Numerical and experimental studies of territorial binding of counterions in polyelectrolyte solutions including the added salt case

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This paper provides an extension of a procedure for calculating counterion binding ratios in a polyelectrolyte solution based on the Poisson–Boltzmann formulation of territorial counterion binding to include the presence of excess salt of the counterion. It is an extension of an earlier version which dealt with two counterions with different charge numbers without excess salt. The relative binding parameter of sodium to poly(galacturonic acid) as a function of the degree of neutralization in the presence of excess sodium chloride is determined by ^{23}Na n.m.r. and compared with the numerical results from the Poisson–Boltzmann and the Manning condensation theories. Agreement is found with the Poisson–Boltzmann results at degrees of neutralization greater than the critical condensation point predicted by the Manning theory. Qualitative elements of both theories appear in the experimental results.

(Keywords: counterion binding; weak polyelectrolyte; ^{23}Na n.m.r.)

INTRODUCTION

Interest in polyelectrolytes is often focused on solutions containing excess salts. An important property of a polyelectrolyte in solution is the binding ratio, P_b, defined as the fraction of the charges on the polyion compensated by condensation of the counterions. The Manning condensation (MC) theory[1] for calculating P_b is independent of the polyelectrolyte concentration and the concentration of excess salt. In contrast, in the Poisson–Boltzmann (PB) theory[2-4] P_b is a function of both the polyelectrolyte concentration and the excess concentration of salt.

This paper contains the mathematical equations implemented in a computer application called PolyElectrolyte which runs on an Apple Macintosh II[5]. This application is an extension of an earlier version which dealt with two counterions with charge numbers z_1 and z_2 of the same sign. The new version gives the user the option of choosing z_2 to have a sign opposite to z_1 and hence extends the numerical method to include excess salt of the counterion. The method is used to calculate the relative binding parameter, Γ^α, the binding ratio at a selected degree of neutralization (α) of a weak polyelectrolyte normalized to the binding ratio at complete neutralization, i.e. at $\alpha = 1$, for poly(galacturonic acid) (PGA) partially neutralized by NaOH in excess concentrations of NaCl. Values of Γ^α have also been determined experimentally for this system using ^{23}Na n.m.r. and the experimental values are compared with the results calculated by the MC and PB theories.

MATHEMATICAL MODEL

The polyelectrolyte is treated as a solution consisting of negatively charged polyions, co-ions and a single species of counterions. The accumulation of the small ions near the polyion will be examined. Length will be measured in nanometres (nm) and charge in electrostatic units (esu). The mathematical model of Dolar and Peterlin[3] will be used, in which the polyion is modelled as an infinitely long cylinder of radius a (nm) which carries a specified number of negative charges. Let $1/l$ denote the number of negative charges per unit length of the polyion. Each infinite length polyion is surrounded by a concentric infinite length cylindrical cell of radius R (nm), determined by the concentration of the charges on the polyion in the solution, c (molar), according to:

$$R = \frac{1}{\sqrt{0.6023\pi lc}} \qquad (1)$$

The domain of this so-called cell model, is this cylindrical cell.

Following Dolar and Peterlin[3] and using their notation, it is assumed that only electrostatic forces are acting and the counterions are treated as point charges. Total charge neutrality is assumed inside the cylindrical cell. Given the

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fraction N_1^0 of positive charge due to the counterion where the electrostatic potential is zero, i.e. at the cell boundary, the fraction $\bar{N}_1$ of the volume average charge due to the counterions and co-ions is found. This process defines a function $\bar{N}_1 = G(N_1^0)$ which is strictly increasing. In the n.m.r. experiments, a value for $\bar{N}_1$ is specified and measurements are made to determine the fraction of the counterions of charge number z_1 bound to the polyion. Numerically, given $\bar{N}_1$, a zero finding method is applied to the function $F(N_1^0) := G(N_1^0) - \bar{N}_1$. Once N_1^0 has been found, the mole fraction of each counterion bound to the polyion can be computed and compared with the n.m.r. results.

Let T denote the absolute temperature of the polyelectrolyte in Kelvin; ε, the dielectric constant of the solvent; e, the charge on a proton (esu); and k, the Boltzmann constant.

