Ion Specific Surface Forces between Membrane Surfaces

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Entities such as ion distributions and forces between lipid membranes depend on effects due to the intervening salt solution that have not been recognized previously. These specific ion or Hofmeister effects influence membrane fusion. A typical illustrative example is this: measurements of forces between double-chained cationic bilayers adsorbed onto molecularly smooth mica surfaces across different 0.6−2 mM salt solutions have revealed a large degree of ion specificity [Pashley et al. *J. Phys. Chem.* **1986**, *90*, 1637]. This has been interpreted in terms of very specific anion "binding" to the adsorbed bilayers, as it would too for micelles and other self-assembled systems. However, we show here that inclusion of nonelectrostatic (NES) or ionic dispersion potentials acting between ions and the two surfaces explains such "ion binding". The observed Hofmeister sequence for the calculated pressure without any direct ion binding is given correctly. This demonstrates the importance of a source of ion specificity that has been ignored. It is due to ionic physisorption caused by attractive NES ionic dispersion potentials. There appear to be some far reaching consequences for interpretations of membrane intermolecular interactions in salt solutions.

Introduction

To understand transport in the microbiological domain in the sub-pore, or interfacial, scale from the Ångstrom to micrometer dimensions,[1] one needs to understand the electrostatic properties of membranes[2−5] and the underlying double layer theory. We will give a few examples that demonstrate why forces between charged surfaces across salt solutions can be ion pair specific.

Hofmeister specific ion effects have been with us for a very long time. They have been observed in a large variety of systems.[6] A few examples include growth rates of Staphylococcus Aureus,[7] solubility of protein solutions,[6] surface tension of salt solutions,[8] behavior of microemulsions,[9] surfactant aggregation,[10] and hydrolytic activity of Aspergillus Niger lipase.[11] There are very many other examples in biochemistry, biology, and physical chemistry.[6] The origin of these specific ion effects has not been understood. Recently there has been some progress.[6,12] In a series of papers, Boström et al. have demonstrated that some of the specific ion effects fall into place if quantum mechanical NES forces acting between each ion and a macromolecule (e.g., a protein)[8,13−21] are included consistently. These many-body potentials due to the totality of electrodynamic many-body fluctuation forces are accessible, in principle, via Lifshitz theory.[12] They are not included in standard theories which, by and large, are limited to electrostatic effects alone. At and above biological concentrations (∼0.15M) electrostatic effects are strongly screened, and these ionic dispersion potentials dominate. In this regime, highly ion specific forces and "ion binding" emerge as dominant. Rydall and Macdonald, for example, used NMR to demonstrate that anions "bind" to lipid membranes following a so-called Hofmeister series. The ^{2}H NMR quadropole splitting near a charge neutral phosphotidylcholine membrane increased in the order $NO3^- \ll I^- < SCN^- < ClO4^-$.[22] McLaughlin et al.[4] showed that the surface potentials of bilayer membranes follow the same Hofmeister sequence. The conclusion is that large polarizable ions such as perchlorate and thiocyanate "adsorb" to phospholipid bilayers to a much larger degree than chloride. We have shown that this circumstance can be traced to, and is largely due to, these NES or ionic dispersion potentials.[16,17]

However, there has been no understanding of how ions can influence forces between bilayers and ion binding, with high specificity at salt concentrations below the typical biological regime (which we take as around 0.1 M). Ionic dispersion potentials can be expected to give rise to large Hofmeister effects (ion specificity) at and much above biological (>0.1 M) salt concentrations where electrostatic effects are screened. Surprisingly, there are also specific counterion effects even at much lower salt concentrations. This is so for both intermolecular forces and for ion distributions. In the illustrative system considered below, co-ion distributions, but not intermolecular forces, are also co-ion specific at 1−10 mM salt solutions.

At biological salt concentrations (around 0.1 M) and above we will show that there is large ion specificity in good agreement with our earlier results.[13]

We will also pay some attention to the important role of divalent cations in membrane adhesion.[3] In biological systems there are often millimolar concentrations of divalent cations (e.g., Ca^{2+} and/or Ba^{2+}). Deutsch et al.[23] investigated the influence of Mg^{2+} (2−15 mM) and Ba^{2+} (2−10mM) on potassium ion channels. While 10 mM barium ions cause almost complete blockage of the currents, one had to add more than 15 mM of magnesium ions to achieve the same effect. While some of these effects may be due to unidentified "chemical" binding of these ions, there is a clear case that similar effects occur by physisorption of these ions caused by nonelectrostatic forces with a vital role for these ionic dispersion potentials. There are

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clear and direct links between the way ions apparently "bind" to surfaces, and experimentally observed phenomena such as surface potentials, ion currents through membranes, surface charge of proteins, pH, and surface forces.

