**Ion-specific thermodynamic properties of colloids and proteins**

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**Abstract**

Franz Hofmeister established in 1888 that different salt solutions with the same ionic charges have different efficiencies in precipitating proteins from whole egg white. We will discuss how this can be understood from the modified Poisson–Boltzmann equation that accounts for ion specificity via the ion-surface non-electrostatic potential of mean force (NE-PMF) from molecular dynamics simulations. Using this approach, it is at least in principle possible to capture the important physics of the system due to the inclusion of ion-surface van der Waals forces, short range hydration, image potential and different solvent-mediated forces. The method has been proved to be efficient and suitable for describing phenomena where the water structure close to the interface plays an essential role. As an illustrative example, we demonstrate why the double layer force between two gold electrodes coated with hydrophobic self-assembled monolayers in different electrolytes can be highly ion specific. Important thermodynamic properties related to protein aggregation, essential in biotechnology and pharmaceutical industries, can be obtained from the method shown here.

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1. Introduction

Ion-specific effects in biological and biochemical systems [1] have been known since 1888 when Franz Hofmeister [2] established an efficiency series in precipitating proteins from whole egg white when the species of anions were changed and the choice of cation kept constant. Similarly for fixed anion and varying cation, and the series can sometimes even be reversed [3–7]. Hofmeister (specific ion) effects have been found everywhere: in studies of protein stability and unfolding, enzymatic activity, membrane permeability to anions, growth of bacteria, uptake of water by wool and leather, in molecular forces in colloid science, pH measurements, electrolyte activities and viscosities, ion binding to micelles, ionic microemulsions, vesicle formation, cloud points of non-ionic surfactants. The list appears to be endless [8–14].

The overall aim of this paper is to discuss how one can put an understanding of systematic Hofmeister effects to work in solution chemistry, biophysical chemistry, and in chemical engineering. The proposed program for such an ambitious goal is to show how a modified Poisson–Boltzmann equation that accounts for short range ion-surface non-electrostatic potentials of mean force (NE-PMF) from molecular dynamics simulations can be exploited to provide long range PMF between colloidal particles. With PMF between colloidal or protein surfaces one can calculate thermodynamic properties of colloid and protein solutions. The number of areas that depend on a better theoretical understanding of specific ion effects is so large that insights into even one would have significant long-term economic and scientific benefits. A better foundation could also provide optimal directions for experiment [14].

The shared property of these ion-specific phenomena is that none are accommodated by classical theory! So what to do? One way of testing specific ion effects in colloid science is to consider the air–solution interface of simple aqueous salt solutions. In a pioneering work Jungwirth and Tobias [15] could show that it is probably crucial to take into account the polarizability of the ions, much as Ninham and Yaminsky [1] proposed in their landmark paper several years earlier. But in contrast to Ninham and Yaminsky, Jungwirth and Tobias used molecular dynamic simulations in order to predict surface tensions. They found out that it is probably necessary to consider the influence of the ion polarizability on the solvent structure in order to get the right ordering of the surface tension. However, although MD simulations roughly predicted the right Hofmeister series of surface tensions, such simulation techniques are computer heavy to carry out, give rather bad results for surface tension of pure water, and are too complicated to be used in many practical applications.

In any case, MD simulations are not appropriate for rapid calculations of surface properties. In this respect the approach by Ninham and Yaminsky [1] is much easier to use. In principle the...
influence on the ion-surface potential from some solvent effects can be taken into account within the DLVO model by using a convenient Lifshitz-like ansatz [3–7]. There, the relevant non-electrostatic (NES) interactions are taken into account via frequency summations over all electromagnetic interactions that take place in the solutions. If done rigorously, the result will be quite accurate. As a proof of principle, Boström et al. made a first attempt in this direction [16,17]. The classical DLVO ansatz was replaced by a modified Poisson–Boltzmann equation (MPBE), in which a dispersion term was added to the electrostatic interaction [16,17]. In this way ion specificity came in natural via the polarizability and the ionization potential of the ions. However, it turned out that this approximation of the non-electrostatic interactions was not sufficient to predict the Hofmeister series of surface tension [17]. The problem apparently comes at least partly from the neglect of ion–water interactions and their changes near the surface. To introduce such interactions in primitive model calculations Boström et al. [18] used Jungwirth and Tobias [15] water profile perpendicular to the surface as a basis to model a distance dependent electrostatic function, instead of a spatially constant dielectric constant.

