$, which is typical for metal–metal interactions through vacuum ($10^{-30} \times 10^{-20} \text{ J}$ [27]). If the ‘Hamaker constants’ $A_{13}$ of ion–water interactions would be of this order of magnitude, then the water–water interaction ($A_{33} = 3.7 \times 10^{-20} \text{ J}$) can be neglected in Eq. (11). However, the derivation of Eq. (10) is based on the (macroscopic) hypothesis that the ‘ion sphere’ replaces a ‘water sphere’ of the same size. If the ions are thought as occupying interstitial places in a (rigid) water lattice, the displacement of ions is not followed by that of water. In such a case, the effect of the ‘intervening medium’ has to be discarded and the Hamaker constants calculated (in the hypothesis of pairwise additivity) as through vacuum.

Furthermore, these van der Waals interactions are important only near the interface, where it is unlikely that either Lifshitz or Hamaker approaches are accurate for spheres of molecular sizes. For example, the magnitude of the interaction for $\text{Na}^+$ ions at 5 Å from the interface is only approximately $0.02kT$ (the values of $B$ used in the calculation, $B_{\text{Na}} = -1 \times 10^{-50} \text{ J m}^3$ was obtained from fit by Boström et al. [17] and $B_{\text{Na}} = +0.8 \times 10^{-50} \text{ J m}^3$ was calculated by Karraker and Radke [18]). Eq. (8) might provide a convenient way to account for the interfacial interactions, if suitable values for $B_i$ (not related to the ‘macroscopic’ Hamaker constants) would be selected.

There are, however, some more important qualitative issues, which should be discussed. If the cations would be attracted by the interface, they will condense
there (since this attraction diverges for $x \to 0$) and the accumulation of ions on the interface will lead to an infinite decrease of the interfacial tension. Boström et al. [17] avoided this ‘cation catastrophe’ by selecting a cut-off of 2 Å in the calculations and obtained good agreement with experiment by fitting the values of $B$. As will be shown in the next section, if a cut-off of approximately 4 Å is used, good agreement with experiment can be obtained by completely disregarding the van der Waals interactions of ions.

More dramatic are the long-range consequences of the van der Waals attraction, even when a cut-off is included. As shown by Boström et al. [16], the double layer interactions in electrolytes of physiological concentrations become in this case attractive at distances less than 30 Å. This unexpected theoretical prediction has yet to be verified experimentally.

Recent molecular dynamics simulations [28] showed that the ‘commonly held opinion’ that the interfacial region is depleted of electrolyte ions might not be true, and that some ions might approach the interface. Their accumulation on the interface can be predicted by a suitable negative value for the parameter $B$, in the van der Waals interactions of the ions (coupled with an interaction cut-off). However, there are the large negative ions ($\text{Cl}^-$, $\text{Br}^-$) which prefer to accumulate in the vicinity of the interface [28], and not the less-polarizable small and positive ions, as expected from the van der Waals interactions.

In the treatment of Karraker and Radke [18], the interaction coefficients $B_i$ are always positive, and the cation catastrophe is avoided. However, the van der Waals repulsions are still larger for the negative ions than for the positive ones; therefore, the accounting for the van der Waals interaction alone would imply that all air/electrolyte interfaces should have a positive surface potential. Boström et al. [17] argued that this might be indeed the case, and that the negative values of the potentials typically obtained experimentally might be caused by the double layers generated around the electrodes used in the experiments, and do not represent intrinsic properties of the water/air interface. Karraker and Radke [18] suggested that the negative potentials of the surfaces are due to the preference of $\text{OH}^-$ for the surface, thus including another interaction (in their treatment, the van der Waals interactions still repel the $\text{OH}^-$ ions from the interface, stronger than they repel the cations).

The increase of the surface tension of water by the addition of an electrolyte was traditionally related (via Gibbs adsorption equation) to the negative adsorption of ions on the interface. However, some electrolytes decrease the interfacial tension [29], hence should be positively adsorbed. Therefore, if the van der Waals interactions would repel all the ions from the interface, some additional interactions have to be included to explain the positive adsorption.

The accounting for the van der Waals interactions of ions has the advantage of simplicity, since the determination of the values of the $B_i$ coefficients for all the ions could lead to a quantitative treatment of ion specific effects within the Poisson–Boltzmann framework. However, as mentioned above, this treatment provides the debatable prediction that the cations would approach the interface closer than the anions.
The change in ion hydration between bulk and interface was suspected since a long time [13] to be responsible for the distribution of ions in the vicinity of the interface; whereas this effect can be easily understood qualitatively, a consistent quantitative theory has not yet been developed. The reason is that accurate information about the structure of water in the vicinity of an interface and about the corresponding changes in the ion hydration with the distance are yet beyond our reach. In the next section, a simple modality to account in a semi-quantitative manner for the ion hydration effects will be suggested. The effects of the van der Waals interactions and image forces will be compared with those of hydration.

3. A simple treatment of ion hydration. General behavior

It is well known that, in general, there is a strong correlation between the standard enthalpy of hydration of an electrolyte and the modification of the surface tension by that electrolyte [30]. The effect of ion hydration on interfacial tension can be easily understood qualitatively. For the structure-making ions, their approach to the interface is unfavorable, because they can better organize the water dipoles in bulk water than at the interface. The opposite is true for the structure-breaking ions; in such cases, the total free energy of the system is minimized by pushing the structure-breaking ions toward the interface, because the bulk water molecules can better organize their hydrogen bonding network without these ions.

The surface tension can either increase or decrease with electrolyte concentration, depending whether the depletion of the structure-making ions in the vicinity of the surface or the adsorption of the structure-breaking ions dominates the process. The distribution of ions in the vicinity of the interface could be calculated if accurate expressions for $\Delta W_i(x)$ would be available.

There is, however, a simple manner to obtain reasonable estimations of ion distribution, even when the expressions $\Delta W_i(x)$ are not known. The hydration free energy per ion, in bulk water, is of the order of $-10^2 kT$ [31]. An increase in the total free energy by $5kT$ implies (via the Boltzmann distribution) a concentration decrease by more than two orders of magnitude. Therefore, if at a particular distance $d_i$ from the interface, the hydration free energy of a structure-making ion is increased by only a few percent from the bulk hydration free energy, one can consider, for calculation purposes, that the region from the interface to the distance $d_i$ is totally depleted of those ions.

Hence, one can describe the hydration interaction of a structure-making ion by a parameter, representing a distance of closest approach to the surface. It is plausible to consider $d_i$ related to the hydrated radii of the ions of species ’i’; however, they are not the same because the structure of water is different in the vicinity of the interface from that in the bulk.

This approach might seem to be rather crude; however, it should be noted that recent molecular simulations of simple electrolytes interfaces [28] show that the variation of the electrolyte concentrations is about as steep as the variation of water density at the interface. Therefore, if one assumes a sharp water/air interface, one can also assume step distributions for the ions of the electrolyte.
A similar simple treatment is less accurate for the structure-breaking ions. The change in the total free energy between surface and bulk cannot exceed a few $kT$, because otherwise the ions would be trapped at the interface and generate a large surface potential, possibility ruled out by experiment. Since $\Delta W_i(x)$ is not very large, it cannot be well approximated, in general, by a step function. However, in the spirit of the above approximation and in the absence of more accurate information, we will assume that it can be described by a potential well and will examine the consequences.

In this section, we will investigate the effect of the changes in the free energies of ions between bulk and interfacial region, on the ion distributions in the vicinity of the interface, and consequently on the surface tension, for an uni-univalent electrolyte in the following cases:

1. Both kinds of ions are structure-making, and $d_1=d_2$;
2. Both kinds of ions are structure-making, but the cations (2) are repelled more strongly than the anions (1): $d_2>d_1$;
3. The cations are structure-making ($d_2>0$) but the anions are structure-breaking, hence positively adsorbed on the interface.