Improving understanding at a more fundamental level is vital for a better understanding of a large number of industrially and medically important phenomena.

The outline of the paper is as follows. We rehearse the ion specific double layer theory in Section II and present numerical results in Section III for forces between charged bilayers. Finally, in Section IV we wrap up our story with a few concluding remarks.

II. Theoretical Modeling of Ion Specific Double Layer Forces

In the standard DLVO theory of particle interactions in colloid science, the forces operating repulsive electrostatic double layer, and attractive quantum mechanical, and van der Waals−Lifshitz forces are treated separately. This ansatz is incorrect and results in the ion specific forces being ignored. (They are included but contribute insignificantly because the theory is linear). In a correct theory, they must be treated at the same level as electrostatic forces acting on ions.[12] This has been demonstrated in a number of previous papers.[8,13−21] Following this earlier work, we therefore, use an ion specific Poisson−Boltzmann equation with a constant charge boundary condition. This allows the determination of the ion distributions between two charged membrane surfaces a distance L apart. The appropriate equations are as follows:[13]

$$\frac{d^2\phi}{dx^2} = -\frac{ec_0}{\epsilon_w\epsilon_0}(\exp[-(e\phi + U_+(x))/kT] - \exp[(e\phi - U_-(x))/kT]) \quad (1)$$

$$\left.\frac{d\phi}{dx}\right|_{x=L/2} = 0, \left.\frac{d\phi}{dx}\right|_{\text{surface}} = \frac{\sigma}{\epsilon_w\epsilon_0} \quad (2)$$

Here ϵ_w is the dielectric constant of water, ϕ is the self-consistent electric potential, and σ is the surface charge (here taken to be constant). $U_\pm$ is the ionic dispersion potential acting between each ion and the two surfaces,[13]

$$U_\pm = B_\pm\left(\frac{1}{x^3} + \frac{1}{(L-x)^3}\right) \quad (3)$$

Here the dispersion coefficient ($B_\pm$) for different combinations of ion and membrane can be calculated from the frequency-dependent ionic excess polarizability (this is the difference in polarizability compared to the surrounding water), and the dielectric functions of water and of the surface. In a complete theory the B coefficients will include contributions from not just the visible to UV frequency region van der Waals dispersion forces. They also include (many body) dipole−induced dipole, and permanent dipole−dipole forces.

We chose, in our first example, the number of charges per unit area of a positively charged model surface to be 1.7×10^{18} m^{-2} for the double chained cationic surfactant adsorbed on mica. This is the experimental system considered by Pashley et al.[24] For sodium, chloride, bromide, and thiocyanate, the following values for the ionic dispersion coefficient have been used: -0.45×10^{-50}Jm^3; -3.57×10^{-50}Jm^3; -10×10^{-50}Jm^3; and -15×10^{-50}Jm^3.[17] The magnitudes of these values are consistent with refractive index data and with other ion specific experiments, such as surface tension of electrolytes,[8] and surface potentials of membranes in salt solutions.[4,16,17,25] As we have shown in a series of papers, these ionic dispersion potentials are also important for ion binding to micelles,[14] microemulsions,[9,10,12,26−28] and polyelectrolytes,[15] as well as for ion transport across membranes.[21]

In our second example we consider a system with 25% acidic lipid membranes and 75% charge neutral lipids (e.g., a 3:1 PC:PG membrane[2]). Each lipid in our example has an estimated area of 68 Å^2.[2] To illustrate the general principles, we use, as an example, the same ionic dispersion coefficients as above for sodium and chloride. By comparison we estimate that the ionic dispersion potential acting on the cesium ion to be at least -5×10^{-50}Jm^3 (the static polarizability is roughly 20 times larger for Cs^+ than for Na^+). We will also consider the effect of 20 mM Ca^{2+}, with an estimated ionic dispersion coefficient -1.3×10^{-50}Jm^3,[29] on the short-range interaction and surface potentials between two lipid bilayers at physiological NaCl concentrations. This enables us to hazard a reasonable estimate of the influence of addition of calcium on cell adhesion.

