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Enhancement of charge inversion by multivalent interfacial groups

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In this Brief Report, we perform molecular-dynamics simulations of an interface containing charged functional groups of different valences in contact with 2:1 ionic solution. We take into account both the finite sizes of the ions in solution and the functional groups but we neglect the structural details of the solvent (primitive model). We show that the interaction between a charged interface (of given surface charge density) and electrolyte depends strongly on the individual charges of the interfacial groups originating the surface charge. In particular, we show that charge inversion (i.e., interfacial charges attracting counterions in excess of their own nominal charge) is enhanced by the presence of multivalent interfacial groups (such as certain phospholipids). Overall, our results reveal that in primitive models of the ion-interface interaction not only the ionic size and valence are important but also the size and valence of the interfacial charged groups have a significant impact.

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The interaction of charged interfaces with ions immersed in an aqueous solution is a subject of great importance in many areas of science such as colloidal science, soft matter physics, and biophysics [1]. The electrostatic stabilization of micro and nanoparticles [2] or the binding of polyelectrolytes such as DNA at membranes are clear examples [3].

The case in which the counterions are multivalent is attracting a great experimental and theoretical interest due to their ability to induce complex and rich unique phenomena [4]. A classical example is the inversion of the electrostatic force between equally charged interfaces: charged surfaces which repel in presence of monovalent electrolyte develop strong electrostatic attractive forces in presence of multivalent counterions [5–7]. Another example is the inversion of electrokinetic quantities such as electrophoretic mobility or streaming current [4,8]: in presence of large enough concentrations of multivalent ions, the mobility or the current is opposite to what is observed with a monovalent electrolyte. This puzzling effect, known as charge inversion (or equivalently charge reversal or overcharging) [8], has been observed in many different systems: phospholipid liposomes [9], DNA [10], colloids [11–13], and silica nanochannels [14] to mention only a few examples.

The driving force responsible for charge inversion is still a subject of debate [8]. In a few particular cases, specific chemical forces such as the hydrophobic effect have been unequivocally identified as responsible for charge inversion [15] but in most cases the driving force remains unclear. It is interesting to recall that in many recent experiments, charge inversion has been reported to be largely independent of the chemical details of the system but it has been shown to strongly correlate with quantities such as the density of the charged interfacial groups and the valence of counterions (see, for example, [7,10,13,14] for experimental examples). From the theoretical side, modern statistical-mechanical theories of electrolyte solutions show that multivalent counterions develop strong correlations near surfaces with high charge density, which may be responsible for charge inversion [16–19]. Several comparisons between predictions of theories including ion correlations and experimental results have been reported recently by different groups [12,13], supporting the view that ion correlations are a major driving force for charge inversion in colloids. The way the problem is solved differs between the different groups although they share the same basic assumptions: these descriptions are typically primitive models in which the ionic solution is modeled as a system of point charges or charged hard spheres in a dielectric medium (all molecular details of the solvent are neglected). In this way, it is possible to go beyond the mean-field approximation employed in the classical theory.

It is important to emphasize that these studies typically neglect the details of the interface, which is represented by an uniformly charged plane. However, a recent theoretical proposal [20] emphasizes the possibility of electrostatic binding between multivalent counterions and the specific group carrying the interfacial charge. In particular, the theory predicts that the explicit effect of the interfacial groups will be particularly clear for multivalent interfacial groups in contact with an electrolyte containing multivalent counterions. This situation may seem artificial, but let us recall that it is not unusual in the case of phospholipids present in biological membranes. A particularly interesting case is the dimiristoylphosphatidic acid (DMPA) phospholipid, which plays a relevant role in signaling processes in biological membranes. This phospholipid has a switchable charge (0, $-1e$, or $-2e$) in biological conditions, which is employed to bind divalent cations such as Ca^{2+} or Mg^{2+} to membranes with a particularly high affinity [21]. Even the case of interfaces containing interfacial groups with charges as large as $q=-4e$ is possible. This is the case, for example, of the phosphatidylinositol 4,5-bisphosphate lipid (also known as PIP2), a biologically active membrane lipid which has a charge between $-2e$ and $-4e$ depending on the environmental conditions [22]. Molecular-dynamics simulations of these complex systems [20–22] suggest that the properties of the interfacial groups play an important role in the process of cation bind-