With such a modification the description of ion profiles on surfaces became more physical within this modified DLVO approach. However, not all profiles were satisfactory, partly because of the still too crude approximation when hydration effects [5–7] and the effects from the anisotropy of the water surface layer near the interface on the dispersion potential were not included.

In a very interesting paper Luo et al. [19] used molecular simulations that included a finite size ion and explicit water molecules to calculate NE-PMF acting on an ion near an interface. As shown by Luo et al. this NE-PMF approximate reasonably well the ion-specific short range potential acting between an ion and a liquid–liquid surface. Similar simulations were recently performed for an ion near a self-assembled monolayer (SAM) [20] and for an ion near an air–water interface [21]. In parallel with this work Parsons et al. recently calculated non-electrostatic potentials that accounted for hydration effects through the use of both ion and water polarizabilities [5]. The hydration model assigns an explicit hydration shell to kosmotropic (strong hydrated) ions only. The different Hofmeister series appears to be coming out correct from a combination of ion-surface dispersion interactions and hydrated ion size. These two complementary approaches are very promising. The modified Poisson–Boltzmann equation with a proper ion-specific potential provides reasonable result for interactions across salt solutions between two surfaces that are not too close together. For interactions when the colloids come closer together it should be preferable to use simulations that include ion-specific potentials [19–26].

One question that could be raised is if ion size correlation and electrostatic correlation not accounted for in MPBE may influence the result. Solvent averaged Monte Carlo (MC) simulations were performed by Boström et al. [25] for ion distributions outside a single globular macroion in different salt solutions. The model used included both electrostatic, hard-sphere finite ion size, and NES interactions between ions and between ions and macroions. Simulation results were then compared with the predictions of the Ornstein–Zernike equation (OZ) with the hypernetted-chain (HNC) closure approximation and the non-linear Poisson–Boltzmann equation in spherical coordinates, both extended to include NES potentials. We show in Fig. 1 that there is good agreement between modified Poisson–Boltzmann theory, MC simulations, and OZ-HNC calculations when the counterions and co-ions are monovalent. This suggest that short range ion dispersion potentials, or as an alternative the ion-surface NE-PMF from simulations that include solvation effects, can be used in solvent averaged mean-field theories such as the modified Poisson–Boltzmann equation. We present in Section 2 some discussions about how density functional theory can be used to verify under what conditions Poisson–Boltzmann is a valid theory.

We have in a series of papers reported that inclusion of short range ion-surface potentials obtained from simulation [27–30], or from extended Lifshitz theory that accounts for hydration [5], probably is essential to obtain good results. It may also be important to account for the spatial variation of the local dielectric constant near the interface [27].

The outline of this article is as follow. In Section 2, we present a discussion on how Poisson–Boltzmann theory comes out as a limiting form of the density functional theory (DFT). We also compare ion distributions obtained from DFT and PB. The conclusion is that Poisson–Boltzmann theory works well for monovalent ions, at least when the salt concentrations or surface charge densities are not too high. In Section 3 we recapitulate briefly the story of ion-surface NE-PMF from molecular dynamics simulations. Then in Section 4 we describe how the non-linear modified Poisson–Boltzmann (MPB) equation that account for such short range ion-surface NE-PMF can be exploited to obtain the long range potential of mean force between colloidal particles or proteins. This interaction between colloidal particles can then be used to calculate thermodynamic properties (e.g., phase diagrams or second virial coefficients). In Section 4 we show that the experimentally observed reversal of the Hofmeister series when pH passes the isoelectric point comes
out right when the NE-PMF is included in the MPB. We end with some conclusions and a brief discussion about the potential use of our theoretical work in chemical engineering in Section 5.

2. From Debye–Hückel to DFT: limits of Poisson–Boltzmann theory

For different systems, we have shown that the Poisson–Boltzmann equation (PBE) is a reasonable approximation for systems with monovalent ions and not too high salt concentrations or surface charges. PBE is often useful for studying systems containing simple electrolyte solutions. However, as a mean-field theory, Poisson–Boltzmann has some intrinsic limitations. Some modifications, such as those that will be presented in Section 3, where some additional features are captured from molecular dynamics, have succeeded in minimizing these limitations, while keeping the low computational effort required for engineering applications. Nevertheless, even when using the MPBE, one must be aware of its limits. PBE has never been supposed, e.g., to be used for very high salt concentrations, but this is usually not a problem, because it has been proven that it works quite well at the salt concentrations of biological solutions [25].

