Overcharging by macroions: above all, an entropy effect.

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(October 27, 2018)

Model macroion solutions next to a charged wall show interface true overcharging, charge reversal and inversion, and layering. Macroion layering is present, even if the wall or the macroparticle are uncharged or if the wall and macroions are like-charged. An effective long-range attractive force between the adsorbed macroions is implied. The results are obtained through an integral equation theory and a new extended Poisson-Boltzmann theory, and are in accordance with experiments on confined macroions and polymer layering.

PACS: 68.08.-p, 61.20.Qg, 82.70.Dd

The restricted primitive model (RPM) for an electrolyte solution includes the two main forces in this system: the long range Coulombic and the short-range repulsive forces. In RPM the ions are taken to be hard spheres of diameter $a$ and charge $e\varepsilon_i$ ($\varepsilon$ is the protonic charge and $e_i$ is the ionic valence), embedded in a dielectric medium of dielectric constant $\varepsilon$. This model has been shown to be in agreement with Monte Carlo (MC) simulations and experimental results of bulk and confined electrolyte systems.

When a divalent electrolyte, at high concentration, is next to a charged wall, the charge of the adsorbed counterions to the wall overcome that on the wall. This effect produces a second layer of ions, where the coions outnumber the counterions. These effects are known as charge reversal (CR), and charge inversion (CI), respectively. Although these phenomena have been reported, both theoretically and by computer simulations, since 1980, important implications to protein electrophoresis and medicine were later recognized. On the other hand, the long-range attraction between confined like-charged macroparticles or the adsorption of macroions onto oppositely charged or like-charged surfaces have received much attention. The understanding of these phenomena have been recognized as relevant for the colloid science and technology, the oil industry, and molecular self-assembly (e.g., DNA encapsulation) and nanostructured films (e.g., polyelectrolyte layering).

Here, we extend the hypernetted chain/mean spherical approximation (HNC/MSA) integral equation to be applied to model macroion solutions next to a charged wall. The HNC/MSA has been proved to be in good agreement with Monte Carlo data for the electrical double layer (EDL) of closely related models. Because of the larger macroion’s size, this theory is expected to be even more reliable than for the simple electrolyte case. The macroparticle is taken as a charged, hard sphere of diameter $a_M$, concentration $\rho_M$ and valence $z_M$, whereas the little ions are modeled by the RPM. The wall has uniform surface charge density $\sigma_0$. The wall dielectric constant is chosen to be equal to that of the solvent, to avoid image potentials. The ionic distribution, as a function of the distance $x$ from the surface of the wall, gives the structure of the equilibrium EDL, and is expressed in terms of the concentration profiles, $\rho_{wi}(x) = \rho_i g_{wi}(x)$. $\rho_i$ is the bulk concentration, of the ionic species $i$, and $g_{wi}(x)$ is the species $i$ reduced concentration profile (RCP). The HNC/MSA integral equations for the RCPs are given by $\iiint g_{wi}(x) \equiv \exp[-\beta W_i(x)] = \exp[-\beta (e\varepsilon_i \psi_i(x) + J_i(x))]$. $W_i(x)$ is the potential of mean force, i.e., the effective total wall- ion interaction potential. $W_i(x)$ has two contributions: the electrostatic potential part, given by the mean electrostatic potential,$\psi(x)$, plus the short range repulsive potential part, due to the ionic size, given by $J_i(x)$. Both functions are functionals of $\rho_{wi}(x)$. $\beta=1/(K_BT)$, where $K_B$ is the Boltzmann constant and $T$ is the absolute temperature. The ion-ion and the macro-ion ion direct interaction potentials are given by a hard-sphere potential plus the Coulombic potential. In the limiting case of $a=0$ HNC/MSA reduces to the integral equation form of a new extended inhomogeneous Poisson-Boltzmann (PB) theory for point ions plus macroions, next to a charged wall. Since macroions are considered at finite concentration, this approach is an improvement to the classical PB equation for confined macroions, at infinite dilution, where only two macroions are considered: i.e., in our theory macroion-macroion correlations are included. For $a=0$ and $\rho_M=0$, we recover the integral equation version of the classical Gouy-Chapman (GC) theory for point-ions next to a charged wall. A point-ion model (PIM) for an electrolyte solution is like the RPM, but $a=0$.

