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Specific ion effects on double layer forces through ion hydration

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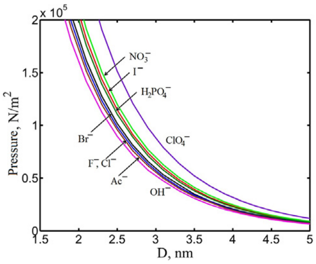
HIGHLIGHTS

- The hydration of ions generates a negative excess entropy.
- The nonideality caused by hydration is responsible for the specificity of ions.
- The specificity provides an ion order as that observed by Hofmeister.

GRAPHICAL ABSTRACT



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ABSTRACT

An attempt is made to explain the dependence of the strength of repulsion between two charged parallel plates immersed into an electrolyte solution on the nature of the electrolyte. The theory provides a sequence of ions which almost coincides with the Hofmeister series for both anions and cations. The repulsive force is calculated by taking into account that the ions are hydrated; this hydration generates a negative volume exclusion entropy, which is considered to be responsible for ion specificity. In contrast to the traditional theory in which the electrolyte solution is considered to be ideal, the present one includes a nonideal contribution caused by ion hydration. It will be also shown that at high salts concentrations the anions of the same counterion provide strong specificities (large differences between the repulsive interactions of successive ions) for positively charged surfaces, and the cations of the same counterion strong specificities for negatively charged surfaces.

1. Introduction

At the end of 19th century, Hofmeister observed a sequence for the ability of salts to precipitate the egg white [1]. He suggested that this ability depends on their water ordering capacity. Since then, numerous physicochemical properties of electrolyte solutions were found to be dependent on the nature of the salt employed. They include the surface tension at the air/water interface [2–4], the hydrogen bond network of water [5], the repulsive force between two charged surfaces [6,7], the micelle formation [8], the osmotic stress of macromolecular solutions [9], and many more, the sequence of their strengths being that observed by Hofmeisters for proteins.

A number of attempts have been made to explain the physical mechanism which provides ion-specificity [10–18]. Ruckenstein and Schiby derived an expression for the excess chemical potential of ions caused by their hydration [10,11]. The resulted negative volume exclusion entropy is responsible for ion specificity.

The dispersion interactions, which are dependent on the ion polarizability, were suggested to provide ion specificity [12]. The dispersion interactions predict repulsive forces between the water–air interface and the highly polarizable ions (Cl^-, Br^-, I^-) and attractive ones between the interface and the less polarizable ions (Na^+, Li^+, K^+). However, the old experiments of Frumkin [13]

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revealed that the more polarizable anions are positively adsorbed on the interface and the less polarizable cations are negatively adsorbed on the interface, opposite to the predictions of the ion dispersion theory [14]. Collins suggested that the surface charge density of hydrated ions constitutes an important parameter that controls ion specificity [15]. Recently, a model was proposed which explains the ion-specificity of the surface tension of electrolyte solutions and their surface potentials [16]. In both cases the specificity has the order provided by Hofmeister. These authors suggested that ionic hydration is the consequence of a competition between cavitational and electrostatic energies. The cavitational energy is a result of the perturbation by the ion of the hydrogen bond network of water and results in a force which drives the ion toward the interface. This force is counterbalanced by an electrostatic Born force. For weakly polarizable ions, the Born energy is much larger than the cavitational one favoring bulk solvation. In contrast, for large polarizable ions the balance is shifted toward the interface. An interaction potential that quantifies this effect was derived.

The quantitative evaluation of the repulsive force between two charged parallel plates in an electrolyte solution is relevant for colloidal systems and biological processes. In most cases, such forces have been calculated using the DLVO theory [17]. In that approach the ions are treated as point charges and the ion specificity is disregarded. The corrected version of the traditional DLVO theory [18] also disregards ion specificity. However, numerous experiments revealed that ion specificity is present in the interaction between colloidal particles [19–22]. For this reason, in addition to the interactions involved in the DLVO theory, other interactions which account for ion specificity must be included into the theory.

In solution, the ions are hydrated and for this reason are relatively large. This means that the number of possibilities to locate a hydrated ion is smaller than that of a nonhydrated one. Compared to the case in which the ions are not hydrated [17,18], the entropy is smaller when the ions are hydrated because a larger number of sites are occupied. This excess negative entropy changes the chemical potential and introduces in this manner the specificity of ions. In other words, the present theory considers the electrolyte solution to be nonideal with a nonideality caused by ion hydration. In contrast, the corrected traditional theory considers the electrolyte solution to be ideal.

In the present paper, the effect of volume exclusion of hydrated ions on the double layer repulsion is examined in more details than in our recent short letter [23].

