Supporting Information

Equation Chapter (Next) Section 1

The Electrostatic Free Energy of SMPBE

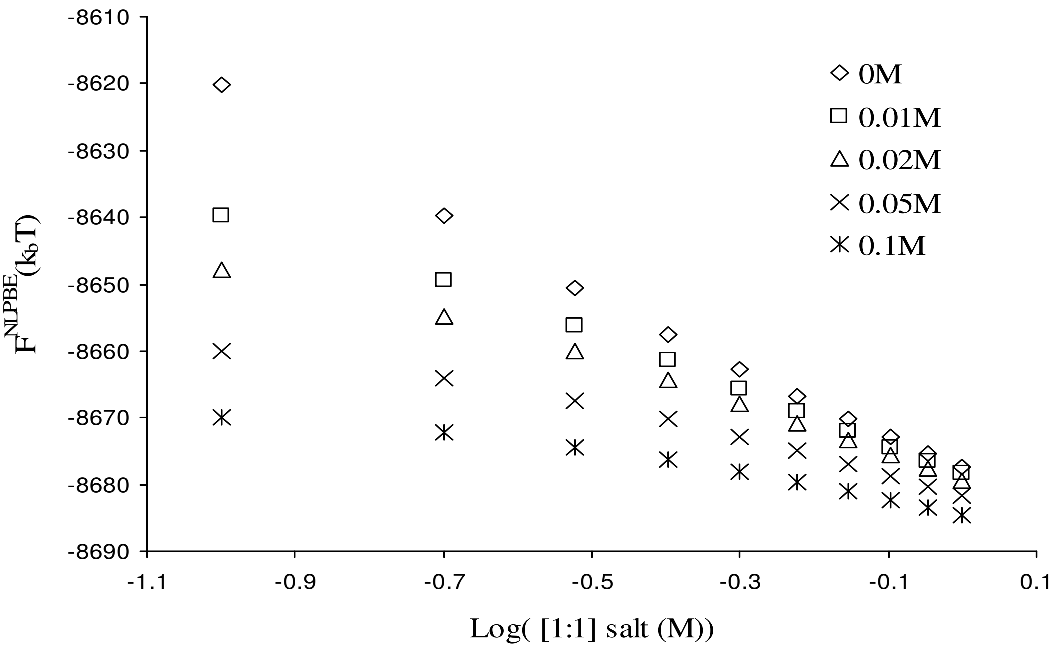
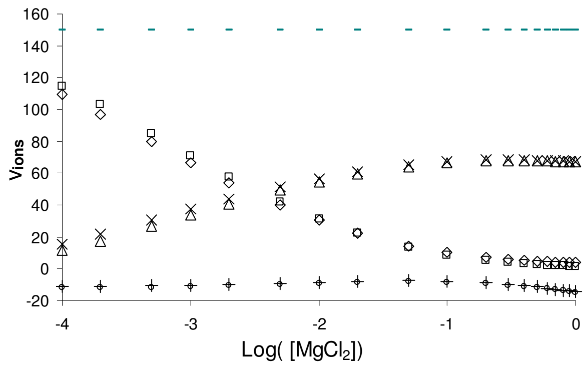
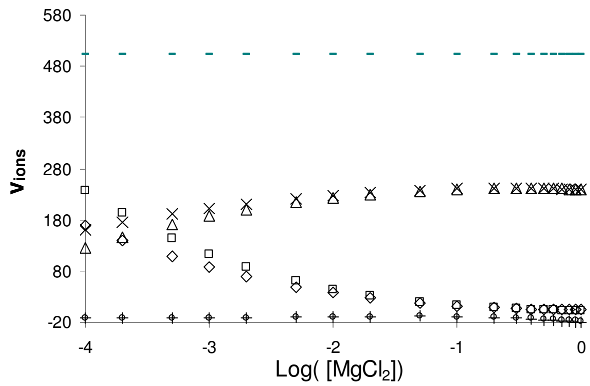


Figure A.1. The electrostatic free energy (in k_bT) computed with the nonlinear Poisson-Boltzmann equation, F^{NLPBE}, of a spherical cavity of radius 20 Å and a central charge of –50e at concentrations of 2:1 salt, [$MgCl_2$], of 0, 0.01, 0.02, 0.05, and 0.1 M and Stern layer of width 1.5 Å is plotted against the logarithm of the concentration of 1:1 salt, [NaCl].