3.1. $d_1=d_2=d_E$

In this case (in the absence of a surface charge) the interface is neutral. The dependence of the interfacial tension $\gamma$ on the uni-univalent electrolyte concentration $c_E$ can be calculated using the Gibbs adsorption equation:

$$d\gamma = -\sum_{i=1,2} \Gamma_i d\mu_i,$$

where $\mu_i$ is the (total) electrochemical potential and $\Gamma_i$ is the surface excess of ion $i$:

$$\Gamma_i(c_E) = \int_0^\infty (c_i(x) - c_E) dx$$

with the water/air interface located at $x=0$. The total electrochemical potential, which is independent of the distance from the interface, can be related to the bulk electrolyte concentration $c_E=c_i(\infty)$ via:

$$d\mu_i = d(kT \ln(c_i(\infty) f_i)),$$

where $f_i$ is the activity coefficient of the electrolyte in the bulk.

Using Eqs. (12)–(14) and assuming $f_i \equiv 1$, the change in the interfacial tension due to the addition of an electrolyte is given by:

$$\frac{1}{kT} \frac{d\gamma}{dc_E} = - \frac{\Gamma_1 + \Gamma_2}{c_E} = 2\Delta,$$
where the ratio $-(\Gamma_1 + \Gamma_2)/2c_E$ has the dimension of a length which is denoted by $\Delta$, the depletion thickness.

The surface tension as a function of electrolyte concentration can be obtained by integrating Eq. (15):

$$\gamma(c_E) - \gamma(0) = \int_{c=0}^{c_E} \frac{\partial \gamma}{\partial c} dc = -kT \int_{0}^{c_E} \frac{\Gamma_1(c) + \Gamma_2(c)}{c} dc.$$

(16)

In the present case, there is no surface charge and $d_1 = d_2 = d_E$, therefore $c_i(x) = c$ for $x > d_E$ and $c_i(x) = 0$ for $0 < x < d_E$, which provides $\Gamma_i(c_i) = -c\Delta = -cd_E$ and

$$\Delta \gamma(c_E) = (2kTd_E)c_E \alpha c_E.$$

(17)

This expression was employed before to account for the dependence of $\gamma$ on the electrolyte concentration [30], which is roughly linear up to large electrolyte concentrations. It should be noted that this simple model is in better agreement with experiment up to large ionic concentrations [29] than the Onsager–Samaras theory [15], which assumes that the image forces are screened by the electrolyte and hence are small at large electrolyte concentrations. However, $d_E$ has to be regarded as a parameter, which depends on both kinds of ions of the electrolyte; therefore, the ‘specific ion effects’ are transformed into ‘specific electrolyte effects’. For some electrolytes, the value of $d_E$ determined through fitting is reasonable and seems to be close to the hydrated ion radius, for example $d_E = 3.9$ Å for NaCl and $d_E = 3.8$ Å for KCl [30]. For these electrolytes, the selection of a cut-off distance equal to $d_E (\approx 4$ Å) in the Poisson–Boltzmann equation would lead to an excellent agreement with surface tension experiments, even if the van der Waals interactions and other interactions that decorate the Poisson–Boltzmann approach are disregarded [30].

It is instructive to compare how the ion-interface interactions (image force, van der Waals interactions, ion hydration) affect the depletion thickness at various electrolyte concentrations. To estimate the magnitudes of these effects, it will be assumed that the interactions are non ion-specific (which implies to use Eq. (6a) for the potential of the image force, and $B_1 = B_2 = B$ in Eq. (8) for the van der Waals interactions). Consequently, the interface is neutral and the surface adsorption can be calculated from the simple expression:

$$\frac{\Gamma_1}{c_E} = \frac{\Gamma_2}{c_E} = -\Delta = \int_{0}^{\infty} \exp\left(-\frac{\Delta W(x)}{kT}\right) - 1 \right) dx.$$

(18)

As that generated by ion hydration for $d_1 = d_2$, the depletion thickness generated by the van der Waals interactions, when $B_1 = B_2$, does not depend on concentration. When only the van der Waals interactions are accounted for, Eqs. (8) and (18) lead
Fig. 1. Comparison between the depletion distances generated by several symmetric (the same for both ions) interactions: the image forces (Eq. (6a), $\varepsilon=80$, $\varepsilon'=1$, $T=300$ K), the van der Waals interaction (Eq. (8), $B_1=B_2=31 \times 10^{-50}$ or $1 \times 10^{-50}$ J m$^3$) and ion hydration ($d_1=d_2=d_3=4$ Å). The interactions accounted for on each curve are: (1) the ion hydration and the image forces; (2) the image forces alone; (3) the ion hydration and the van der Waals interactions, $B=31 \times 10^{-50}$ J m$^3$; (4) the van der Waals interactions alone, $B=31 \times 10^{-50}$ J m$^3$; (5) the ion hydration and the van der Waals interactions, $B=1 \times 10^{-50}$ J m$^3$; (6) the ion hydration alone; (7) the van der Waals interactions alone, $B=1 \times 10^{-50}$ J m$^3$.

to the following depletion distance [17]:
\[
\Delta \equiv \int_0^\infty \left( 1 - \exp\left( -\frac{B}{kT} \right) \right) dx = \left( \frac{B}{kT} \right)^{1/3} \int_0^\infty \left( 1 - \exp\left( -\frac{1}{y^3} \right) \right) dy \approx 1.354 \left( \frac{B}{kT} \right)^{1/3}.
\]  
(19a)

while when both the ion hydration and van der Waals are accounted, the effect of the van der Waals interactions is to increase (decrease) the cut-off distance:
\[
\Delta \equiv \int_0^{d_E} dx + \int_{d_E}^\infty \left( 1 - \exp\left( -\frac{B}{kT}\frac{1}{x^3} \right) \right) dx \approx d_E + \frac{B}{2kTd_E^2}.
\]  
(19b)

The correction of the cut-off distance in Eq. (19b) is significant only for large values of $B$. 

\[
\Delta \equiv \int_0^{d_E} dx + \int_{d_E}^\infty \left( 1 - \exp\left( -\frac{B}{kT}\frac{1}{x^3} \right) \right) dx \approx d_E + \frac{B}{2kTd_E^2}.
\]  
(19b)
There is no reason to assume that $B_1 = B_2$ or that $d_1 = d_2$. However, when the surface potential is low (hence in the absence of a surface charge and at sufficiently low electrolyte concentrations), Eq. (18) can be used to calculate separately the depletion thicknesses for each kind of ions.

For comparison purposes, the depletion thickness is plotted in Fig. 1 as a function of electrolyte concentration ($\varepsilon = 80$, $\varepsilon' = 1$, $T = 300 \text{ K}$) for a number of cases listed there. The value of the cut-off distance $d_E = 4 \text{ Å}$ was selected to obtain agreement with the surface tension data for the aqueous solutions of some common electrolytes (NaCl, KCl) at high ionic strengths. The effects of the van der Waals interactions or of ion hydration on the depletion thickness are qualitatively the same. When $B$ is large ($B = 31 \times 10^{-50} \text{ Jm}^3$), the additional accounting of ion hydration provides only a small correction to the result obtained with van der Waals interactions alone. When $B$ is small, the additional accounting of the van der Waals interactions does not affect much the result obtained with ion hydration interactions alone. It should be noted than neither $B$ nor $d_E$ are precisely known; what can be inferred from the data on surface tension at high ionic strengths is that both effects together should lead to a depletion thickness of approximately $4 \text{ Å}$. Therefore, the rather large value $B_{\text{Cl}} = 31 \times 10^{-50} \text{ Jm}^3$, evaluated from fitting in Ref. [17], might have been obtained because the ion hydration was neglected.

Assuming an electrolyte with a depletion thickness of approximately $4 \text{ Å}$ at high ionic strengths, Fig. 1 suggests that the image forces play a dominant role at very low electrolyte concentrations ($c_0 < 1.0 \times 10^{-4} \text{ M}$), but are negligible at relatively large concentrations ($c_0 > 0.1 \text{ M}$).

For some electrolytes, the ‘characteristic distance’ $d_E$ required to fit the experimental data on surface tension with Eq. (17) is smaller than the hydrated radius of the ions and might even become negative (e.g. HCl, HNO$_3$, HCIO$_4$ [29]). This means that at least one component of the electrolyte is preferentially adsorbed on the interface. Therefore, $d_E$ can be regarded only as a parameter in an extremely simplified theory.

### 3.2. $d_1 < d_2$

The differences in the hydration energies of the ions and in their hydrated radii are expected to lead to $d_1 \neq d_2$. As indicated by simulations [28], the negative ions are less repelled, therefore they can approach the interface closer than the positive ions. The asymmetric ion depletions generate a surface potential, even in the absence of an ‘external’ surface charge. The charge that generates the diffuse double layer is located a few Ångstroms from the interface, and is due to the anions.