A cylindrical coordinate system with the z-axis coincident with the axis of the polyion is used. The electrostatic potential, ψ, will depend only on the radial distance, r. In the cell model it is assumed that the electrostatic force is zero at the cell boundary $r = R$ and it is convenient to normalize the potential so that $\psi(R) = 0$. Let n_1^0 and n_2^0 denote the numbers of counterions and co-ions per unit volume at this boundary where the electrostatic potential is zero, and let $\bar{n}_1$ and $\bar{n}_2$ denote the volume average numbers of the counterions and co-ions per unit volume, where z_1 and z_2 denote the valences, or charge numbers, of the counterions and co-ions, respectively. It will be required that $z_1 > 0$, while z_2 can be positive or negative, although it will be negative for the excess salt case. The PB equation for this system of charges is:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}\psi}{\mathrm{d}r}\right) = -\frac{4\pi e}{\varepsilon} r\left[z_1 n_1^0 \exp\left(\frac{-z_1 e\psi}{kT}\right) + z_2 n_2^0 \exp\left(\frac{-z_2 e\psi}{kT}\right)\right] \quad (a \leqslant r \leqslant R) \qquad (2)$$

At $r = R$, we have the boundary conditions:

$$\frac{\mathrm{d}\psi}{\mathrm{d}r}(R) = 0 \qquad (3a)$$

$$\psi(R) = 0 \qquad (3b)$$

The gradient of the potential at the surface of the polyion is related to the parameter l by:

$$\frac{\mathrm{d}\psi}{\mathrm{d}r}(a) = \frac{2e}{\varepsilon a l} \qquad (4)$$

The parameters $\bar{n}_1$ and $\bar{n}_2$ are given by:

$$\frac{\bar{n}_1}{n_1^0} = \frac{2}{(R^2 - a^2)} \int_a^R \exp\left(\frac{-z_1 e\psi}{kT}\right) r\,\mathrm{d}r \qquad (5a)$$

$$\frac{\bar{n}_2}{n_2^0} = \frac{2}{(R^2 - a^2)} \int_a^R \exp\left(\frac{-z_2 e\psi}{kT}\right) r\,\mathrm{d}r \qquad (5b)$$

and total charge neutrality implies that:

$$\frac{1}{l} = (z_1\bar{n}_1 + z_2\bar{n}_2)\pi(R^2 - a^2) \qquad (6)$$

Equation (6) can be derived from equation (3a) along with equations (2) and (4).

It is convenient to introduce the equivalent fractions N_1^0, N_2^0, $\bar{N}_1$, $\bar{N}_2$, the ratio η, dimensionless variables x and ϕ, and dimensionless parameters $\bar{R}$, and λ by:

$$N_1^0 := \frac{z_1 n_1^0}{z_1 n_1^0 + |z_2| n_2^0} \qquad (7a)$$

$$N_2^0 := 1 - N_1^0 \qquad (7b)$$

$$\bar{N}_1 := \frac{z_1 \bar{n}_1}{z_1 \bar{n}_1 + |z_2| \bar{n}_2} \qquad (7c)$$

$$\bar{N}_2 := 1 - \bar{N}_1 \qquad (7d)$$

$$\eta := \frac{z_1\bar{n}_1 + z_2\bar{n}_2}{z_1 n_1^0 + |z_2| n_2^0} \qquad (7e)$$

$$x := \frac{r}{a} \qquad (7f)$$

$$\phi(x) := \frac{-e\psi(r)}{kT} \qquad (7g)$$

$$\bar{R} := \frac{R}{a} \qquad (7h)$$

$$\lambda := \frac{e^2}{\varepsilon k T l} \qquad (7i)$$

Specification of N_1^0 together with equations (2), (3) and (4) uniquely determines ψ, n_1^0 and n_2^0. The average number densities $\bar{n}_1$ and $\bar{n}_2$ can then be found from equation (5). A more convenient dimensionless form for this problem is obtained by substituting (7) into equations (2)–(6). We find the boundary value problem (BVP). Given N_1^0, $0 \leqslant N_1^0 \leqslant 1$ in the case $z_2 > 0$, and $0.5 < N_1^0 \leqslant 1$ in the case $z_2 < 0$, we find a positive real number η and a function $\phi = \phi(x)$ which is twice continuously differentiable for $1 \leqslant x \leqslant \bar{R}$ so that:

