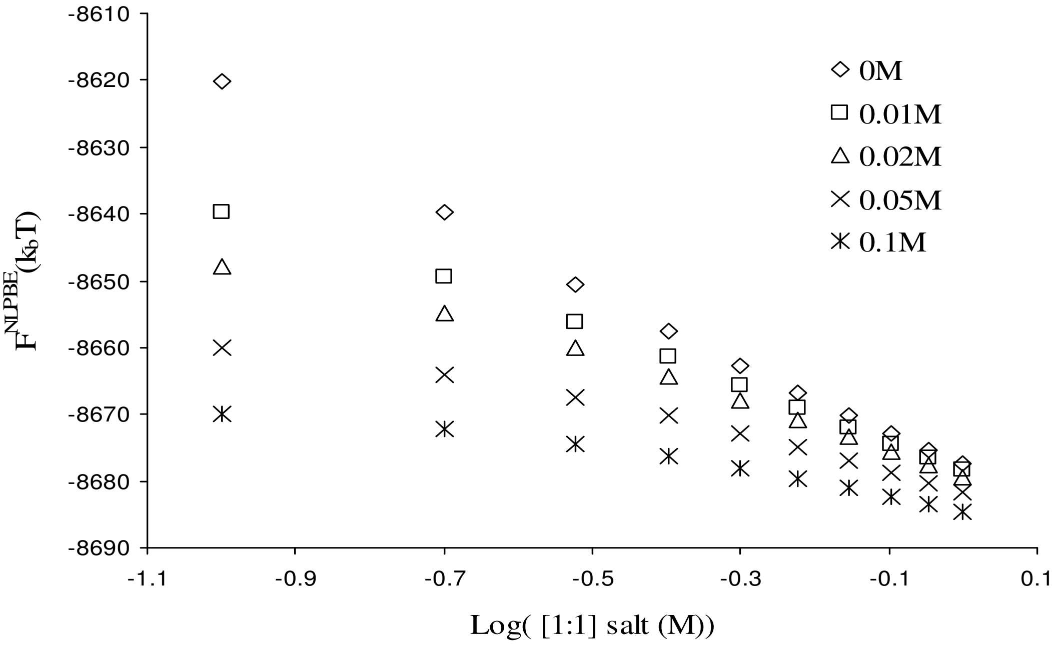
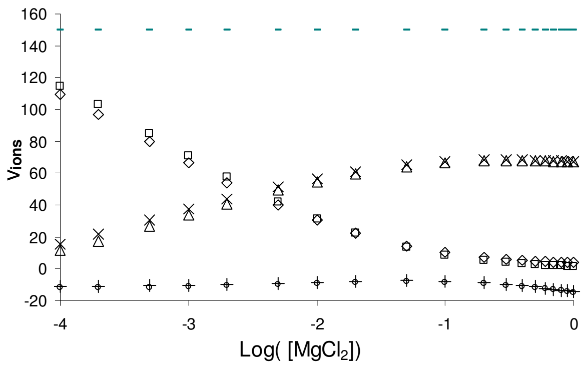
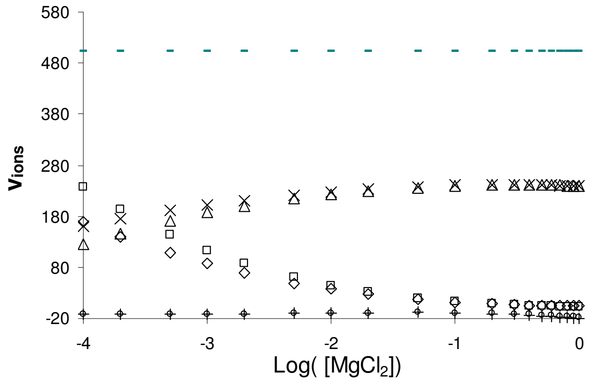



**Figure A.1.** The electrostatic free energy (in $k_bT$) computed with the nonlinear Poisson-Boltzmann equation, $F^{NLPBE}$, of a spherical cavity of radius 20 Å and a central charge of –50e at concentrations of 2:1 salt, [$MgCl_2$], of 0, 0.01, 0.02, 0.05, and 0.1 M and Stern layer of width 1.5 Å is plotted against the logarithm of the concentration of 1:1 salt, [NaCl]. The dielectric constant of spherical cavity is 4 and the dielectric constant of the solvent is 78.5.




(a)




(b)

**Figure A.2.** The numbers of bound $Mg^{2+}$, $Na^{+}$, and $Cl^{-}$ ions ( $\nu_{Mg}$, $\nu_{Na}$, and $\nu_{Cl}$ ) for a spherical cavity of radius 20 Å and a 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 $(\Delta, \square, o)$, and the size-modified Poisson-Boltzmann equation $(\times, \Diamond, +)$ are plotted as a function of $[MgCl_2]$. The NLPBE calculations were performed with a Stern layer of 1.4 Å. The ion radius is approximately equal to one half of $a$, the size of the lattice spacing used in the SMPBE theory. The dielectric constant of spherical cavity is 4 and the dielectric constant of the solvent is 78.5.

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

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

where $\Gamma$ is the boundary of the molecule and $R_L$ is chosen far enough from the molecule so that for $R_L < r < \infty$, $\xi_i$ 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.