The corresponding modified Poisson–Boltzmann equations for the planar interface located at $x = 0$ are:

\[
\frac{d^2 \psi}{dx^2} = 0 \quad 0 < x < d_1, \tag{20a}
\]
\[
\frac{d^2\psi}{dx^2} = \frac{e\epsilon_F}{\epsilon \epsilon_0} \exp\left(\frac{e\psi}{kT}\right) d_1 < x < d_2, \tag{20b}
\]
\[
\frac{d^2\psi}{dx^2} = \frac{2e\epsilon_F}{\epsilon \epsilon_0} \sin h\left(\frac{e\psi}{kT}\right) d_2 < x < \infty, \tag{20c}
\]

where \( e \) is the protonic charge. Eqs. (20a), (20b) and (20c) can be solved for the boundary conditions:
\[
\frac{d\psi(x)}{dx} = 0 \quad \text{(no surface charge density) } x = 0, \tag{21a}
\]
\[
\psi(x) \to 0 \quad x \to \infty. \tag{21b}
\]

The surface potential generated by the asymmetric distribution of the ions in the vicinity of the surface is small when the electrolyte concentration is sufficiently low. It is, therefore, worthwhile to obtain an analytical solution in the linear approximation. The general solution of the linear approximation of Eqs. (20a), (20b) and (20c) is:
\[
\psi_1(x) = C_1 x + C_2 \quad 0 < x < d_1, \tag{22a}
\]
\[
\psi_2(x) = -\frac{kT}{e} + C_3 \exp\left(\frac{x - d_1}{2\lambda}\right) + C_4 \exp\left(-\frac{x - d_1}{2\lambda}\right) d_1 < x < d_2, \tag{22b}
\]
\[
\psi_3(x) = C_5 \exp\left(\frac{x - d_2}{\lambda}\right) + C_6 \exp\left(-\frac{x - d_2}{\lambda}\right) d_2 < x < \infty, \tag{22c}
\]

where \( \lambda \) is the Debye–Hückel length, \( \lambda = \sqrt{(\epsilon \epsilon_0 kT/2e^2\epsilon_F)} \).

The boundary condition Eq. (21a) leads to \( C_1 = 0 \) and the boundary condition Eq. (21b) to \( C_5 = 0 \). The continuity of \( \psi \) and \( d\psi/dx \) at \( x = d_1 \) and \( x = d_2 \) leads finally to the solution:
\[
\psi_1(x) = -\frac{kT}{e} \left(1 - \frac{1}{\cosh\left(\frac{d_2 - d_1}{\lambda \sqrt{2}}\right)} + \frac{1}{2}\sin h\left(\frac{d_2 - d_1}{\lambda \sqrt{2}}\right)\right) 0 < x < d_1, \tag{23a}
\]
\[
\psi_2(x) = -\frac{kT}{e} \left(1 - \cosh\left(\frac{x - d_1}{\lambda \sqrt{2}}\right) + \frac{1}{2}\sin h\left(\frac{x - d_1}{\lambda \sqrt{2}}\right)\right) d_1 < x < d_2, \tag{23b}
\]
\[
\psi_3(x) = -\frac{kT}{e} \left(\cosh\left(\frac{x - d_2}{\lambda \sqrt{2}}\right) - 1\right) d_2 < x < \infty. \tag{23c}
\]
The power generated by the asymmetric distribution of the electrolyte ions \( d_1 = 2 \, \text{Å}, d_2 = 5 \, \text{Å}, \varepsilon = 80, T = 300 \, \text{K} \) provided by Eq. (23a), Eq. (23b) and Eq. (23c) is compared with the numerical solution of Eqs. (20a), (20b) and (20c) for various electrolyte concentrations. (b) The distribution of electrolyte ions in the vicinity of the interface \( d_1 = 2 \, \text{Å}, d_2 = 5 \, \text{Å}, c_E = 1 \, \text{M}, \varepsilon = 80, T = 300 \, \text{K} \). (c) The depletion thickness for \( d_1 = 5 \, \text{Å} \) and \( d_1 = 0, 1, 2, 3, 4 \) and 5 Å, as a function of electrolyte concentration \( \varepsilon = 80, T = 300 \, \text{K} \). (d) The change in surface tension as a function of electrolyte concentration, for \( d_2 = 5 \, \text{Å} \) and \( d_1 = 0, 1, 2, 3, 4 \) and 5 Å. The value \( \gamma_0 \) corresponds to \( c_E = 0 \).

\[
\psi_{m}(x) = -\frac{kT}{e} \frac{1}{1 + \sqrt{2} \left( \tan h \left( \frac{d_2 - d_1}{\lambda / 2} \right) \right)^{-1}} \exp \left( -\frac{x - d_2}{\lambda} \right) \quad d_2 < x < \infty .
\]

(23c)

The magnitude of the potential is larger for larger values of \( (d_2 - d_1)/\lambda \), but is everywhere smaller than \( kT/e = 0.026 \, \text{V} \). The potential is generated by the asymmetric distributions of the two kinds of ions (it vanishes for \( d_1 = d_2 \)) and increases with increasing \( c_E \). At sufficiently low electrolyte concentrations, the linear approximation is always accurate; however, at sufficiently high ionic strengths, the linear approximation is no longer valid and the magnitude of the surface potential can exceed \( kT/e \). The potential obtained via the numerical integration of Eqs. (20a), (20b) and (20c) is compared with Eqs. (23a), (23b) and (23c) in Fig. 2a, for \( d_1 = \)}
2 Å, \( d_2 = 5 \) Å and various electrolyte concentrations. Up to \( c_E = 1 \) M (\( \lambda = 3 \) Å), the numerical integration of the nonlinear Eqs. (20a), (20b) and (20c) provides a solution \( \psi(x) \) within a few percents from the analytical solution of the linear approximation. The distributions of electrolyte ions for \( c = 1.0 \) M are plotted in Fig. 2b.

The change in the interfacial tension due to the electrolyte ions can be calculated using the Gibbs adsorption equation (Eqs. (12)–(14)). The surface adsorptions are given by:

\[
\Gamma_1 = \int_0^\infty (c_1(x) - c_E) \, dx = \int_0^{d_1} -c_E \, dx + \int_{d_1}^{d_2} (c_1(x) - c_E) \, dx + \int_{d_2}^\infty (c_1(x) - c_E) \, dx \\
= -c_E d_2 + \int_{d_2}^\infty (c_1(x) - c_E) \, dx + \int_{d_1}^{d_2} c_1(x) \, dx 
\]

(24a)

and

\[
\Gamma_2 = \int_0^\infty (c_2(x) - c_E) \, dx = -c_E d_2 + \int_{d_2}^\infty (c_2(x) - c_E) \, dx.
\]

For small values of \( \psi_{II} \), the last integral in Eq. (24a) can be evaluated using Eq. (23b):

\[
\int_{d_1}^{d_2} cE \exp \left( \frac{e\psi_{II} \lambda}{kT} \right) = cE \int_{d_1}^{d_2} \cos h \left( \frac{x-d_1}{\lambda/2} \right) + \frac{1}{\lambda} \sin h \left( \frac{d_2-d_1}{\lambda/2} \right) \, dx \\
= 2cE \lambda \frac{1}{1 + \sqrt{2} \tan^{-1} \left( \frac{d_2-d_1}{\lambda/2} \right)}. 
\]

(25)

Since in the linear approximation the second integrals in Eqs. (24a) and (24b) cancel each other, Eq. (15) becomes:

\[
\frac{1}{kT} \frac{\partial \gamma}{\partial c_E} = -\frac{\Gamma_1 + \Gamma_2}{c_E} = 2\Delta = 2 \left( d_2 - \frac{\lambda}{1 + \sqrt{2} \tan^{-1} \left( \frac{d_2-d_1}{\lambda/2} \right)} \right). 
\]

(26)

The slope of the surface tension as a function of electrolyte concentration is no longer constant, since \( \lambda \) depends on \( c_E \). For low electrolyte concentrations,
2\Delta = (d_1 + d_2) + \frac{(d_2 - d_1)^2}{2\lambda^2} - \frac{(d_2 - d_1)^3}{12\lambda^3} + \cdots \quad (27a)

For $c_E \rightarrow 0$, the surface potential generated by the asymmetry of the ion concentrations vanishes, the anions are uniformly distributed from $d_1$ to infinity, and the total depletion thickness is given by the sum of the depletion thicknesses of each kind of ions, calculated independently.