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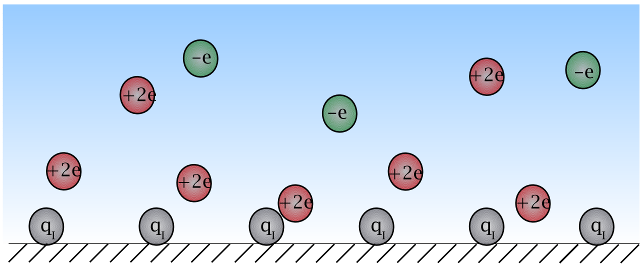

FIG. 1. (Color online) Cartoon of the model considered in our simulations. The charged interfacial groups are located on top of an impenetrable wall at the *XY* plane. The charged surface is in contact with a 2:1 electrolyte located in the region $z>0$.

ing (rather than the averaged surface charge density). However, due to the complexity of the models with atomic resolution considered in these simulations, it is very difficult to disentangle this effect from other, more complex processes such as hydrogen bonding, solvent effects.

Here, we perform molecular-dynamics simulations of a simple model of an interface with explicit interfacial charged groups interacting with 2:1 electrolyte. We show that, for surfaces with the same charge density, the presence of multivalent charged groups has a deep impact on the interaction between electrolyte and the interface.

Let us briefly summarize the model and simulation procedures (extensive details can be found in [24]). The simulation box contains a symmetric system consisting of two equal interfaces (modeled as described above) located at $z=0$ and $z=L_z$. Each interface is modeled as shown schematically in Fig. 1. The charged interface is made of fixed equally spaced spheres with charge q_I and centers at $z=0$ over a perfectly reflecting impenetrable wall. The interfaces are in contact with a 2:1 electrolyte solution (counterions of charge $+2e$ and coions of charge $-e$) in a dielectric medium with $\epsilon_r=78$ (primitive model). The values of L_z are always selected to be large enough so that any interaction between the two interfaces is negligible and the central region of the simulation box (of at least several nm) can be considered as bulk electrolyte at concentration c_B. All the results presented here will be symmetrized in the z direction since the two copies of the interface are equivalent, simply representing two states of the same system. The numbers of coions and counterions inside the simulation box were selected according to the algorithm described in [24] in order to obtain the desired concentration c_B in the central region (bulk electrolyte). Also, the overall system has to be neutral. Typical numbers of counterions employed in our simulations are between 1200 and 3200; the sizes of the simulation box in the parallel and perpendicular directions depend on each simulation, but are around 300 and 150 Å, respectively (see [24]). Periodic boundary conditions were applied along the directions parallel to the interfaces (x and y directions) but not in the z direction. The electrostatic interactions were computed using the slab version of the Ewald summation technique included in LAMMPS [23]. Basically, the program treats the system as if it were periodic in z, but inserting empty volume between slabs and removing dipole interslab interactions so that slab-slab interactions are effectively turned off [25].

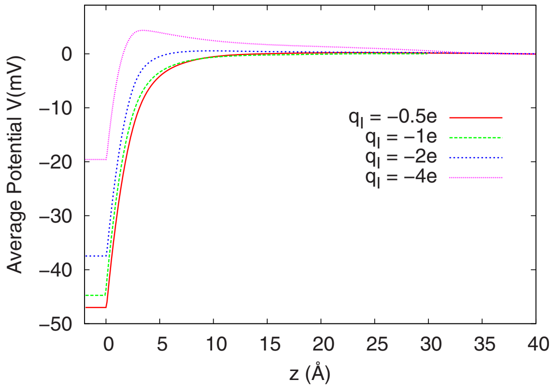

FIG. 2. (Color online) Average electrostatic potential for simulations with $\sigma_0=-0.9e/\text{nm}^2$, $c_B=0.1M$ and different values of the charge of the interfacial groups ($q_I=-0.5e,-1e,-2e,-4e$).