The density functional theory (DFT) is a powerful technique that accounts for excluded volume effect, electrostatic and size correlations. By taking into account these additional effects, DFT is an excellent alternative for systems where the classical PB approach is not enough. Different from molecular simulations, DFT accounts for the microscopic details of a many-body system without explicitly dealing with thermal fluctuations. Its computational cost is for the microscopic details of a many-body system without explicitly dealing with thermal fluctuations. Its computational cost is in between molecular simulations and PBE. The superior numerical efficiency and concomitant physical clarity enable both MPBE and DFT to bridge multiple length and time scales spanning from molecular events to meso/macroscopic phase transitions [31].

Whereas DFT provides an exact mathematical framework based on statistical mechanics, its performance entirely depends on the formulation of the grand potential or equivalently, of the Helmholtz energy functional $F$ in terms of the molecular density profiles. The central task for the application of DFT is therefore to derive an analytical expression of the Helmholtz energy as a functional of the density profiles. In general, the Helmholtz energy functional can be formally expressed as the sum of an ideal-gas term, $F^{id}$, that preserves the bond connectivity for polyelectrolytes, and an excess, $F^{ex}$, that takes into account all nonbonded interactions. While the ideal-gas Helmholtz energy is known exactly by using the polymer-field theory for a continuous model of chain connectivity [32], the excess Helmholtz energy arising from nonbonded interactions, i.e., hard-sphere repulsion and Coulomb interactions in the primitive model of polyelectrolytes, can only be formulated at various levels of mean-field approximations. Here we use the approach proposed by Li and Wu (2006) [33], that accounts for the contributions to the Helmholtz energy from multibody correlations by using a modified fundamental measure theory (FMT) [34] and a quadratic functional expansion (or hypernetted-chain approximation, HNC) for the electrostatic interactions [35]. FMT is a geometry-based approach that uses weighted densities to account for hard-sphere repulsions. The numerical details about FMT, not in the scope of this paper, involve geometric functions as presented by Yu and Wu (2002) [34].

The equilibrium molecular density profiles correspond to the minimization of the grand potential. This minimization yields the Euler–Lagrange equation for the density profiles of ions:

$$c_i(x) = \exp \left[ \left( \frac{\mu_i - \psi(x)}{k_B T} - \frac{\delta F^{ex} / \delta c_i(x)}{k_B T} \right) \right],$$

where $\mu_i$ is the chemical potential of the ion $i$ and $\psi$ is the external potential due to the presence of a charged surface.

The Helmholtz energy functional of the ions can be decomposed into four contributions:

$$F = F^{id} + F_{el}^{ex} + F_{C}^{ex} + F_{RS}^{ex},$$

where $F^{id}$ is the intrinsic Helmholtz energy functional for an ideal gas, $F_{el}^{ex}$ stands for the contribution due to hard-sphere repulsions, $F_{C}^{ex}$ represents the direct Coulomb energy, and $F_{RS}^{ex}$ is the excess Helmholtz energy functional arising from the electrostatic correlations. The term $F^{id}$ in Eq. (1) is the sum of the last three terms in the right hand side of Eq. (2) and the contribution of the ideal term $F^{id}$ is implicit in the chemical potential $\mu_i$ in Eq. (1).

The electrostatic potential $\psi(x)$ used in PBE is given by the sum external potential and the direct Coulomb energy:

$$\gamma \psi(x) = \psi_i(x) + \frac{\delta F^{ex}_{el}}{\delta c_i(x)}.$$  

Hence, neglecting the size effects ($\delta F^{ex}_{el} / \delta c_i = 0$) and correlations ($\delta F^{ex}_{el} / \delta c_i = 0$) reduces the Helmholtz energy $F$ to that used in the PB approach, and Eq. (1) is reduced to

$$c_i(x) = c_{i,0} \exp \left[ \frac{\gamma \psi(x)}{k_B T} \right],$$

that is the density profile predicted by the classical PB, where $c_{i,0} = \exp[\mu_{i,0} - \gamma \psi(0)] / k_B T$ (with $\mu^*$ being the reference chemical potential), i.e., the chemical potential in the bulk is directly related to the bulk density of ion $i$.

Henderson and Boda [36] compared results obtained from the Poisson–Boltzmann theory for the double layer around an electrode with those obtained from molecular simulations and DFT. They found that PB equation give good results for the diffuse layer potential and ion profiles of monovalent ions. However, the PB equation did not present good results for multivalent ions, high salt concentrations, high surface charge densities, low temperature or solvents with low dielectric constant. This is a good tutorial of the general well-known limitations of the classical PB equation. When using the classical DLVO theory we must have in mind that it is a convenient but limited theory and we should not expect results beyond what it was developed for. That is the reason why we and other groups propose a MPBE.