For sufficiently high ionic strengths, but low enough for the linear approximation to remain still valid, Eq. (26) leads to:

\[ 2\Delta \equiv 2d_2 - \frac{\lambda}{1 + \sqrt{2}}. \quad (27b) \]

The latter equation shows that the cation hydration (described by the cut-off distance $d_2$) dominates the process. Because of the increase in potential with electrolyte concentration, the region between $d_1$ and $d_2$ is practically depleted of anions.

The depletion distance $2\Delta$ (given by Eq. (26)) is plotted in Fig. 2c as a function of electrolyte concentrations for $d_2 = 5$ Å and various values of $d_1$. The slope increases with ionic strength because the surface potential increases. The change in interfacial tension (obtained by integrating Eq. (26)) is represented for the same cases in Fig. 2d. The dependence is well approximated in all cases by a straight line, with a slope dependent on both $d_2$ and $d_1$.

As already noted in Section 3.1, for neutral systems with $d_1 = d_2$ and $B_1 = B_2$, the accounting of ion hydration through a cut-off distance provides similar results as the ion-surface van der Waals interactions. The surface potential generated by the asymmetric distribution of ions, due to van der Waals interaction alone (with $B_1 \neq B_2$) is plotted in Fig. 3a. We employed for curve (1) the values $B_1 = +15 \times 10^{-50}$ J m$^3$ and $B_2 = +0.8 \times 10^{-50}$ J m$^3$, which were calculated for Cl$^-$ and Na$^+$ in Ref. [18]. The values $B_1 = +31 \times 10^{-50}$ J m$^3$ and $B_2 = -1.0 \times 10^{-50}$ J m$^3$, employed for the curves (2–4), were obtained in Ref. [17] by fitting the experimental surface tension data. In the latter case, it was necessary to use a cut-off, $\Delta_{\text{cut-off}}$, in the cation interactions, to avoid their infinite accumulation on the interface. The value $\Delta_{\text{cut-off}} = 2$ Å was suggested in Ref. [17]; as shown in Fig. 3, the results are strongly dependent upon this choice. The corresponding dependence of surface tension on electrolyte concentration is presented in Fig. 3b.

The only significant difference between the two models (one accounting for hydration alone and the other for van der Waals interactions alone) is that the surface potential is always positive in the latter method, because always $B_1 > B_2$. At sufficiently large electrolyte concentrations, both models predict an almost linear increase of the surface tension, and agreement with experiment can be obtained by using suitable choices for the parameters ($d_i$ or $B_i$).
Fig. 3. (a) The surface potential and (b) the surface tension vs. electrolyte concentration, calculated by accounting for the van der Waals interactions alone in the Poisson–Boltzmann formalism ($\varepsilon = 80$, $T = 300$ K), for (1) $B_1 = 15 \times 10^{-50} \text{ J m}^3$ and $B_2 = 0.8 \times 10^{-50} \text{ J m}^3$; (2) $B_1 = 31 \times 10^{-50} \text{ J m}^3$, $B_2 = -1 \times 10^{-50} \text{ J m}^3$ and $\Delta_{\text{cut-off}} = 1 \text{ Å}$; (3) $B_1 = 31 \times 10^{-50} \text{ J m}^3$, $B_2 = -1 \times 10^{-50} \text{ J m}^3$ and $\Delta_{\text{cut-off}} = 2 \text{ Å}$; (4) $B_1 = 31 \times 10^{-50} \text{ J m}^3$, $B_2 = -1 \times 10^{-50} \text{ J m}^3$ and $\Delta_{\text{cut-off}} = 4 \text{ Å}$. 
3.3. The anions are adsorbed on and the cations are repelled by the interface

The change in hydration energy for the cations will be assumed, as before, given by:

$$\Delta W_2(x) = \infty \quad 0 < x < d_2$$

$$\Delta W_2(x) = 0 \quad d_2 < x < \infty$$

(28a)
(28b)

The interactions between anions and the interface will be, however, approximated by a potential of the type:

$$\Delta W_1(x) = -W_1 \quad 0 < x < d_1$$

$$\Delta W_1(x) = 0 \quad d_1 < x < \infty$$

(29a)
(29b)

In this case, two parameters \((W_1, d_1)\) are used to describe the interfacial interactions of the anions. The modified Poisson–Boltzmann equation is (for \(d_1 < d_2\)):

$$\frac{d^2 \psi_1}{dx^2} = \frac{ec_E}{\varepsilon \varepsilon_0} \exp \left( \frac{W_1}{kT} \right) \exp \left( \frac{e \psi_1}{kT} \right) \quad 0 < x < d_1,$$

(30a)

$$\frac{d^2 \psi_1}{dx^2} = \frac{ec_E}{\varepsilon \varepsilon_0} \exp \left( \frac{e \psi_1}{kT} \right) \quad d_1 < x < d_2,$$

(30b)

$$\frac{d^2 \psi_1}{dx^2} = \frac{2ec_E}{\varepsilon \varepsilon_0} \sinh \left( \frac{e \psi_1}{kT} \right) \quad d_2 < x < \infty$$

(30c)

with the same boundary conditions as before:

$$\frac{d \psi}{dx} = 0 \quad x = 0,$$

(31a)

$$\psi \to 0 \quad x \to \infty.$$

(31b)

To evaluate the effect of the potential well on the ion distributions, it will be assumed that \(d_1 = d_2 = d_E\).

3.3.1. \(d_1 = d_2 = d_E\). Linear approximation

For sufficiently small electrolyte concentrations, the surface potential generated is small and the linear approximation is valid. The solution of Eqs. (30a), (30b) and (30c) for the boundary conditions Eqs. (31a) and (31b), is given in this
Fig. 4. The anion (1) and cation (2) distributions and the potential (3) in the vicinity of an interface,
d_1 = d_2 = 4 Å, W_1 = 1kT, c_0 = 0.1 M, ε = 80, T = 300 K.

approximation by:

\[ \psi_1(x) = -\frac{kT}{e} \left( 1 - \frac{\cos h \left( \frac{x}{\lambda} \sqrt{\frac{A}{2}} \right)}{\cos h \left( \frac{d_E}{\lambda} \sqrt{\frac{A}{2}} \right) + \sqrt{\frac{A}{2}} \sin h \left( \frac{d_E}{\lambda} \sqrt{\frac{A}{2}} \right)} \right) \quad 0 < x < d_E, \quad (32a) \]

\[ \psi_2(x) = -\frac{kT}{e} \frac{1}{1 + \sqrt{\frac{1}{A} \tan h^{-1} \left( \frac{d_E}{\lambda} \sqrt{\frac{A}{2}} \right)}} \exp \left( -\frac{x}{\lambda} \right) \quad d_E < x < \infty, \quad (32b) \]

where \( A = \exp (W_1/kT) \). The potential in the diffuse layer and the corresponding ion distributions are presented in Fig. 4 for \( d_E = 4 \ Å, c_0 = 0.1 \ M \) and \( W_1 = 1kT \).

For the depletion thickness, one obtains in the linear approximation:

\[ -\frac{\Gamma_1 + \Gamma_2}{c_0} \equiv 2\Delta = 2d_E - \exp \left( \frac{W_1}{kT} \right) \int_0^{d_E} \exp \left( \frac{e\psi_1}{kT} \right) dx \]

\[ = 2d_E - \frac{2\lambda}{1 + \sqrt{\frac{1}{A} \tan h^{-1} \left( \frac{d_E}{\lambda} \sqrt{\frac{A}{2}} \right)}} \approx d_E \left( 2 - \frac{A}{1 + \frac{Ad_E}{2\lambda}} \right). \quad (33) \]
The last approximate expression shows that, at low electrolyte concentrations \((\lambda \to \infty)\), the total adsorption is positive when the potential well is sufficiently deep \((A \equiv \exp(W_1/kT) > 2)\). In this case, the surface tension decreases almost linearly with increasing electrolyte concentration. However, the slope does not remain constant, its magnitude decreasing with increasing electrolyte concentration, because of the surface potential generated by the asymmetric distribution of electrolyte ions. The slope \(\partial \gamma / \partial c\) becomes positive at concentrations higher than a critical electrolyte concentration, obtained from:

\[
2 - \frac{A}{1 + \frac{Ad_E}{2\lambda_c}} = 0 \Rightarrow \lambda_c = \frac{d_E}{2} \frac{1}{1 - \frac{1}{A}}.
\]  

(34)

3.3.2. \(d_1 = d_2 = d_E\): Approximate solution of the nonlinear equation

At high electrolyte concentrations, the linear approximation fails and Eqs. (31a), (31b), (32a), (32b) and (33) are no longer valid. A simple solution, even approximate, of the non-linear Poisson–Boltzmann equation is more difficult to obtain; however, the general behavior of the system can be understood from the following semi-quantitative analysis.