We have solved HNC/MSA for several values of $Z_M$, $a_M$, $\rho_M$, $\sigma_0$ and salt parameters: $z_+ = z_-$, $\rho_i$, and $a$. We calculated $g_{wi}(x)$, $\psi(x)$ and the effective charge density, $\sigma(x) = -\int_x^\infty \rho_{ei}(y)dy$ [10,13]. The charge profile...
in the solution is given by \( \rho_{el}(x) = \sum_{m=1}^{3} e z_m \rho_m g_m(x) \), where we have omitted the sub-index \( w \), for notation simplicity. \( x = a/2 \) is the distance of closest approach, to the wall, of the small ions. Hence, \( \sigma_0 = -\int_0^{a/2} \rho_{el}(y)\,dy \), by the electroneutrality condition, and

\[
\sigma'(x) = \int_{a/2}^{x} \rho_{el}(y)\,dy
\]

is the charge induced by the wall, on the fluid, between the wall and the distance \( x \) to the wall. Hence, \( \sigma(x) = \sigma'(x) + \sigma_0 \) is the effective or net charge (wall plus fluid) at the distance \( x \) away from the wall. \( \sigma(x) \) measures overcharging, CR or CI at the interface. The effective electrostatic force on an ion is \( f^i(x) = -e z_i \frac{\partial \rho_i(x)}{\partial x} = \frac{4 \pi e z_i \sigma(x)}{\epsilon} \). Therefore, \( \sigma(x) \) is not only a measure of the over (under)-charging but also of the wall-particle effective electrical force. \( F_i(x) = \frac{\partial W_i(x)}{\partial x} = \frac{1}{3} \frac{\partial \ln \rho_i(x)}{\partial x} \) is the net effective, many-body force between the wall and an ion of species \( i \). Hence, \( F_i(x) = f^i(x) + f^g(x) \), where \( f^g(x) = \frac{\partial J_i(x)}{\partial x} \) contains the non-electrostatic contributions. The larger the ionic size, the larger the confinement excluded volume (CEV) and the smaller the accessible volume. In our case, \( f^g(x) \) has the ionic excluded volume contributions. Since both \( \psi(x) \) and \( J_i(x) \) are functionals of \( \rho_{el}(y) \) and are in a non-linear equation, the charge and size correlations are, in general, not independent \([10,13]\) and, hence, our theory predicts that overcharging, if present, is related to both the electrical charge and the ionic size. It is an elementary statistical mechanics result that the smaller the accessible volume the smaller the entropy of the system. Thus, the larger the ionic size the lower the entropy of the system. Charge correlations of like-charged ions have the effect of also reducing the system’s accessible volume and, thus, of reducing its entropy.

In all our calculations \( T = 298 \) K, \( \epsilon = 78.5 \) and \( \rho_M = 0.01 \) M. In the RPM calculations \( a = 4.25 \) Å. The 4.25 Å ionic size approximately corresponds to that of a hydrated ion. In Fig. 1, the macroion has negative charge, which is opposite to that of the wall and the divalent salt ion. The macroion RCP shows a very strong adsorption to the wall. A second layer of macroions is adsorbed, with an intermediate layer of divalent positive ions, followed by monovalent negative little ions. A layer of positive divalent ions, followed by a monovalent negative ions layer, also mediates a third layer of adsorbed negative macroions. The macroions of the first layer are surrounded by counterions. Subsequent layers of, less concentrated, macroions are observed, also mediated by layers of positive and negative little ions. Considering that the bulk macroion concentration is 0.01M, the local macroion concentration at the second peak, \( \approx 0.035 \) M, is not negligible. The first peak is \( \approx 20 \) M. Hence, large macroions, next to a highly charged wall, assemble next to the wall. In the inset, at a distance of one macroion radius, a deep minimum is observed, corresponding to a very strong CR. The maximum located around \( 15a/2 \) show a CI. For \( x \) lower than one macroion radius, true overcharging of the wall is present: That is, wall’s divalent ions, are adsorbed to the wall and their charge exceeds that of the wall plus the adsorbed negative little ions. This effect has not been reported before and is probably present only in macroions solutions. The effective wall electrical field, which is proportional to \( \sigma(x) \), is positive before the first layer of macroions and then negative, before the second layer. Hence, the electrical force is first attractive and then repulsive to negative ions. The behavior of the total force on an ion of species \( i \), however, is implicit in the RCP, i.e., a \( g_i(x) \) above (below) 1 implies that \( F_i(x) \) is attractive (repulsive). At \( x = a/2 \), \( \sigma(x) \) is equal to the wall’s charge, whereas for \( x \to \infty \), \( \sigma(x) \to 0 \), as it should be if electroneutrality is satisfied. Lower wall charge density or lower macroion’s charge, size or concentration produce lower adsorption. The 2:1 electrolyte solution does not show CR.