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(x\frac{\mathrm{d}\phi}{\mathrm{d}x}\right) = \frac{4\lambda x}{(\bar{R}^2 - 1)\eta}\left[N_1^0 \exp(z_1\phi) + \frac{z_2}{|z_2|}(1 - N_1^0)\exp(z_2\phi)\right] \quad (1 \leqslant x \leqslant \bar{R}) \qquad (8)$$

$$\frac{\mathrm{d}\phi}{\mathrm{d}x}(\bar{R}) = 0 \qquad (9a)$$

$$\phi(\bar{R}) = 0 \qquad (9b)$$

$$\frac{\mathrm{d}\phi}{\mathrm{d}x}(1) = -2\lambda \qquad (10)$$

Once this BVP has been solved, the fraction $\bar{N}_1$ can be computed from:

$$\bar{N}_1 = \frac{2N_1^0}{(\bar{R}^2 - 1)\eta} \int_1^{\bar{R}} \exp(\phi) x\,\mathrm{d}x \qquad (11)$$

The fraction of each counterion bound to the polyion can also be computed. Let the thicknesses of the regions over which the counterions and co-ions are bound to the polyion be denoted by Δ_1 and Δ_2 (nm). These thicknesses are taken to be the diameters of the hydrated counterions. Let $X_{\mathrm{b}1}$ and $X_{\mathrm{b}2}$ denote the corresponding fraction of each ion bound to the polyion defined by:

$$X_{\mathrm{b1}} := \frac{\int_a^{a+\Delta_1} \exp\left(\frac{-z_1 e\psi}{kT}\right) r\,\mathrm{d}r}{\int_a^R \exp\left(\frac{-z_1 e\psi}{kT}\right) r\,\mathrm{d}r} = \frac{\int_1^{1+\Delta_1/a} \exp(z_1\phi) x\,\mathrm{d}x}{\int_1^{\bar{R}} \exp(z_1\phi) x\,\mathrm{d}x} \tag{12}$$

$$X_{\mathrm{b2}} := \frac{\int_a^{a+\Delta_2} \exp\left(\frac{-z_2 e\psi}{kT}\right) r\,\mathrm{d}r}{\int_a^R \exp\left(\frac{-z_2 e\psi}{kT}\right) r\,\mathrm{d}r} = \frac{\int_1^{1+\Delta_2/a} \exp(z_2\phi) x\,\mathrm{d}x}{\int_1^{\bar{R}} \exp(z_2\phi) x\,\mathrm{d}x} \tag{13}$$

The above BVP has a solution. If z_1 and z_2 are positive, then given $\bar{N}_1$, $0 \leqslant \bar{N}_1 \leqslant 1$, it is possible to find N_1^0, $0 \leqslant N_1^0 \leqslant 1$, and $\eta \geqslant 1$ so that the BVP has a solution which yields the given value for $\bar{N}_1$. For the added salt case, it is conjectured that for any $\bar{N}_1$, $0.5 \leqslant \bar{N}_1 \leqslant 1$, it is again possible to find N_1^0, $0.5 < N_1^0 \leqslant 1$, and $\eta \geqslant 0$ so that the BVP has a solution which yields the given value for $\bar{N}_1$. In our computer application, the lower bound of N_1^0 has arbitrarily been placed at 0.50001. This puts a slightly higher lower bound on $\bar{N}_1$.

EXPERIMENTAL

The PGA ($M_w = 30\,000$) was obtained from Polysciences, Inc. The experimental procedures used for preparing the PGA solutions at different degrees of neutralization, α, and the same polyelectrolyte concentration on a monomer basis, i.e. fixed charge concentration at $\alpha = 1$, c^*, were previously described in detail[6]. However, in this investigation excess NaCl was also added to the $c^* = 20$ mM PGA solution to obtain solutions having added salt concentrations, c_s, of 5, 10 and 20 mM NaCl. The method of obtaining and analysing the ^{23}Na n.m.r. spectra has also been previously described[6]. Spectra were obtained on Bruker AC-200 and Bruker AC-500 instruments. The uncertainty of the Γ^α determined from results obtained with these instruments for the solutions used in this investigation is $\sim \pm 0.03$.