The diffuse double layer is generated by the anions trapped in the potential well. The ‘surface charge density’, due to their distribution between 0 and \(d_E\), is given by:

\[
\sigma = \int_0^{d_E} \rho(x)dx = -e\bar{c}_E \exp\left(\frac{W_1}{kT}\right)\int_0^{d_E} \exp\left(\frac{e\psi(x)}{kT}\right)dx = -e\bar{c}_E d_E \exp\left(\frac{W_1 + e\bar{\psi}}{kT}\right).
\]  

(35)

where \(\bar{\psi}\) is a suitable average value between \(\psi(0)\) and \(\psi(d_E)\).

Starting from Poisson equation, one can show that, because of the electroneutrality, the potential gradient at distance \(d_E\) is related to the ‘surface charge density’ via:

\[
\frac{d\psi}{dx}\bigg|_{x=d_E} = -\int_{d_E}^{\infty} \frac{d^2\psi}{dx^2} dx = \int_{d_E}^{\infty} \frac{\rho(x)}{\varepsilon\varepsilon_0} dx = -\int_0^{d_E} \frac{\rho(x)}{\varepsilon\varepsilon_0} dx \equiv -\frac{\sigma}{\varepsilon\varepsilon_0}.
\]  

(36)

Outside the well, the integration of the Poisson–Boltzmann equation (with the boundary condition Eq. (31a)) leads to [27]:

\[
\frac{d\psi(x)}{dx} = \frac{2kT}{e\lambda} \sin h\left(-\frac{e\psi(x)}{2kT}\right) \quad d_E < x < \infty.
\]  

(37)
Fig. 5. Graphical solution of Eq. (38). If $W_0 > 0$, there is a positive adsorption of anions in the potential well if the electrolyte concentration is sufficiently low. The increase of the electrolyte concentration displaces $|\tilde{\psi}|$ toward larger values. If the electrolyte concentration is sufficiently high, the anion adsorption in the well becomes negative ($\exp\left((W_1 + e\tilde{\psi})/kT\right) < 1$).
Combining Eqs. (35)–(37), yields:

\[
\exp\left(\frac{W_i + e\tilde{\psi}}{kT}\right) = \frac{4\lambda}{d_E} \sin h\left(-\frac{e\tilde{\psi}(d_E)}{2kT}\right).
\] (38)

If the well is not very broad and the potential is sufficiently large, then the potential varies slowly between 0 and \(d_E\) and one can approximate \(\tilde{\psi} \approx \psi(d_E)\). Under such conditions, Eq. (38) allows to calculate \(\psi(d_E)\) at any electrolyte concentration. In Fig. 5, the left-hand-side term of Eq. (38) is plotted against \(-e\tilde{\psi}/kT\) (\(\tilde{\psi}\) is negative) for \(W_i = 0\), \(1kT\) and \(3kT\). The right-hand-side term is plotted for \(4\lambda/d_E = 0.1, 1, 10\). The intersection of the two curves provides \(\tilde{\psi}\) for the value selected for \(4\lambda/d_E\).

The cations cannot approach the interface closer than \(d_E\). When \(W_i = 0\), the region \(0 < x < d_E\), which is depleted of cations, is also partially depleted of anions, since \(\exp((W_i + e\tilde{\psi})/kT) < 1\), because of the potential generated by the asymmetric distributions of ions. At low electrolyte concentrations (curve (1) in Fig. 5), the potential is small and the anion depletion negligible. The increase of the electrolyte concentration displaces the intersection toward larger magnitudes of \(\tilde{\psi}\), and at high electrolyte concentrations (curve (3) in Fig. 5) the potential well can be considered as being completely depleted of anions, because \(\exp((W_i + e\tilde{\psi})/kT) \approx 0\). When \(W_i > 0\), there is a positive adsorption of anions at the interface if the electrolyte concentration is sufficiently low, but the unbounded increase of the surface potential with increasing ionic strength generates a negative adsorption of the anions in the potential well at large electrolyte concentrations. Consequently, the surface tension can first decrease (if the potential well is deep enough) and then increase with increasing electrolyte concentration.

When the surface potential is large, the hyperbolic sinus in the right term can be approximated by its largest exponential term and Eq. (38) becomes:

\[
\tilde{\psi} = -\frac{2}{3} \left(\frac{W_i}{e}\right) \ln(\frac{d_E}{2\lambda}),
\] (39)

which shows that the surface potential increases without bound with the electrolyte concentration. Therefore, the potential well will be always depleted by the anions at sufficiently high electrolyte concentrations, in spite of their favorable interaction with the interface.

To illustrate the above discussions, the surface potential and the surface tension are plotted vs. electrolyte concentration in Fig. 6a and b, respectively, for \(d_1 = d_2 = d_E = 5\) Å and various values for \(W_i\). The Poisson–Boltzmann Eq. (30b) was integrated numerically and its solution was employed in Eq. (15) to calculate the surface tension. If the potential well for anions is shallow, the total depletion thickness is positive at any electrolyte concentration and the surface tension always
Fig. 6. (a) The surface potential and (b) the surface tension vs. electrolyte concentration, calculated for a potential well, with \( d_1 = d_2 = 5 \ \text{Å}, \ \varepsilon = 80, \ T = 300 \ \text{K} \).

increases with increasing ionic strength. If the potential well is sufficiently deep \( A \equiv \exp(W_y/kT) > 2 \), the total depletion thickness is negative at low ionic strength (because of the anion adsorption in the potential well) and the surface tension is decreased by the addition of electrolyte. However, the increase in surface potential with ionic strength expels the anions from the potential well and, at large electrolyte concentrations, the depletion thickness becomes positive. Consequently, the surface tension passes through a minimum. For \( W_y = 2kT \), the minimum is at approximately
c_s = 0.8 M; the position of the minimum depends on the parameters of the interactions and increases with the depth of the well.

4. Applications

4.1. Zeta potential

As noted above, the surface potential generated by the asymmetric distributions of electrolyte ions increases with increasing ionic strength. In contrast, electrophoretic experiments on air bubbles indicated that the surface potential decreases with the addition of electrolyte and depends strongly on the pH of the solution. For this reason, the effect of pH was included in the model, by assuming that the OH\(^-\) ions are adsorbed on the interface. The adsorption of the H\(^+\) will be neglected in comparison to that of OH\(^-\).

Assuming an equilibrium constant \(K_{\text{OH}}\) for the adsorption of OH\(^-\) on the interface sites, one can write:

\[
K_{\text{OH}} = \frac{(1-x)[\text{OH}^-]_S}{x},
\]

where \((1-x)\) is the fraction of free sites and \([\text{OH}^-]_S\) the concentration of OH\(^-\) in the vicinity of the interface sites. Consequently, the surface charge density is given by:

\[
\sigma_{\text{OH}} = -eN = - \frac{eN}{1 + \frac{K_{\text{OH}}}{[\text{OH}^-]_S}},
\]

where \(N\) is the number of adsorption sites per unit area of the interface.

It will be assumed that the pH value was attained by adding an acid (or a base) with the same anion (cation) as the electrolyte. The salt and the acid or base will be assumed totally dissociated. The surface charge is therefore screened by monovalent ions with a total bulk concentration \(c' = c_E + c_A + c_B\), where \(c_A(c_B)\) is the concentration of the added acid (base).