In Fig. 1, the wall and macroion have negative charge. Here, the positive divalent little ions are counterions of the wall and macroion. A layer of positive ions, followed by negative ions is adsorbed to the wall. Then, a strong adsorption of macroions is observed. In the inset, a CR is followed by a CI. In Fig. 2, the macroions are responsible for the first CR, whereas, in Fig. 3, they are responsible for the first CI. The 2:1 electrolyte does show CR. Thus, if no macroions are present, monovalent counterions do not produce CR, whereas divalent counterions do. The first peak corresponds to a 0.2 M macroion concentration. This implies a long-range effective attraction, between the adsorbed macroions. This attraction is lower, as the macroions-wall distance increases or for smaller macroions. Our results show that the macroion adsorption depends on \( \rho_M^2 \equiv \rho_+ a^+ + \rho_- a^- + \rho_M \phi_M^3 \), i.e., it depends on the CEV. Hence, adsorption of larger macroions implies longer range and more strong effective macroion-macroion attraction. These findings are suggestive, in relation to experimentally reported attraction between like-charged macroions, next to a like-charged wall, where \( \mu \) size confined macroions show the same behavior \([6]\).

In Fig. 2, uncharged, large particles, immersed into a 1:1 RPM electrolyte are next to a negatively charged wall. A slight CR is observed in the inset, even though that the counterions are monovalent. EDL studies for 1:1 electrolytes show that there is no charge or RCP oscillations around 1 \([4]\). Hence, in Fig. 3, the oscillations in the little ions RCP are due to size correlations related to the macroparticle adsorption to the wall. Thus, macroion charge is not necessary to have macroparticle adsorption and their presence induce ionic oscillations for 1:1 electrolytes.

In Fig. 4, the wall is uncharged. Since the macroion has a larger size, \( a_M = 6.5a \), we have increased the macroion’s charge to have the same macroion’s surface charge den-
sity. The result is a strong adsorption of macroions to the wall. The local macroion concentration, at contact with the wall is \( \approx 6.63 \text{M} \). In the inset, strong positive and negative true overcharging of the wall is seen. If \( a_M=4.5a \) or \( Z_M=-40 \) (not shown) the maximum of the second layer of macroions decreases from 1.7, in Fig. 1, to 1.2, but the RCP’s and \( \sigma(x) \) curves are qualitatively equal. If no macroions are present, \( \sigma(x) = 0, \forall x > 0 \). Since the wall is uncharged, the strong macroion adsorption and wall overcharging is due to the large CEV, imposed by the macroions size. Thus less accessible volume, which implies less entropy, impose more order at the interface, i.e., more adsorption to the wall.

In Fig. 2, we repeat the calculation of Fig. 1, but, now, the electrolyte species have zero diameter (PIM) and the macroion has a smaller diameter, \( a_M=4.5a \). This case corresponds to an extension of the PB theory, where only two macroions are considered [6]. In the inset, before one macroion radius, positive overcharging is present. The maximum is at \( x = a_M/2 \). The maximum of negative overcharging is at \( x \approx 9.6a/2 \). If no macroions are present, \( \sigma(x) = 0, \forall x > 0 \). Notice the oscillations in the point-ion RCP. This oscillatory behavior is in accordance with the exact second moment condition (SMC) of Stillinger and Lovett [14]. However, it is well known that the RCPs obtained from the PB equation for PIM electrolytes in bulk, next to a charged wall or around two macroions (DLVO theory [5]), do not show oscillations and the macroion-macroion interaction is purely repulsive [6]. In fact, it is a mathematical theorem that the PB equation can not predict and attractiv force for two like-charged macroions, between them or with the wall, at infinite dilution [5]. The adsorption of macroions to the wall implies an effective attraction between them and with the wall. The difference of our Fig. 2 result with the classical PB result is the finite concentration of macroions, which implies a proper consideration of entropy.

In summary, CR, CI and true overcharging of a wall depend on electrostatic interactions and on the CEV, which depends on \( \rho_T^* = \rho_+ a_+^3 + \rho_- a_-^3 + \rho_M a_M^3 \) (larger \( \rho_T^* \) implies more adsorption). On one hand: a) Higher wall or macroion charge, enhance adsorption; b) Typical hydrated monovalent counterions (e.g., Na\(^+\), \( a \approx 4.25 \text{Å} \)) do not show CR (Fig. 1), whereas typical divalent counterions do (Fig. 3). This is due to a greater efficiency of divalent counterions to store charge [6]. On the other hand: 1) Overcharging can be present for uncharged walls or macroions, or for like charged wall and macroions, provided \( \rho_T^* \) is sufficiently large; 2) Point ions can never overcharge a surface [1][2][3][4]. In a pure electrolyte solution, larger monovalent counterions, such as hydrated Li\(^+\) (\( a \approx 7 \text{Å} \)), show CR [7]. Therefore, while that CR, CI and true overcharging result from the competition between energy vs. entropy, our results show that entropy has a much more important role than has been recognized in the past, and give some insight on the experimentally found long range effective attraction of like-charged macroions next to a wall [dechter97], and self-assembled complexes [6] [6].