On the other hand, the linearization of the PB equation results in the well-known Debye–Hückel (DH) equation. The problem in this case is that, in the linearization process, many important features are lost. One point here is to show that DH is an oversimplified equation and there is no reason to use it except for the convenience of the analytical solution.

Fig. 2a shows a comparison between the half distance – distance from the surface where the electrostatic potential equals half of the surface potential – predicted by DFT, non-linear PBE and by the Debye–Hückel (DH) approximation, as a function of the surface potential $\phi_0$, for a monovalent electrolyte solution. The nondimensional distance is defined as $X = \kappa \cdot x$, where $\kappa$ is the inverse of the Debye screening length. The great agreement between DFT and PB calculations shows that PB equation works quite well in this condition. In these DFT simple electrolyte calculations we follow the method described by Li and Wu (2006) [33], considering ions of size $0.2 \text{nm}$. We notice from Fig. 2a that, even for monovalent ions, DH approximation fails to predict the half distance except for low surface potentials, not higher than $\phi_0 = 1.0$, which corresponds to 0.026 V. One can also see a non-smooth behavior for the DFT curve, what reveals a problem of numerical convergence for high surface potentials. This convergence problem is not experienced by the simpler PB approach. Fig. 2b shows that the agreement of DFT and PBE is not so good for divalent ions. In fact, the breakdown of the classical PB theory for 2:2 electrolytes has been known for a long time. In 1982, Torrie and Valleau [37] compared Gouy-Chapman (Poisson–Boltzmann) classical results with those obtained from

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Monte Carlo (MC) simulations for 2:1 and 2:2 aqueous electrolytes at concentrations up to 0.5 M. They show that when the counterions in the 2:1 system are singly charged, the success of the MPB theory is similar to those found previously for 1:1 electrolytes. However, for doubly charged counterions in both the 2:2 and 2:1 systems, the MC results show the PB theory to be totally inadequate. They concluded that for divalent counterions the PB theory greatly overestimates the surface potential even at quite low surface charges and electrolyte concentrations. Moreover, it has already been shown by our group some examples where even the modified version of PBE used here does not work well for divalent counterions [37]. This occurs because it does not include size and electrostatic correlation effects between the ions, and these effects become important when the counterions are divalent.

In Fig. 3, we compare the concentration profiles of counterions predicted by the same 3 theories as a function of the distance for a fixed surface potential \( \phi_0 = 2 \), and for (a) \( z = 1 \) and (b) \( z = 2 \). Note that, for monovalent ions, the profiles predicted by these 3 theories are very similar. However, for divalent ions, there is a considerable difference between the profile predicted by PB and DH theories again. Interestingly, in this case the DFT profile – supposed to be the more accurate here – agrees with DH profile at very low distances (probably due to the compensation of errors) and with PB results at higher distances.

3. Non-electrostatic potential of mean force from simulations

Horinek and Netz [20] obtained the ion-surface non-electrostatic potential of mean force for 3 different halide anions and for sodium at infinite dilution near a hydrophobic self-assembled monolayer (SAM), using MD simulations with polarizable force fields. Later the same group presented results that suggest that MD simulations with optimized non-polarizable force fields may work well [21]. All these simulations included explicit water molecules and the conclusion was that the heavier anions do adsorb, whereas the small cations like sodium are repelled from the surface. Examples of such NE-PMF curves are shown in Fig. 4. The potential which we here call NE-PMF includes unscreened image-charge effects, van der Waals interactions between ion, water, and substrate and ion hydration. The reader is referred to the cited paper [20] for simulation details. We point out that the NE-PMFs from these simulations not only include ion-surface van der Waals forces but also solvent-mediated forces, for which no reliable simple theory is known. The NE-PMFs obtained by molecular dynamics simulation were fitted using heuristic functions. For the SAM data [19–22] the function used is

\[
\frac{V(x)}{k_B T} = \frac{A}{(x-x')^2} - \frac{B}{(x-x')^6} + C_1(x-C_2) e^{-C_3(x-C_2)^2} + D_1 e^{-D_2(x-D_2)^2}.
\] (5)
The parameters of Eq. (5) for sodium, chloride, bromide, and iodide are given in Ref. [20].