2. Theoretical framework

2.1. Free energy of formation of the double layer

The system examined in the present paper involves two charged parallel plates immersed in a reservoir containing an electrolyte solution. The free energy of the double layer is given by the sum of the following three contributions

$$F = F_{ele} + F_{ion} + F_v \tag{1}$$

where F_{ele} is the electrostatic free energy, F_{ion} is the free energy of ions in the double layer minus the free energy of the same ions under the conditions in the reservoir, F_v is the change in the free energy of ions and water due to the volume exclusion generated by hydration.

At constant surface potential, the electrostatic free energy has the form [17]

$$F_{ele} = \frac{1}{2}\varepsilon\varepsilon_0 \int_{-D/2}^{D/2} \left(\frac{d\varphi}{dx}\right)^2 dx - 2\varphi_S\sigma \tag{2}$$

whereas at constant surface charge density, the electrostatic free energy is given by

$$F_{ele} = \frac{1}{2}\varepsilon\varepsilon_0 \int_{-D/2}^{D/2} \left(\frac{d\varphi}{dx}\right)^2 dx \tag{3}$$

where D is the distance between the two plates; φ, the electrical potential; φ_S, the surface potential; ε, the dielectric constant; ε_0, the vacuum permittivity; and σ, the surface charge density.

Assuming the solution to be ideal, the electrolyte contribution to the free energy is provided by the difference between the entropies of ions in the double layer and (of the same ions) under the conditions in the reservoir. Consequently, for ideal solutions, one can write

$$\begin{aligned} F_{ion} &= k_B T \int_{-D/2}^{D/2} \left[\sum\nolimits_{i=1,2} \left(c_i \ln \frac{x_i}{x_{i,b}}\right) + c_w \ln \frac{x_w}{x_{w,b}}\right] dx \\ &= k_B T \int_{-D/2}^{D/2} \left[\sum\nolimits_{i=1,2} \left(c_i \ln \frac{x_i}{x_{i,b}}\right) + c_w \ln \frac{1-\sum_{i=1,2} x_i}{1-\sum_{i=1,2} x_{i,b}}\right] dx \end{aligned} \tag{4}$$

where k_B is the Boltzmann constant, T is the temperature in K, c_i and x_i are the concentrations (number densities) and the mole fractions of the ions of the electrolyte, c_w and x_w are the concentration and the mole fraction of water, and subscript b indicates their values in the reservoir. Because $x_w \gg \sum_{i=1,2} x_i$, one can expand $\ln((1-\sum_{i=1,2} x_i)/(1-\sum_{i=1,2} x_{i,b}))$ in series to obtain [18]

$$F_{ion} \approx k_B T \int_{-D/2}^{D/2} \left[\sum\nolimits_{i=1,2} \left(c_i \ln \frac{c_i}{c_{i,b}} - c_i + c_{i,b}\right)\right] dx \tag{5}$$

2.2. Excess chemical potentials of ions and water

A hydrated ion cannot occupy the space already occupied by other hydrated ions. The number of positions available to locate a hydrated ion is therefore smaller than when it is assumed to be nonhydrated. Assuming that τ_i water molecules are hydrating one ion i, the total fraction of sites occupied by cations ($i = 1$) and anions ($i = 2$) is $\sum_{i=1,2} c_i\tau_i/n$, where n is the number of sites per unit volume (assumed to be the concentration of water). Hence the fraction of free sites is given by $1-\sum_{i=1,2} c_i\tau_i/n$. To locate an ion i, τ_i free neighboring sites are required. The probability $P_i(x)$ of finding τ_i free neighboring sites is approximately given by $\left(1-\sum_{i=1,2} c_i\tau_i/n\right)^{\tau_i}$. Using the Boltzmann relation, this probability provides the following excess entropy for ion i

$$\Delta S_i = k_B \ln P_i(x) = k_B \ln \left(1 - \sum_{i=1,2} c_i\tau_i/n\right)^{\tau_i} \tag{6}$$

As a result, the ions possess excess chemical potentials per ion given by $\mu_i^e = -k_B T \ln \left(1-\sum_{i=1,2} c_i\tau_i/n\right)^{\tau_i}$, which has to be added to the chemical potential of an ideal solution. Therefore, the excess free energy due to the decreased entropy of the two kinds of hydrated ions of the electrolyte is given by the expression

$$F_v = -k_B T \int_{-D/2}^{D/2} \sum_{i=1,2} c_i \ln \left(1 - \sum_{i=1,2} c_i\tau_i/n\right)^{\tau_i} dx + \text{the contribution of water} \tag{7}$$

The excess chemical potential of water can be calculated using the Gibbs–Duhem equation. The excess chemical potential of water can be obtained from