RESULTS AND DISCUSSION

Previously we reported a study of the dependence of sodium ion binding to PGA on the degree of neutralization determined by ^{23}Na n.m.r. and calculated Γ^α using the PB theory for the system without excess salt[6]. The fraction of the sodium ions territorially bound to the polyion was monitored and evaluated following the procedure used by Grasdalen and Kvam[4] which was in turn based on the theory developed by Halle *et al.*[7]. This study indicated good agreement between the Γ^α calculated by the BP theory and the experimental values of Γ^α at α greater than a critical value, α_c, for concentrations of 5 to 50 mM PGA. The critical degree of neutralization, α_c, can be defined from the MC theory as the degree of neutralization at which the reduced charge density is unity, i.e. the distance between the fixed charges projected on the axis of the rod-like polyion is equal to the Bjerrum length. Significant positive deviations from the PB theory occurred at lower values of α for the higher concentrations of PGA. It was stated at that time that the experimental evaluation of Γ^α from ^{23}Na n.m.r. measurements depends on the basic assumptions that the quadrupole coupling constant and correlation time remain constant over the entire range of α. This second assumption appears to describe the system. The correlation times for the ^{23}Na n.m.r. spectra of 20 mM PGA, evaluated for $0.2 < \alpha \leqslant 1$ and $0 \leqslant c_s \leqslant 20$ mM NaCl were 0.90 ± 0.05 ns with no apparent trends. However, it is uncertain whether the first assumption describes the system at low α, i.e. low pH, and there is no independent measurement available for obtaining the quadrupole coupling constant. Also the possibility of a conformational change at some stage of the neutralization, perhaps near α_c as suggested by Manning[8], cannot be excluded as an influence on the values of Γ^α.

The previous computer program was applicable only for polyelectrolyte solutions containing an equivalent amount of the counterion[6]. It has been extended to assign opposite signs to each of the simple ions to make one a counterion and the other a co-ion of the polyion. This extended program provides a means of calculating Γ^α in the presence of excess salt of the counterion that can be compared with experimental n.m.r. results for such solutions. In the present study of PGA solutions with excess sodium salt, the theoretical values of Γ^α are obtained using the results of equation (12) for any given α and $\alpha = 1$ by:

$$\Gamma^\alpha = \left(\frac{X_{\mathrm{b1}}^\alpha}{X_{\mathrm{b1}}}\right)\left(\frac{1 + \frac{c_s}{\alpha c^*}}{1 + \frac{c_s}{c^*}}\right) \tag{14}$$

Equation (14) was also used to convert the experimental values of $(X_{\mathrm{b1}}^\alpha / X_{\mathrm{b1}})$ to Γ^α.

Plots of Γ^α *versus* α calculated for $c^* = 20$ mM PGA and $c_s = 0$, 5, 10 and 20 mM NaCl by the PB theory and for PGA by the MC theory are shown in *Figure 1*. An increase in Γ^α with an increase in c_s at α is indicated only by the PB theory.

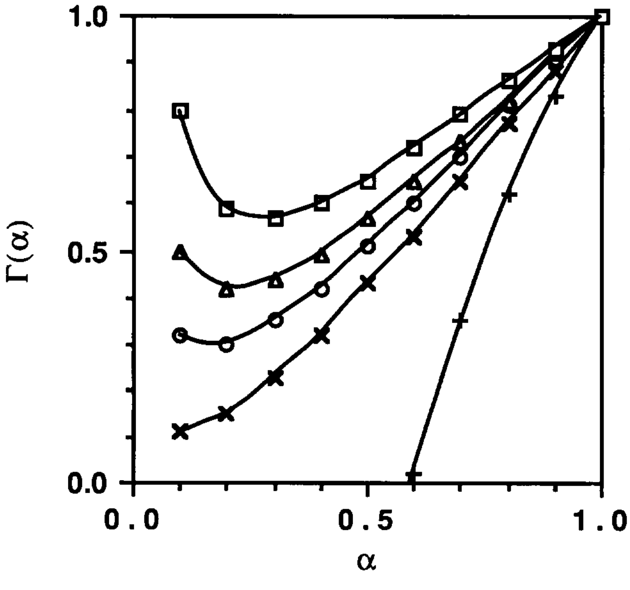

Figure 1 Theoretical Γ^α *versus* α for 20 mM PGA in the presence of added NaCl calculated by the Manning and Poisson–Boltzmann theories: (+) Manning; (×) PB, 0 mM NaCl; (○) PB, 5 mM NaCl; (△) PB, 10 mM NaCl; and (□) PB, 20 mM NaCl