In order to account for the finite size of ions and interfacial groups we need to introduce a repulsive interparticle potential. The specific form of the interaction potential is not essential provided that it is a strongly repulsive potential with an interaction range adjusted to the size of the ions. In this work, we will consider that each pair of particles i,j (being i an ion and j another ion or a fixed interfacial charge) separated a distance r_{ij} interacts with a Lennard-Jones interaction with a cutoff at $r_{ij}=\sigma_{LJ}$. In this way, particles interact nearly as hard spheres of size σ_{LJ}. In all our simulations we set the same values $\sigma_{LJ}=3$ Å and $\epsilon=1$ kJ/mole.

Molecular-dynamics simulations in the canonical ensemble (Nose-Hoover thermostat relaxation constant of 0.5 ps) at $T=300$ K were carried out with the LAMMPS (21May2008 version) [23] package running in the CESVIMA supercomputing center. The equilibration time employed in our simulations and number of time steps employed in the production runs depend on the different cases under study due to the very different sizes of the simulation box and number of particles considered, as described in detail in [24]. A movie, illustrating the simulations reported here, is also available as EPAPS material [24].

For the sake of simplicity, in this work we will consider always the same value for the bare charge density of the interface. We take a value of $\sigma_0=-0.9e/\text{nm}^2$, typical of highly charged interface such as certain phospholipid monolayers or even some solid surfaces such as silica. The effect of explicit interfacial groups is analyzed by considering interfacial groups of charge $q_I=-0.5e,-1e,-2e,-4e$. In order to obtain the same charge density, the separation between interfacial groups is different in each case, being 0.74, 1.05, 1.5, and 2.1 nm, respectively.

Let us first consider a situation in which we have the same bulk electrolyte concentration and bare surface charge but the interfacial charge is built up from groups with different values of q_I. In Fig. 2, we show the average electrostatic potential as a function of the coordinate z perpendicular to the interface for simulations with $c_B=0.1M$, $\sigma_0=-0.9e/\text{nm}^2$ and different values of q_I. The effect of the discreteness of the multivalent interfacial groups can be clearly seen in this figure. The magnitude of the electrostatic potential obtained in the case $q_I=-2e$ is significantly smaller

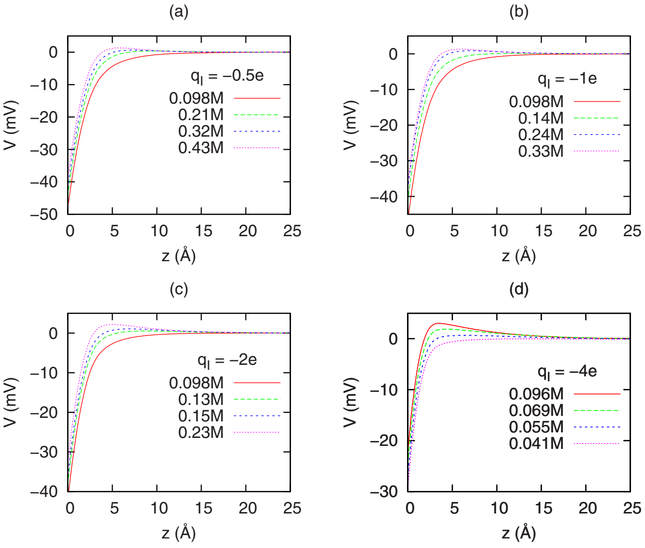

FIG. 3. (Color online) Dependence of the average potential profile on the bulk concentration for $\sigma=-0.9e/\text{nm}^2$ and different charges of interfacial groups, $q_I=-0.5e$, $q_I=-1e$ $q_I=-2e$, and $q_I=-4e$.