With this theory, we take into account some effects neglected in the classical DLVO theory and even in the modified Poisson–Boltzmann equation with a general expression for the NES potential, used previously [3]. One point not discussed in the past is the fact that the NE-PMF includes an unscreened image potential. This means that in order to obtain high accuracy NE-PMF potentials in Monte Carlo simulations [24–26]. To illustrate how specific ion effects can be accounted for, we use as an example proteins as well. In excellent agreement with experiments salt solutions. However the qualitative results would be valid for two planar surfaces assuming the same group density as on the globular protein surface [3].

The purpose was to investigate if one can understand why the Hofmeister sequences can be totally different when the ions are counterions as compared to when they are co-ions. As a reasonable approximation for the ion–surface potential we used an ionic dispersion potential obtained from Lifshitz theory. The calculation was done for lysozyme coated plates (pl ≈ 11.16) for different 0.15 M salt solutions. However the qualitative results would be valid for other proteins as well. In excellent agreement with experiments on a variety of proteins (with lysozyme the experiments could not be done above pl) we see in Fig. 5 that we obtain a reverse Hofmeister sequence for pH < pl and a direct Hofmeister sequence for pH > pl, i.e., the pressure between the planar surfaces is known the potential energy between the surfaces can be obtained in a standard way by integration.

5. Applications of MPB and the reversal of the Hofmeister series

We recall that Tardieu and co-workers used SAXS [38] to demonstrate that the addition of salts not only screens the particle charges, but also induces an additional short range attractive potential between macromolecules that is a function of the anion type. Irrespective of the macromolecule that they studied, e.g., lysozyme, γ- and α-crystallins, they found that when the macromolecule was studied at a pH lower, or higher, than the isoelectric point, the double layer repulsion followed a reversed, or direct, Hofmeister sequence.

We considered a few years ago two planar surfaces coated with lysozyme proteins. The reversal of the Hofmeister effect observed for protein solutions was investigated theoretically by considering a case when the charge groups of the protein was smeared out on two planar surfaces assuming the same group density as on the globular protein surface [3].

The purpose was to investigate if one can understand why the Hofmeister sequences can be totally different when the ions are counterions as compared to when they are co-ions. As a reasonable approximation for the ion–surface potential we used an ionic dispersion potential obtained from Lifshitz theory. The calculation was done for lysozyme coated plates (pl ≈ 11.16) for different 0.15 M salt solutions. However the qualitative results would be valid for other proteins as well. In excellent agreement with experiments on a variety of proteins (with lysozyme the experiments could not be done above pl) we see in Fig. 5 that we obtain a reverse Hofmeister sequence for pH < pl and a direct Hofmeister sequence for pH > pl, i.e., the pressure between the protein coated plates was reversed in the same way as the experimental second virial coefficient of protein solutions when pH passes the pl. Close to the isoelectric point where electrostatic effects are very small one can even have attraction with very polarizable anions such as thiocyanate. This means that the reversal of the Hofmeister series can be explained by including NES potentials in the non-linear modified Poisson–Boltzmann equation [3,4].

We will show that the reversal of the Hofmeister sequence also comes out right when we include ion–specific NE-PMF for the interaction between ions and two hydrophobic surface [30]. When the
two surfaces are very close together no distinct reversal of the Hofmeister series is obtained. However, when the two surfaces are 1.0–1.5 nm apart we see in Figs. 6 and 7 clear specific ion effects. We observe a clear reversal of the Hofmeister series when the anions go from being co-ions to being counterions (i.e., depending on the surface charge). The result is consistent with previous work using NES potentials [2–4] and with simulations from Jungwirth and co-workers [39,40].

Interestingly, the reversal of the Hofmeister sequence does not occur exactly at the zero charge point, but it is a little dislocated to the positive charge region, where the anions are counterions. It would be very interesting if one could provide some experimental results to confirm these predictions. We also see that, as expected, the ion specificity between Cl\(^-\) and I\(^-\) is more pronounced when these anions are counterions. For a distance of 0.1 nm the pressure is repulsive for NaCl and attractive for NaI and the repulsion increases with the surface charge for NaCl, but the attraction increases with the charge for NaI. This behaviour for NaI is completely different from that predicted by the classical PB equation and it is dominated by the strong NE interactions for the iodide ions.