The ion distributions obtained are used to calculate the pressure between two parallel charged membranes. The double layer pressure between two planar plates a distance L apart can then be written as[13,30]

$$P = kT\sum_i[c_i(L/2) - c_{o,i}] - 2\sum_i\int_{x_o}^{L/2} c_i\frac{dU_i}{dL}dx - \frac{H}{6\pi L^3} \quad (4)$$

where k, T, $c_{0,i}$, $c_i(L/2)$, $x_0 = 2$ Å, and U_i are Boltzmann's constant, temperature, ion density in bulk solution, ion density at the mid plane between the two surfaces, ion size (which is the closest distance the ions can come to the interface), and the ionic dispersion potential acting between each ion and the two interacting surfaces. The last term is the direct van der Waals interaction between the two planar surfaces across water. H is the Hamaker constant, which is here estimated to be 10^{-20} J.[24] In general, of course, the Hamaker constant is different for different surfaces. It should be quite different for lipid−water, 10 times lower, and modeled as a triple film. Treating the surface as a triple film and taking into account retardation effects can change the interaction by a factor of 10 or more. The use of a Hamaker constant, or non retarded Lifshitz theory, for the direct van der Waals interaction is equivalent to the statement that an intervening liquid between the surfaces has uniform density and molecular orientation profile; i.e., we ignore perturbations of the profile, hydration forces, caused by interactions. In any real cell membrane interaction, that seems reasonable since hundreds of atmospheres of pressure would then be involved.

III. Numerical Results: Double Layer Forces

Pashley et al.[24] demonstrated that there can be large ion specificity for the pressure between mica surfaces coated with bilayers of double-chained quaternary ammonium acetate and bromide surfactants. The force could be up to 10 times smaller with more polarizable bromide ions than in a solution with acetate. We stress again that the same Hofmeister phenomena holds for ion binding to micelles, cationic or anionic, for microemulsions and for polyelectrolytes. For such systems, the phenomenological ion binding model, used, for example, for interpretation of NMR measurements of binding is exactly equivalent to an electrostatics-only model. It "works", loosely only in the limit of strong counterion binding due to electrostatics. For other counterions and co-ions, e.g., Ac vs Cl, the binding makes no sense.[10,26−28] For such systems, one needs to include ionic dispersion and other NES forces in the ion binding theory

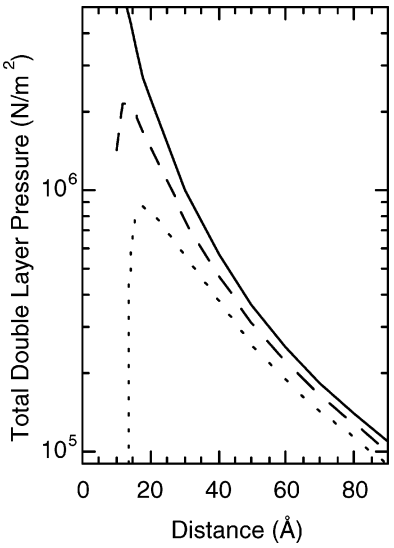

Figure 1. The calculated total double layer force between a pair of bilayers as described in the text across a 1 mM salt solution of NaCl (solid line), NaBr (dashed line), or NaSCN (dotted line).

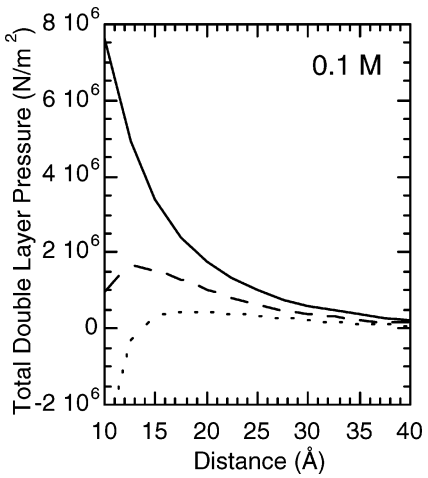

Figure 2. The calculated total double layer force between a pair of bilayers as described in the text across a 0.1 M solution of NaCl (solid line), NaBr (dashed line), or NaSCN (dotted line).