The concentration of OH\(^-\) ions in the vicinity of the surface, \([\text{OH}^-]_S\), is related to the bulk concentration \([\text{OH}^-]\) through:

\[
[\text{OH}^-]_S = [\text{OH}^-] \exp \left( -\frac{\Delta W_{\text{OH}}(0)}{kT} \right) \exp \left( \frac{e\psi_S}{kT} \right),
\]

where \(\psi_S = \psi(x = 0)\) is the surface potential, which is negative, \([\text{OH}^-]\) is the bulk concentration, and \(\Delta W_{\text{OH}}\) includes all the ion interactions which are not contained in the mean field \(\psi\). The latter interactions can be accounted for by using a new
apparent dissociation constant $K'_{\text{OH}}$. With this choice, Eq. (41a) becomes:

$$\sigma_{\text{OH}} = -\frac{eN}{1 + K'_{\text{OH}}[\text{OH}^-] \exp\left(-\frac{e\psi_s}{kT}\right)}$$  \hspace{1cm} (42b)

A more complete treatment should include in the Poisson–Boltzmann formalism all the interactions between the electrolyte ions and the interface, summarized in Section 2. Here it will be shown that, by accounting only for the hydration interaction of the electrolyte ions, one can capture the experimental dependence of the surface potential on pH and electrolyte concentration.

It will be assumed that the cations are structure-making, with a cut-off distance $d_s=d_E$ and the anions structure-breaking, with interactions given by Eq. (29a) and Eq. (29b). For simplicity, it will be assumed that $d_s=d_a=d_B$, and that the interactions of $H^+$ and $\text{OH}^-$ with the interface ($\Delta W_H(x)$, $\Delta W_{\text{OH}}(x)$) are negligible. The latter approximation affects the results only at very low or very high pH values.

Consequently, the potential satisfies the equations:

$$\frac{d^2\psi}{dx^2} = \left((c_E+c_A)\exp\left(\frac{W_1}{kT}\right) + c_B\right)\frac{e}{\varepsilon\varepsilon_0}\exp\left(\frac{e\psi}{kT}\right) + c_A\frac{e}{\varepsilon\varepsilon_0}\exp\left(-\frac{e\psi}{kT}\right) \hspace{1cm} 0<x<d_E \hspace{1cm} (43a)$$

$$\frac{d^2\psi}{dx^2} = \frac{2e(c_E+c_A+c_B)}{\varepsilon\varepsilon_0}\sin h\left(\frac{e\psi}{kT}\right) \hspace{1cm} d_E<x<\infty \hspace{1cm} (43b)$$

where $c_E$ is the electrolyte concentration and $c_A(c_B)$ is the concentration of the added acid (base). The boundary conditions are:

$$\frac{d\psi}{dx}\bigg|_{x=0} = -\frac{\sigma_{\text{OH}}}{\varepsilon\varepsilon_0} = \frac{eN}{\varepsilon\varepsilon_0} \frac{1}{1 + K'_{\text{OH}}[\text{OH}^-] \exp\left(-\frac{e\psi_s}{kT}\right)}$$  \hspace{1cm} (44a)

and:

$$\psi(x)|_{x=\infty} = 0$$  \hspace{1cm} (44b)

A boundary condition, which is equivalent to Eq. (44b), but is more convenient for calculations, is provided by Eq. (37), which is valid because for $x>d_E$ the potential satisfies the traditional Poisson–Boltzmann equation. In this case, it is enough to solve Eq. (43a) for $0<x<d_E$, with the boundary conditions Eq. (44a) and Eq. (37).
Fig. 7. The experimental values of the zeta potential for water/air interface in presence of NaCl, as a function of pH, from Ref. [32] (triangles: 0.1 M; circles: 0.01 M; squares: 0.00001 M) are compared with the potential values ($\psi_S$ and $\psi_d$) predicted by the present model: $d_1 = d_2 = 4$ Å, $W_i = 0.5kT$, $K_{OH} = 10^{-10}$ M, $N = 5.0 \times 10^{16}$ sites/m², $e = 80$ and $T = 300$ K.

The numerical solution for the surface potential as a function of pH is compared in Fig. 7, for various NaCl concentrations, with the experimental results provided by Li and Somasundaran [32]. The potentials $-\psi_S = -\psi(0)$ and $-\psi_d = -\psi(d_E)$ are plotted as functions of distance, since the zeta potential determined by electrophoresis is not defined at the surface, but at an unknown location, the ‘plane of slip’. The magnitude of $\psi_S$ is always larger than that of $\psi_d$, since the potential decays with the distance. The value $d_E = 4$ Å, which is provided by the dependence of the surface tension of water on the NaCl concentration at high ionic strengths was employed. For the equilibrium constant, the value $K_{OH} = 10^{-10}$ M, which is consistent with the experimental data for pH values between 3 and 6, was selected. A reasonable agreement with the data (which have a rather large error) was obtained by selecting $N = 5.0 \times 10^{16}$ sites/m² and $W_i = 0.5kT$.

One important consequence of the present hydration model is that the predicted surface potential does not vanish at high ionic strength, because of the cut-off distance for cations. Since there is no screening in the cation depletion region, the surface potential at large electrolyte concentrations is roughly given by:

$$\psi_{Sl-E} \rightarrow \approx \frac{\sigma d_E}{\varepsilon_0}$$

Another consequence is that the asymmetric distributions of electrolyte ions, due to their different hydration interactions, generate themselves a surface potential, which increases with increasing electrolyte concentration. At sufficiently high pH values (larger than $\approx 3$) the surface charge generated by the adsorption of OH$^-$ on
the interface provides the dominant contribution to the surface potential. In this case, the increase of the electrolyte concentration enhances the screening of the surface charge and hence the absolute value of the surface potential decreases. However, at low pH values, the adsorption of the OH\(^-\) ion is negligible and the surface potential is generated by the asymmetric distributions of the two kinds of ions. In this case, the absolute value of the surface potential is increased by the addition of electrolyte. The decrease of the absolute value of the surface potential with increasing electrolyte concentration at most pH values and its increase at very low pH values (Fig. 7) appears to be supported by experiment [32].

Karraker and Radke [18] compared the same experimental data with a model in which the surface potential was generated by the charge of the [OH\(^-\)] adsorbed on the interface, which is screened by the ions of the electrolyte. While good agreement for the surface potential was obtained for \(c_E = 1 \times 10^{-5} \) M, the predicted potential was much lower than the calculated one for \(10^{-2}\) and particularly for \(10^{-1}\) M. They have taken into account the image and van der Waals forces acting on the ions while we accounted only for the ion hydration instead. As noted in Section 3.2, the two approaches can lead to similar results, for suitable choices of the values of the parameters. However, for the values of \(B_1\) and \(B_2\) calculated from the polarizabilities of ions [18], the surface potential is positive at low pH values, and not negative, as indicated by experiment. Its magnitude at 0.1 M, (≈0.003 V, Fig. 3a) is also smaller than that provided by experiment. At large pH values, the adsorption of the OH\(^-\) ions on the interface is responsible for the negative surface potential.

A possibility to generate large surface potentials, at low pH values, would be to employ values for \(B_1\) and \(B_2\) of different signs. If one would select \(B_1 < 0\) and \(B_2 > 0\) and a suitable cut-off distance (to avoid the divergent accumulation of anions at the interface), results similar to those obtained here would be obtained. However, this implies that the van der Waals interactions attract the anions toward and repel the cations from the interface, which contradicts the general theory of the van der Waals interactions.

4.2. Surface tension at low ionic strength. Jones–Ray effect

The dependence of interfacial tension on electrolyte concentration can be related, via the Gibbs adsorption equation, to the depletion of the interfacial region of ions. At relatively large concentrations (between 0.1 and 1 M) of simple electrolytes (NaCl, KCl), the increase in surface tension with increasing ionic strength has an almost constant slope [29]. In the absence of accurate experimental data, it was reasonable to expect that this trend can be extended to low ionic strengths. The Wagner–Onsager–Samaras theory supported this expectation by predicting a positive slope at all electrolyte concentrations, which decreases with increasing ionic strength.

However, a few years after the Onsager–Samaras theory, experiments performed by Jones and Ray [33] indicated that the surface tension at the water/air interface is decreased by the addition of small amounts of KCl and exhibits a minimum at approximately \(c_E = 0.001\) M. Because the relative changes in surface tension are of
the order of 0.01% at that electrolyte concentration, hence very susceptible to experimental error, the existence of this minimum was doubted. The negative slope of the surface tension at low ionic strength contradicted the Onsager–Samaras theory, which was considered valid in that range. Dole and Swartout [34] confirmed, however, the experimental results of Jones and Ray.