We thank CONACYT (L007E and C086A) and NE-GROMEX.

[1] P. Attard, Advances in Chemical Physics Vol. XCII (Wiley, New York, 1996).
[2] M. Lozada-Cassou et al., J. Chem. Phys. 77, 5150 (1982).
[3] W. van Megen and I. Snook, J. Chem. Phys. 73, 4656 (1980).
[4] M. Lozada-Cassou et al., Phys. Rev. E 60, R17 (1999).
[5] W. M. Gelbart, et al., Physics Today 53, 38 (2000).
[6] G. M. Kepler and S. Fraden, Phys. Rev. Lett. 73, 356 (1994); J. C. Crocker and D. Grier, Phys. Rev. Lett. 77, 1897 (1996); W. R. Bowen and A. O. Sharif, Nature 393, 663 (1998).
[7] E. Gurovitch and P. Sens, Phys. Rev. Lett. 82, 339 (1999).
[8] G. Decher, Science 277, 1232 (1997).
[9] K. S. Schmitz, Macroions in Solution and Colloidal Suspensions (VCH Publishers, New York, 1993).
[10] M. Lozada-Cassou and J. Yu, Phys. Rev. Lett. 77, 4019 (1996); ibid 56, 2958 (1997).
[11] L. Degrève and M. Lozada-Cassou, Phys. Rev. E 57, 2978 (1998).
[12] M. Lozada-Cassou, et al., Phys. Rev. E 53, 522 (1996).
[13] M. Lozada-Cassou and E. Díaz-Herrera, J. Chem. Phys. 92, 1194 (1990); ibid 93, 1386 (1990).
[14] F. H. Stillinger and R. Lovett, J. Chem. Phys. 48, 3858 (1968); S. L. Carnie and D. Y. C. Chan, Chem. Phys. Lett. 77, 437 (1981).
[15] J. C. Neu, Phys. Rev. Lett. 82, 1072 (1999); J. E. Sader and D. Y. C. Chan, Langmuir 16, 324 (2000).
[16] R. Messina et al., Phys. Rev. Lett. 85, 872 (2000), which is a zero temperature study.
[17] E. Gonzales-Tovar et al., J. Chem. Phys. 83, 361 (1985), see Fig. 21.
FIG. 1. Inhomogeneous RCP for macroions in a 2:1 RPM electrolyte solution, as function of the distance to the wall $\rho_M = 0.1M$, $\rho_+ = 0.7M$, $\rho_- = 1.0M$, $\sigma_0 = 0.272C/m^2$, $a_M = 4.5a$, $Z_M = -40$, $z_+ = 2$, $z_- = -1$. The solid, dash, and dot lines are the macroion (M), negative (-) ion, and positive (+) ion RCP, respectively. In the inset the solid line is the effective charge density profile, $\sigma(x)$, as a function of the distance to the wall, for the macroion solution, whereas the dash line is $\sigma(x)$ for a 2:1 RPM electrolyte ($\rho_+ = 0.5M$, $\rho_- = 1.0M$, $z_+ = 2$, $z_- = -1$), when no macroions are present. The sketch roughly represent the distribution of ions indicated by their RCP.

FIG. 2. As in Fig. 1 but, $\sigma_0 = -0.272C/m^2$. In the inset, the dash line is $\sigma(x)$ for a 2:1 RPM electrolyte, when no macroions are present, $\rho_+ = 0.7M$, $\rho_- = 1.4M$, $z_+ = 2$, $z_- = -1$.

FIG. 3. As in Fig. 1 but the salt is a 1:1 RPM electrolyte solution and $\rho_+ = 1.0M$, $\rho_- = 1.0M$, $\sigma_0 = -0.272C/m^2$, $a_M = 6.5a$, $Z_M = 0$, $z_+ = 1$, $z_- = -1$.

FIG. 4. As in Fig. 1 but $\rho_+ = 0.915M$, $\rho_- = 1.0M$, $\sigma_0 = 0.0C/m^2$, $a_M = 6.5a$, $Z_M = -83$.

FIG. 5. As in Fig. 1 but the salt is a 2:1 PIM electrolyte solution $\sigma_0 = 0.0C/m^2$, $Z_M = -40$. 