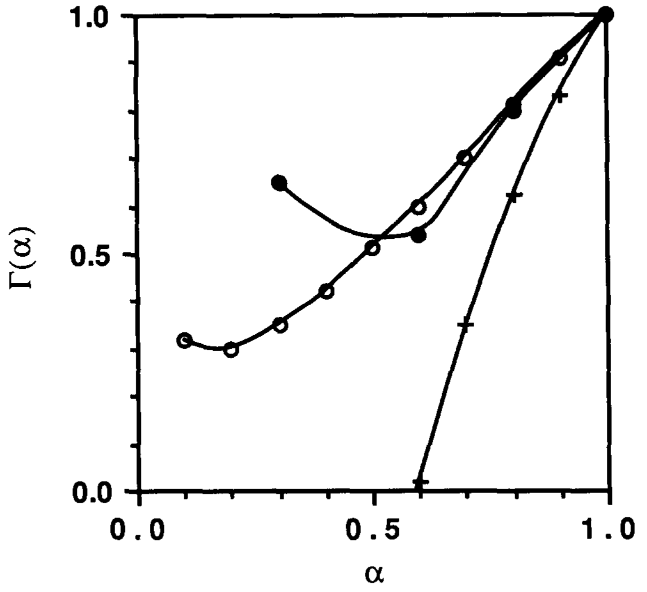

Figure 2 Experimental Γ^{α} *versus* α for 20 mM PGA in 5 mM NaCl, with curves calculated by the Manning and Poisson–Boltzmann theories: (●) experimental points; (+) Manning theory; and (○) PB theory

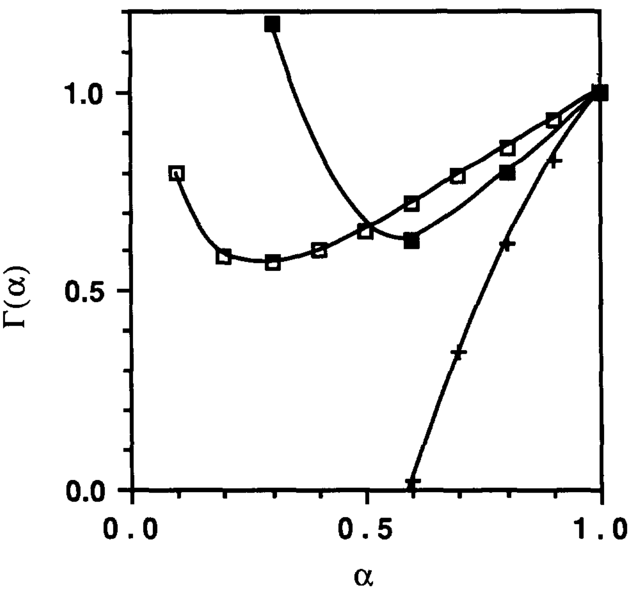

Figure 3 Experimental Γ^{α} *versus* α for 20 mM PGA in 20 mM NaCl, with curves calculated by the Manning and Poisson–Boltzmann theories: (■) experimental points; (+) Manning theory; and (□) PB theory

Values of Γ^{α} obtained by the n.m.r. experiments for $c_s = 5$ and 20 mM NaCl are plotted *versus* α with the MC curve and the PB curve for the appropriate value of c_s in *Figures 2* and *3* to provide a visual means of comparing the experimental results with the curves calculated by these theories. A similar plot of Γ^{α} *versus* α for $c^* = 20$ mM and $c_s = 0$ presented previously[6] (Figure 3 in ref. 6) showed agreement of the experiment Γ^{α} *versus* α with the curve calculated by the PB theory at $\alpha > \alpha_c$, where $\alpha_c = 0.60$ calculated by the MC theory. In *Figures 2* and *3* for $\alpha > \alpha_c$, the experimental Γ^{α} increase with increasing c_s, i.e. the slopes of Γ^{α} *versus* α decrease, and the dependence of Γ^{α} on α is similar to that calculated by the PB theory in this region of α, although the experimental curves lie as much as 10% below the PB theory curves for the corresponding c_s. A serious lack of agreement between the experimental Γ^{α} results and the MC theory curve is apparent at all α, especially at $\alpha < \alpha_c$, where the MC theory projects that Γ^{α} should be zero. However, changes in slope, resulting in minima, in the experimental Γ^{α} *versus* α curves occur near α_c. Minima also occur in the theoretical curves of Γ^{α} *versus* α calculated by the PB theory, as a result of the effect of α in equation (14), but at much lower α than the α at the experimental minima.

Elements of both theories appear qualitatively in the experimental results. The trends in the dependence of the experimental Γ^{α} on α are in agreement with the PB theory at $\alpha > \alpha_c$, with the PB theory providing a curve of slightly gentler slope than the experimental curve for each c_s.

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