than that obtained for $q_I=-1e$. The effect is also more impressive in the case $q_I=-4e$. In this case, the potential experiences an inversion of sign and a nonmonotonic behavior. It is negative at $z=0$ but changes sign at $z\sim 1$ Å and has a maximum at around 3 Å (the distance of closest approach between counterions and interfacial groups). For larger z is always positive. We can say that this system is in a charge inversion situation since an interface with a (highly) negative bare charge induces a positive electrostatic potential outside the interface. On the other hand, the results for the cases $q_I=-0.5e$ and $-1e$ are not significantly different. This suggests a small effect of explicit interfacial groups in the case of monovalent interfacial groups, in agreement with previous Monte Carlo studies [26].

This result suggests that the onset of charge inversion could be different for surfaces with the same value of σ_0 but different values of q_I. This is indeed the case as is demonstrated in Fig. 3. In this figure, we show how the profiles of the electrostatic potential depend with the bulk electrolyte concentration for different values of q_I. In all cases, we observe charge inversion but the concentrations at which this effect is observed and its magnitude depend on q_I.

The analysis of the profiles of the electrostatic potential suggests a method to determine from simulations the electrolyte concentration at which charge inversion appears. This procedure is as follows. For each value of q_I we have performed simulations starting with a system in conditions of charge inversion (for each q_I, the case with higher c_B concentration shown in Fig. 3). Then, we have performed simulations reducing c_B until the electrostatic potential is again monotonic. The charge inversion concentration is taken as the average between the lowest concentration at which the potential is not monotonic and the highest concentration at which is monotonic. The error in this determination can be estimated by the difference between these two concentrations. The results are shown in Fig. 4. As q_I increases, the charge inversion concentration decreases. This figure demonstrates that the onset of charge inversion is sensitive to the explicit modeling of the interfacial groups. For example, the electrolyte concentration required to neutralize the charge of an interface with $q_I=-4e$ is half the amount required for an interface with $q_I=-1e$. The strong dependence with q_I observed in Fig. 4 suggest that correlations between interfacial groups and counterions are a major driving force contributing to charge inversion. Ion-ion electrostatic correlations are very important when the electrostatic coupling constant [defined as $\Gamma=(e^3q_C^3\sigma_0/\pi)^{1/2}/4k_BT\epsilon_r\epsilon_0$ [7]] is $\Gamma \gg 1$. In spite of the high charge density of the surface, the fact that counterions are divalent gives $\Gamma \simeq 3.4$ so we are not in a high electrostatic coupling regime in our case.

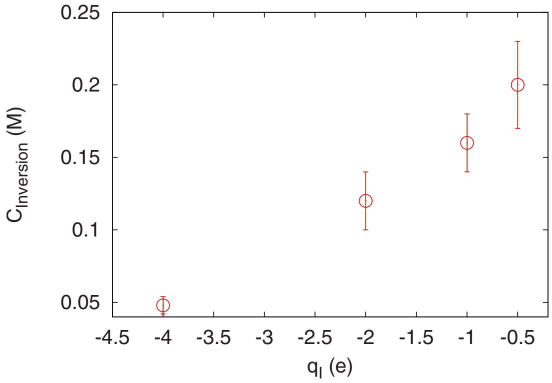

FIG. 4. (Color online) Electrolyte concentration of charge inversion as a function of the different charges of interfacial groups, q_I, for $\sigma=-0.9e/\text{nm}^2$.

In conclusion, our results show that the interaction between multivalent ions and interfaces depends on the individual charges of the interfacial groups making up the charged interface. This effect is particularly clear in the case of multivalent interfacial groups. Multivalent charged groups can be found in soft matter and biophysical systems due to, for example, multivalent charged phospholipids. Up to now, experimental results in these systems (obtained from, e.g., electrokinetic or optical techniques) are routinely interpreted using theories which consider only the surface charge density of the system, regardless of its origin. We hope our results will stimulate the inclusion of the role of the structure of the interface in the interpretation of experimental results.

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