to effect a reconciliation between ion binding required to explain force measurements[13,24] and that for single interfaces such as lipids or micelles.[14,15,26] The pressure shown in Figures 1 and 2 is for two model surfaces corresponding to double chained cationic surfactant adsorbed on mica interacting across different 1 mM and 100 mM salt solutions. It includes the total DLVO pressure (that is, eq 4 using a Hamaker constant of 10^{-20} J[24]). Notice that the standard DLVO theory would give results that not only miss specific ion effects but are also much different in magnitude. One should note that straightforward linearization of the ion distribution in the nonlinear double layer potential gives back the ordinary result from Lifshitz theory.[30] However, to get correct results and to understand ion specificity, one needs the full nonlinear result. As can be seen in Figures 1−2 the pressure between two closely spaced charged bilayers in the presence of either low (1 mM) or high (100 mM) salt can be up to 5−10 times smaller in an electrolyte with highly polarizable anions than in one with no or low polarizability anions. It is important to note that the short-range interaction is influenced more strongly by the ionic species than it is by concentration. There are clear Hofmeister effects observed at these short separation distances. But even more noticeable is the fact that there is a noticeable shift downward in the long-

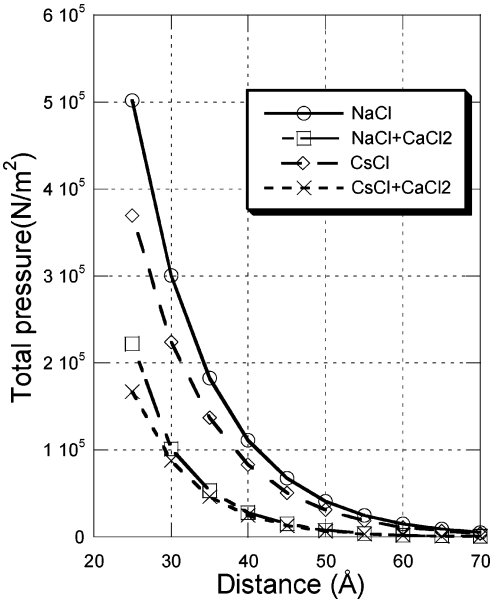

Figure 3. Total pressure (excluding the direct van der Waals interaction between two lipid membranes) as a function of the distance between two phospholipid membrane surfaces (the membranes correspond to 3:1 phosphatidylcholine:phosphoglycerol [1]). The curves correspond to 0.1 M monovalent salt (NaCl or CsCl) with or without added divalent salt (20 mM $CaCl_2$). See the text for details.

range asymptotic pressure for the low salt system (1 mM) with increasing ionic dispersion potentials. While the effects are much more important at biological salt concentrations there are ion specific effects also in the 1−10 millimolar range. This is especially true for ion distributions near the surface but also for intermolecular forces, at least when the ions are counterions. The pressure is more reduced in the salt solution with the more polarizable anions than in the solution with less polarizable anions. This trend is in excellent agreement with the results obtained by Pashley et al.[24] There is a correlation between the resulting pressure and the ionic dispersion potentials, and hence, with the excess polarizabilities. Pashley et al. suggested ion binding of Br^- ions to explain the large deviations between forces measured in bromide compared to in acetate. We are not saying that this is not so. But before considering any direct (chemical) binding one must first do the zeroth order theory correctly without such postulated binding.[6,12] Chemical binding, in contrast to physisorption, is obviously more likely to happen when there is an enhanced surface concentration. Ion binding occurs not only through the influence from electrostatic potentials but also from NES potentials. These new potentials include interaction ionic dispersion potentials. But they also include, for example. solvation energy changes in regions with a varying water density or with changes in hydrated ion size.[20,21] We have recently shown an important role behind the ion specific surface tension of electrolytes for ionic dispersion potentials and the change in the solvation energy (including changes in electrostatic Born self-energy and electrodynamic fluctuation self-energy) as ions move into the air−water interfacial region with its anisotropic water profile with varying water density.

Most work ignores the contribution of co-ions which contribute to forces only via the Debye length. This is because, in a purely electrostatic theory, co-ions are expected to be pushed away from the surface (or pore) by electrostatic forces and, hence, play no role. However with the additional NES forces acting on ions, co-ion adsorption can influence membrane potentials and ion transport through pores. Co-ions can also have