Other measurable properties that can be predicted with our approach are the osmotic second virial coefficient for globular protein systems [41], the mean force between colloidal particles [42], and the mean force between a colloidal particles interacting with a planar surface [43]. The Hofmeister sequences obtained for these properties present almost the same pattern as those reported here for the pressure between planar surfaces, with amazing inversions of the sequence depending on different variables of the system like pH, distance and surface charge. Experimental force measurements using atomic force microscope (AFM) can be made to confirm these force predictions.

6. Conclusions

We have in the past demonstrated that realistic calculations of ion-specific forces between hydrophobic surfaces and colloidal particles in general require a correct treatment of both the ionic potentials of mean force and inhomogeneous dielectric constants near interfaces. Modified Poisson–Boltzmann equation has been used to determine effects of salt identity on the potential of mean force between two proteins or colloidal particles. It has been observed using different methods that large anions appear to be attracted to hydrophobic surfaces while smaller, well solvated ions are repelled. Lund et al. [39,40] used a combination of explicit solvent and continuum model simulations to demonstrate that inclusion of ion-surface NE-PMF leads to ion-specific protein–protein interactions. Such potential of mean forces acting between colloidal particles obtained from modified Poisson–Boltzmann equation or from simulations can be used to calculate phase diagrams [44] and osmotic second virial coefficients for different salt solutions, at different pH and at different ionic strengths. While our model relies on a solvent averaged model the present results are qualitatively consistent with specific-salt effects observed experimentally, starting with the result from Hofmeister for aqueous proteins over 100 years ago. Our calculations emphasize the importance of NES potentials between ions and macroions. These specific forces [1–7,24–30], along with effects related to molecular solvation [15,19–22], may provide a key toward under-

Fig. 5. The double layer pressure in 0.15 M salt solutions between two plates carrying the same charge density and charge groups as lysozyme proteins 20 Å apart [2]. We are in all examples excluding the direct van der Waals pressure between the two plates across a water solution. The different curves correspond to: electrostatics (circles); NaCl (squares); NaI (triangles pointing up); and NaSCN (triangles pointing down) (the lines are only there to aid the eye).

Fig. 6. Pressure between two gold electrodes coated with self-assembled monolayers (SAM) a distance 1.0 nm apart in 0.1 M NaI (solid line) or in 0.1 M NaCl (dashed line).

Fig. 7. Pressure between two gold electrodes coated with self-assembled monolayers (SAM) a distance 1.5 nm apart in 0.1 M NaI (solid line) or in 0.1 M NaCl (dashed line).
standing salt-type effects as observed for colloidal and protein solutions.

Recently theories using ionic dispersion potentials have been improved by using ion-surface NE-PMF from simulations that include explicit water molecules. The method has been proved to be efficient and suitable for describing phenomena where the water structure close to the interface plays an essential role. Important thermodynamic properties related to protein aggregation, essential in biotechnology and pharmaceutical industries, can be obtained from the methods discussed here. The recent experimental work of Zhang and Cremer suggest that positively charged proteins show a strong Hofmeister series only at low salt concentrations and then revert to a direct Hofmeister series at high salt concentrations [45]. This effect may prove a suitable test for further theoretical progress.

We would like to recall that other modifications to the classical Poisson–Boltzmann equations have been designed in the literature to incorporate correlation effects (relevant in particular for systems with multivalent ions, high concentrations or high surface charge densities) [46] (see also Ref. [47]). In any case we believe that we are now getting closer to qualitative understanding of the Hofmeister effect.

List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$c_i$</td>
<td>local concentration (density) of ion $i$</td>
</tr>
<tr>
<td>$c_{i,0}$</td>
<td>bulk concentration of ion $i$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>elementary charge</td>
</tr>
<tr>
<td>$\rho$</td>
<td>pressure between two planar surfaces</td>
</tr>
<tr>
<td>$\phi$</td>
<td>electrostatic potential</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature of the system</td>
</tr>
<tr>
<td>$U_i$</td>
<td>non-electrostatic potential of mean force of ion $i$ between two plates</td>
</tr>
<tr>
<td>$V$</td>
<td>non-electrostatic potential of mean force</td>
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<tr>
<td>$\sigma$</td>
<td>Surface charge density</td>
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References


Glossary

DFT: density functional theory
PBE: Poisson–Boltzmann equation
MPBE: modified Poisson–Boltzmann equation
PMF: potential of mean force
NE-PMF: non-electrostatic potential of mean force
DILVO: the classical theory for colloidal interactions named after Derjaguin, Landau, Verwey and Overbeek
NES: non-electrostatic
SAM: self-assembled monolayer