(a)



(b)

Figure A.2. The numbers of bound Mg^{2+}, Na^{+}, and Cl^{-} ions (ν_{Mg}, ν_{Na}, and ν_{Cl}) for a spherical cavity of radius 20 Å and central charges of (a)-150e and (b)-500e in a mixed salt solution with an ion radius of 1.4 Å with [NaCl] = 0.1 M calculated with both the nonlinear Poisson-Boltzmann equation (Δ,□,o), and the size-modified Poisson-Boltzmann equation ($\times$,◊,+) are plotted as a function of [$MgCl_2$]. The NLPBE calculations were performed with a Stern layer of 1.4 Å.

Volume integration

The volume integral in eq 27 can be evaluated in the limit $c_{bi} \to 0$ by first computing the volume integral, I , which is given by noting that because $\xi(r) \geq 0$ for all r, we can write another integral, I_u that is an upper bound on I:

This integration can be divided into two regions

$$\begin{aligned}\lim_{c_{bi}\to 0} I_u &= \lim_{c_{bi}\to 0} \frac{k_b T}{a^3} \int_{\Gamma}^{R_L} d^3 r \xi_i(r) + \lim_{c_{bi}\to 0} \frac{k_b T}{a^3} \int_{R_L}^{\infty} d^3 r \xi_i^{LPB}(r) \\ &= 0\end{aligned} \tag{A1}$$

where Γ is the boundary of the molecule and R_L is chosen far enough from the molecule so that for $R_L < r < \infty$, ξ_i can be approximated by the linear Poisson-Boltzmann equation. As $c_{bi} \to 0$, both terms in eq A1 go to zero, and I therefore goes to zero.

Taylor series of volume-exclusion factor

The volume exclusion factor $\xi(r)$ is defined from:

$$\frac{1}{1+\xi(r)} = \frac{1-C}{1-C_0} \tag{A.2}$$

, where $\xi(r) = \sum_k \xi_k$ and $\xi(r) = a^3 g(r,a)$, and

$$g(r,a) = \sum_k \{c_{bi}^{+} \exp(-z_i^{+}\phi) + c_{bi}^{-} \exp(z_i^{-}\phi) - (c_{bi}^{+} + c_{bi}^{-})\}\,. \tag{A.3}$$

The NLPB equation is subtracted from SMPB equation in the solvent region

$$\nabla^2(\phi - \phi_{NL}) = -\frac{4\pi}{k_b T \varepsilon}\{\frac{\rho_{NL}(\phi)}{1+\xi(\phi)} - \rho_{NL}(\phi_{NL})\} \tag{A.4}$$

The Taylor expansion of equation on variables $\rho_{NL}(\phi)$ and $\xi(\phi)$ around ϕ_{NL} results in

$$\nabla^2(\phi-\phi_{NL}) = -\frac{4\pi}{k_b T\varepsilon}\{\ -\xi_{NL}(\phi_{NL})\rho_{NL}(\phi_{NL}) + (\phi-\phi_{NL})(1-\xi_{NL}(\phi_{NL}))\frac{d\rho_{NL}(\phi)}{d\phi}\Big|_{\phi=\phi_{NL}}\ \}$$
$$+O(a^3(\phi-\phi_{NL})^2)$$

(A.5)

The term $(\phi-\phi_{NL})$ asymptotically goes to zero as $a\to 0$. If the higher order term $O(a^3(\phi-\phi_{NL})^2$ is ignored, the ansatz $(\phi-\phi_{NL}) = O(a^3)F(\phi_{NL})$ serves as the solution to the equation (A.5). This form of solution gives the derivative of electrostatic potential w.r.t. a as:

$$\frac{d\phi}{da} = O(a^2)F(\phi_{NL}) \qquad \text{(A.6)}$$

with $\lim_{a\to 0}\frac{d\phi}{da} = 0$.

Note that for $\phi_{NL}=0$, the $\phi=0$ and therefore $F(\phi_{NL}=0)=0$.

The Taylor series of volume-exclusion factor $\xi(r)$ around $\phi=\phi_{NL}$ is

$$\begin{aligned}\xi(\phi) &= \xi(\phi_{NL}) - a^3(\phi-\phi_{NL})\rho(\phi_{NL}) + O(a^3(\phi-\phi_{NL})^2)\\ &= a^3 g(r,a=0) - O(a^6)\rho(\phi_{NL})F(\phi_{NL}) + O(a^9F^2(\phi_{NL}))\end{aligned} \qquad \text{(A.7)}$$

Therefore it is valid that in the first order one could approximate the volume-exclusion factor as $\xi(r) = a^3 f(r)$, where $f(r) = g(r,a=0)$ is a function independent of a.