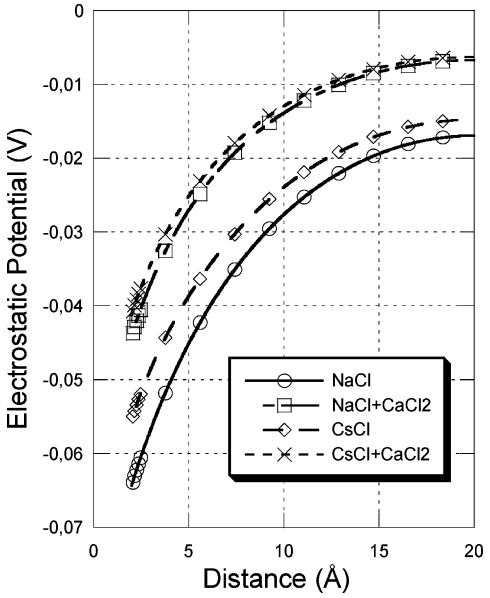

Figure 4. Electrostatic potential profile for the case where the phospholipid membrane surfaces were separated to a distance of 40 Å. The curves correspond to 0.1 M monovalent salt (NaCl or CsCl) with or without added divalent salt (20 mM $CaCl_2$).

an important role in that they can modulate the pH of a solution, pH near a membrane surface,[11,16,19] and membrane potentials.[16,17]

Forces between cells always take place in salt solutions and one should remember that the ionic compositions in cellular fluid and the surrounding compartment often are very different. An example is human red blood cells with its high concentrations of potassium, magnesium, phosphate, and proteins in the intracellular fluid in contrast to the dominating sodium and chloride ions of the surrounding blood plasma. There exists experimental evidence that an initial first step in cell membrane fusion often involves an increase of divalent cations (see references in ref 3). Marcelja[3] showed that the addition of low concentrations of divalent cations strongly reduce the electrostatic double layer repulsion between acidic phospholipid membranes. Since this reduction of the pressure is directly relevant for the cell interactions that are the underlying theme of this paper, we will briefly describe how addition of 20 mM divalent calcium can influence the force between two model membranes (corresponding to 3:1 PC:PG membranes) across 0.1 M NaCl or 0.1 M CsCl. The results presented in Figure 3 demonstrate that the pressure decreases strongly when 0.1 M sodium chloride is replaced with 0.1 M cesium chloride. The more polarizable cesium ions that are attracted toward the membrane surface by nonelectrostatic forces are much more effective at screening the surface charge than sodium ions. It is also more efficient in reducing the electrostatic potential (see Figure 4). The effect on the membrane pressures (Figure 3) and electrostatic potentials (Figure 4) of adding 20 mM divalent salt are in this model system larger, but follow the same trends, as this ion specificity. At the high concentration of the divalent cations used in this example Ca^{2+} have a dominating role on the electrostatic potential. This leads in the present model system to less cation specificity in the presence of divalent cations. This is seen both in the pressure curves (Figure 3) and on the electrostatic potential profiles (Figure 4) and ion distributions (Figure 5) near the membrane. The screening effect of adding calcium ions leads to a reduced concentration of monovalent counterions near the surface. The interplay between electrostatic repulsion and attractive nonelectrostatic forces leads to a minima in the co-ion distribution (Figure 5c). Near the surface, ionic dispersion potential leads to a small accumulation of co-ions, more so as the surface become more electrostatically screened either by more polarizable monovalent cations (Cs^+) or by the presence of divalent cations. It is well-known that potential determining divalent cations have an important role in membrane biology. There is an important role for chemical binding of calcium ions to, for example, membrane bound proteins. But