Dole [35] explained the Jones–Ray effect using a modified Langmuir adsorption equation. He assumed that the interface contains ‘active spots’ which attract anions and that at low electrolyte concentration, the adsorption of the negative ions on these spots provides the main contribution in the Gibbs adsorption equation. By adding electrolyte, all the ‘active spots’ become occupied, no further adsorption of negative ions occurs and the change in surface tension is controlled by the overall depletion of ions due to image forces.

Karraker and Radke [18] proposed another explanation of this minimum. At low electrolyte concentrations, the positive adsorption of OH leads to a decrease of surface tension, while at sufficiently high ionic strengths, the depletion of Cl, repelled by the negative surface charge as well as by the van der Waals and image forces, becomes dominant and the surface tension increases.

A simpler mechanism is suggested here. The adsorption of OH ions does not affect, in a first approximation, the surface tension via the Gibbs adsorption equation. However, it generates a surface charge, which is responsible for the accumulation of cations in the vicinity of the surface. Consequently, the total surface adsorption of ions is positive and the slope of the surface tension, as a function of electrolyte concentration, is negative. The surface potential is, however, decreased by the addition of electrolyte, and the accumulation of cations is compensated by the anion depletion. Hence, by adding electrolyte, the ions depletions of the interfacial region, due to other interactions (ion hydration, image or van der Waals forces) dominate the process, and the slope becomes positive.

The surface adsorption of OH is obviously not negligible. However, the chemical potential of OH in the bulk is given by:

\[ \mu_{\text{OH}} = \mu_{\text{OH}}^0 + kT \ln([\text{OH}^-]f_{\text{OH}}) \]  

and at constant pH, \( \mu_{\text{OH}} \) depends on \( c_E \) only via the activity coefficient, which was taken unity. Therefore, Eq. (15) yields:

\[ \frac{1}{kT} \frac{\partial \gamma}{\partial c_E} = -\frac{\Gamma_{\text{Cl}^-} + \Gamma_{\text{K}^+}}{c_E}. \]  

It should be noted that the same result can be obtained by using an activity coefficient of 1 in Eq. (11) of Ref. [18]. At concentrations of approximately 0.001 M of uni-univalent electrolytes, (relevant for the Jones–Ray effect) \( f = 1 \) is, in general, a good approximation.

Let us evaluate how much the surface potential affects the surface adsorption of electrolyte ions. When only the short-range hydration interactions of ions with the
interface are taken into account, the depletion thickness is given by:

\[
- \frac{\Gamma_{c^-} + \Gamma_{K^+}}{c_E} = \int_0^\infty \left( \frac{2c_E - c_1(x) - c_2(x)}{c_E} \right) dx \\
= \int_0^{d_E} \left( 2 - \frac{c_1(x)}{c_E} - \frac{c_2(x)}{c_E} \right) dx - 2 \int_{d_E}^\infty \left( \cos \left( \frac{e\psi(x)}{kT} \right) - 1 \right) dx,
\]

(48)

where the potential satisfies Eqs. (43a) and (43b). The first term of the right-hand-side is less than 2 \(d_E\), which is approximately 10 Å. At \(c_E = 0.001\) M and assuming \(-e\psi(d_E) = 2kT\), the negative depletion thickness (the adsorption thickness) provided by the second term of the right-hand-side of Eq. (48) is approximately 200 Å, largely exceeding the magnitude of the depletion thickness due to the cut-off distance. This value is so large, that the total surface adsorption remains positive and large, even when other long-range repulsions (such as the image or the van der Waals force) are taken into account. The inclusion of the image potential decreases the adsorption thickness by approximately 10 Å, and a similar effect is obtained by including the van der Waals interactions.

When the electrolyte concentration is increased, the range of the double layer decreases dramatically (the Debye–Hückel length decreases) and the magnitude of the surface potential also decreases. In the linear approximation, \(\psi(x) = \psi(d_E)\exp\left(-\frac{(x - d_E)}{\lambda}\right)\) (for \(x > d_E\)) and the second right-hand-side term of Eq. (48) becomes:

\[
2 \int_{d_E}^\infty \left( \cos \left( \frac{e\psi(x)}{kT} \right) - 1 \right) dx \equiv \int_{d_E}^\infty \left( \frac{e\psi(x)}{kT} \right)^2 dx = \left( \frac{e\psi(d_E)}{kT} \right)^2 \frac{\lambda}{2}
\]

(49)

In summary, at very low electrolyte concentrations (below \(\approx 0.001\) M) and in the absence of a surface charge, the image forces provide the most important contribution to the (negative) ion adsorptions, and the other repulsions (ion hydration, van der Waals interactions) can be neglected. However, if there is a surface charge, the overall accumulation of ions in the vicinity of the surface (the positive overall adsorption) due to the mean field \(\psi\) (the Poisson–Boltzmann effect) becomes important. Furthermore, at electrolyte concentrations smaller than 0.001 M and if \(e\psi(d_E)\) is at least of the order of \(kT\), all the other interactions, including the image forces, become negligible. The overall ion adsorption, which is positive, is well approximated in this case by the traditional (bare-bone) Poisson–Boltzmann equation. At very large electrolyte concentrations, the range of the mean field Poisson–Boltzmann interactions as well as the image forces decrease drastically, since their decay lengths are roughly proportional to \(\lambda\) and \(\lambda/2\), respectively. In this case, other interactions, such as ion hydration or van der Waals forces, become dominant.

In Fig. 8, curve (1) represents the dependence of surface tension on electrolyte concentration, based on the present model. It is assumed that \(\text{OH}^-\) ions are adsorbed on the surface, with an apparent equilibrium constant \(K'_{\text{OH}} = 1 \times 10^{-10}\) M, and that there are a cut-off \(d_E = 4\) Å for the cations, and a potential well of depth \(W_1 = 0.5kT\)
Fig. 8. The change in surface tension at low electrolyte concentrations (the Jones–Ray effect). Circles: Experimental data from Ref. [33]. Curve (1): predicted surface tension for the simple model which accounts for OH\(^-\) adsorption and only ion hydration effects for electrolyte ions, within the Poisson–Boltzmann approach. Curve (2): predicted surface tension when image forces are also included in the model. As noted in Section 3, the image forces cannot be neglected at concentration lower than 0.01 M.

and width \(d_E = 4\) Å for the anions. These values of the parameters are those used in the previous section, which was concerned with the zeta potential of air bubbles determined from electrophoretic experiments. However, to recover the Jones–Ray minimum approximately 0.001 M (for pH 7), a much smaller value for the number of adsorption sites on the interface \(N\) than the one used there had to be employed, namely \(N = 3 \times 10^{15}\) sites/m\(^2\).

At the minimum of the surface tension, the positive adsorption due to the mean field (the Poisson–Boltzmann effect) is compensated by the negative adsorption due to the ion hydration, image forces and van der Waals interactions. As already noted (Fig. 1), at the low ionic strengths where the Jones–Ray minimum occurs (\(\approx 0.001\) M), the image force contribution to the depletion thickness cannot be neglected. By including the image potential in the calculation of the surface adsorption, good agreement with experiment was obtained for \(N = 6 \times 10^{15}\) sites/m\(^2\) (Fig. 8, curve (2)).

From the experimental values of the zeta potentials for air bubbles [32], one could infer that the surface potential should be approximately 0.060 V for 0.001 M NaCl at pH 7. However, this value is much too large to be in agreement with the experiments of Jones and Ray [33]. The depletion thickness vanishes at the minimum of the surface tension, and at this surface potential, the adsorption thickness, due to the Poisson–Boltzmann effect, would be over 200 Å and could not be compensated by the other interactions discussed here. The value which had to be selected for \(N\)
Fig. 9. Approximation of the interactions between ions and the interface: (1) square well for anions; (2) triangular well for anions; (3) hard wall for cations.

\( N = 6 \times 10^{15} \text{ sites/m}^2 \) to provide a good agreement with Jones–Ray minimum, led to a surface potential of only approximately 0.014 V.