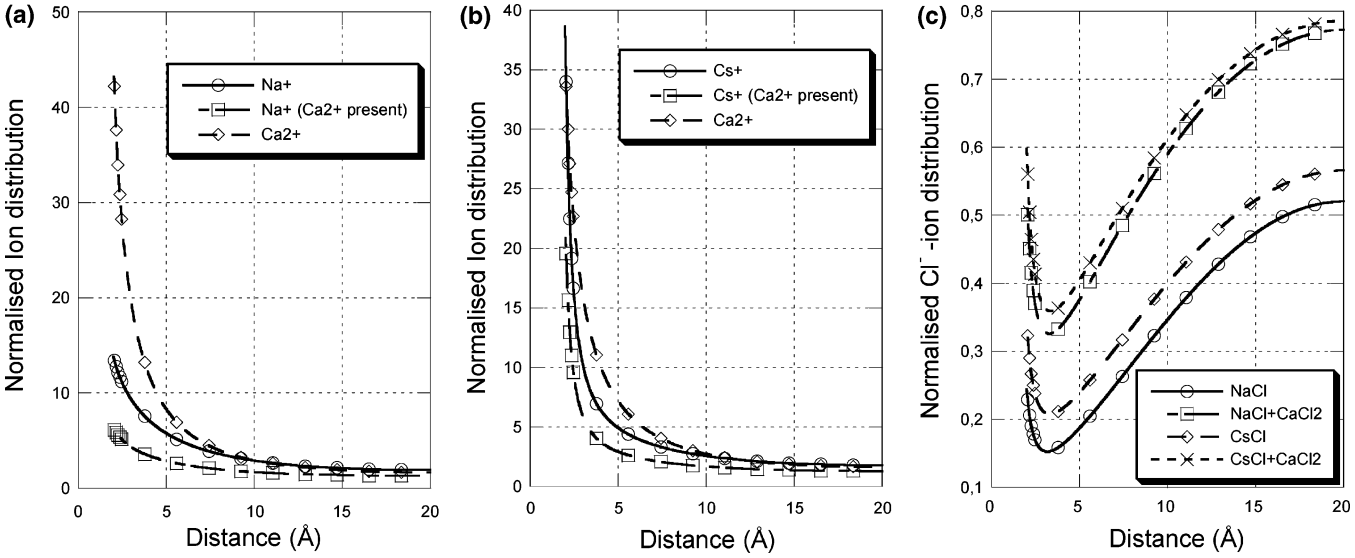

Figure 5. (a) Ion distribution profiles near one of the phospholipid membrane surfaces (with membrane−membrane distance 40 Å) for the case with sodium as monovalent cation. Each ion distribution has been normalized with the bulk concentration of that ionic species. The curves correspond to 0.1 M monovalent salt (NaCl) with (squares) or without (circles) added divalent salt (20 mM $CaCl_2$). (b) Ion distribution profiles near one of the phospholipid membrane surfaces (with membrane−membrane distance 40 Å) for the case with cesium as monovalent cation. Each ion distribution has been normalized with the bulk concentration of that ionic species. The curves correspond to 0.1 M monovalent salt (CsCl) with (squares) or without (circles) added divalent salt (20 mM $CaCl_2$). (c) Chloride ion distribution profiles normalized with the bulk concentration of Cl^- for different salt solutions near one of the phospholipid membrane surfaces (with membrane−membrane distance 40 Å. The curves correspond to 0.1 M monovalent salt (NaCl or CsCl) with (squares) or without (circles) added divalent salt (20 mM $CaCl_2$). (Note that the bulk chloride ion concentration increases from 0.1 to 0.14 M when the divalent salt is added).

our results show that one has also to take into account the NES potentials that act on the ions in solution to obtain correct results.

IV. Conclusions

The pioneering results presented by McLaughlin and co-workers demonstrated that the simplest form of double layer theory is capable of accounting for screening effects due to addition of monovalent and divalent ions on surface potentials of charged phospholipid bilayers. However, the standard text book results, due to Deryaguin, Landau, Verwey, and Overbeek, could never explain the frequently observed ion specificity. The permeability of human red cells can, for example, be reversed when chloride ions is exchanged with salicylate ions. This and the many other observed examples, some discussed here, could not be explained by electrostatic theories alone. While there are, of course, many cases where direct chemical binding of ions are important, one should always first consider the background ion distributions that are ion specific due to nonelectrostatic forces. We have shown that many such ion-specific experiments can be understood when ionic dispersion potentials and solvation energy changes (NES forces) are taken into account.

We would finally like to make the connection between the simple model system considered here with simple nonpermeable lipid membranes and real cell membranes. We can regard the outer cell periphery of many cells as a layer of proteins, lipids, and saccharide in water. This cell coating, or "fuzzy layer", is a region in which the counterions can accumulate. This leads to deviations between the real cell charge and the charge obtained from electrophoretic experiments. What has not yet been discussed in the literature is how the presence of a fuzzy coating influences the force between two cell membranes or ion permeation of membranes. What is clear is that the presence of groups that can bind or give away hydronium ions in this region leads to a different charge of these fuzzy coatings depending on the choice of background salt. Here, we have made some first steps on the way toward understanding the role of salt ions in cell adhesion but it is only a first step. The essential point we have to offer is that in order to understand cell adhesion and a large variety of phenomena that takes place in salt solutions, one needs to include in the theoretical modeling not only electrostatic forces but also non electrostatic forces, such as the ionic dispersion potential and solvation energy changes. This is not a matter of opinion but one of fact, as the previous theories are simply incorrect.[6,8,12−21] More specialized and focused modeling dealing with, for example, processes in microbial transport in natural subsurfaces[1] must now be extended to take into account the role of these non electrostatic forces. Transport clearly involves co-ions as well as counterions. That has major implications for ion transport and the interpretation of membrane potentials that have not been recognized.

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