4.3. Surface tension at high ionic strength

At high ionic strength, the adsorption of OH\(^-\) no longer plays a central role. Because the potential at the surface and its decay length are both small, the behavior of the surface tension is determined by the ion distributions within the first few Ångstroms from the interface.

The almost linear increase of the surface tension with the concentration of the common uni-univalent electrolytes can be easily described by employing a cut-off distance for the cations. However, experiment \cite{29} indicated that for other electrolytes (HCl, HNO\(_3\), HClO\(_4\)) the surface tension decreases with increasing electrolyte concentration up to 1 M. The adsorption thickness due to the Poisson–Boltzmann effect, which is responsible for the Jones–Ray effect at low ionic strength, cannot explain the linear decrease of surface tension at high ionic strength, since it decays too strongly with the electrolyte concentration. The image forces and the repulsive van der Waals interactions \((B_i > 0)\) generate a depletion thickness (a negative adsorption), and, therefore, also cannot explain this behavior.

Can the change in cation hydration, between bulk and interface explain this effect? If the cations (such as Na\(^+\) or K\(^+\)) cannot approach the interface, and the potential well for anions is not very deep, the overall adsorption of ions is negative at any electrolyte concentration. However, if the cations (such as H\(^+\)) can penetrate at least a part of the interfacial potential well of the anions \((d_2 < d_1)\), they are
Fig. 10. The depletion thickness as a function of electrolyte concentration for (a) a square well interaction for anions, with \( d_z = 5 \) Å and \( W_s = 1kT \); (b) a triangular well interaction for anions, with \( d_z = 5 \) Å and \( \Delta W(0) = -2kT \); and a cut-off distance for cations \( d_z = 0, 1, 2, 3, 4 \) and 5 Å; \( \varepsilon = 80 \) and \( T = 300 \) K.

attracted there by the accumulated anions and the overall adsorption can become positive.

Two cases have been investigated. First, the solution of the Poisson–Boltzmann equation was obtained for an interfacial square-well potential for the anions, with \( W_s = kT \) and \( \Delta W(0) = -2kT \); and a cut-off distance for cations \( d_z = 0, 1, 2, 3, 4 \) and 5 Å; \( \varepsilon = 80 \) and \( T = 300 \) K.
For cations, the distance of closest approach to the interface was selected $d_{i}=5$, 4, 3, 2, 1 and 0 Å. The dependence of the slope of the interfacial tension, $(1/kT)(\partial \gamma/\partial c_E) = -(\Gamma_1 + \Gamma_2)/c_E$ on the electrolyte concentration is presented in Fig. 10a (for a square-well) and Fig. 10b (for a triangular well). The results are qualitatively the same: if the cations are allowed to penetrate most of the well, the surface tension decreases with increasing electrolyte concentration. If the cations are not allowed to penetrate the well, the potential is large in the well and the total surface adsorption is negative. At intermediate situations, the total surface adsorption is positive at low electrolyte concentrations (corresponding to a decrease of the surface tension with increasing electrolyte concentration) and negative at high ionic strengths (corresponding to an increase of the surface tension with increasing electrolyte concentration). The corresponding changes in surface tension as a function of electrolyte concentration are presented in Fig. 11a and b, for the square and the triangular well, respectively. While in the intermediate cases the surface tension passes through a minimum, at the extreme cases the dependence of the surface tension on electrolyte concentration is almost linear.

It should be noted that a decrease of the interfacial tension with increasing electrolyte concentration was observed [29] only when the cation was H$. The major differences in the hydration of H$ as compared to those of Na$ or K$, are probably responsible for the fact that the H$ can approach closer the interface than any other cation. Consequently, the simple model suggested here can predict a negative slope for the surface tension when H$ is the cation and a positive slope for the other cations.

### 5. Conclusions

It has been long known that the over-simplified Poisson–Boltzmann equation is accurate in predicting the double layer interaction only in a relatively narrow range of electrolyte concentrations. One obvious weakness of the treatment is the prediction that the ions of the same valence produce the same results, regardless of their nature. In contrast, experiment shows marked differences when different kinds of ions are used. The ion-specific effects can be typically ordered in series (the Hofmeister series [36]), and the placement of ions in this series correlates well with the hydration properties of the ions in bulk water.

It was suggested recently [18,26] that the van der Waals interactions between ions and two media separated by an interface can account, at least partially, for the order in the Hofmeister series and therefore can explain ion specific effects in the distribution of electrolyte ions in the vicinity of an interface. However, there is no consensus regarding the values of the interaction constants which should be used in the van der Waals interactions. It was expected that, due to the van der Waals interactions, the negative ions should be more strongly repelled by the water/air interface than the positive ions. This seems to be, however, contradicted by experiment and simulations.

In this paper, the old idea that the ion hydration should be mainly responsible for the ion-specific effects is reiterated. After a brief review of the Poisson–Boltzmann
Fig. 11. The change in surface tension as a function of electrolyte concentration for (a) a square well interaction for anions, with $d_1 = 5$ Å and $W_s = 1kT$; (b) a triangular well interaction for anions, with $d_1 = 5$ Å and $W_s = -2kT$; and a cut-off distance for cations $d_2 = 0, 1, 2, 3, 4$ and $5$ Å; $e = 80$ and $T = 300$ K.

formalism and of a few approaches that describe ion-specific effects, a simple approach is proposed to account for ion hydration. Assuming that most of the hydration free energy is due to the interaction between ion and its water neighbors, the approach of a structure-making ion to the interface is unfavorable, because it
cannot be fully hydrated there. Since the hydration energy is large, only a minute percentage change of its value can lead to a complete depletion of ions. Therefore, a cut-off distance from the interface can describe well the interaction between ion and the interface. The long-range Wagner–Onsager–Samaras image force is important for neutral interfaces at very low electrolyte concentration, but is negligible when the interface is charged or above the physiological concentrations ($\approx 0.1$ M). The van der Waals interactions can be approximately taken into account by a small change in the cut-off distance.

More difficult is to treat the case of structure-breaking ions, which are pushed toward the interface, because they have there more favorable interactions with water. The consequence of a potential well for the anions in the vicinity of the interface is therefore investigated. However, the depth of the well should not be larger than a few $kT$, otherwise huge surface potentials would be generated at high ionic strengths, and this was not observed experimentally.

It is not yet clear whether the total interaction of ions with the interface can be accounted by a simple function of distance; however, the simple treatment presented here leads to qualitatively appealing predictions. The assumptions that $d_1 = d_2$ or the simple functional form chosen for the anion interaction with the interface were made only to simplify the calculations. Better agreement with experiment can be obtained if other details are included in the model (dependence of the activity coefficient on the electrolyte concentration, additional interactions).

The dependence of the surface potential on the electrolyte concentration and on the pH, determined experimentally, was reasonably well described by the traditional Poisson–Boltzmann equation, using a model involving the OH$^-$ adsorption on the interface and the treatment suggested for ion hydration.

The same simple model can also explain the Jones–Ray effect (a minimum of the surface tension at a concentration of approximately $1.0 \times 10^{-3}$ KCl [33]). At low electrolyte concentrations, the accumulation of the electrolyte ions due to the surface charge (as predicted by the Poisson–Boltzmann equation) overwhelms all the other contribution to the surface adsorptions. Consequently, the interfacial tension first decreases with increasing electrolyte concentration. However, the Poisson–Boltzmann adsorption thickness decays strongly with increasing electrolyte concentration, and the repulsion of ions by the interface (due to image forces, change in ion hydration and van der Waals interactions) becomes dominant, and the slope of the interfacial tension becomes positive.

The behavior of surface tension at high ionic strength also can be understood on the basis of changes in ion hydration changes between bulk and interface. The tendency of the structure-breaking ions to accumulate at the surface can lead to a positive surface adsorption. However, if the cations cannot approach the interface, the asymmetry of the ion distributions generates a potential, which repels the anions from the interface, and the total adsorption becomes negative. Consequently, the surface tension increases with electrolyte concentration; this occurs for simple salts (NaCl, KCl). If the cations can approach the interface, the accumulation of anions in the vicinity of the interface is also followed by an accumulation of cations,
without generating large surface potentials. Consequently, the total adsorption becomes positive and the surface tension decreases with electrolyte concentrations, up to high ionic strengths. This occurs, for example, for acids (HCl, HNO₃, HClO₄), and can be attributed to the ability of the H⁺ ion to approach the interface.

References