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INTERACTIONS BETWEEN IONS AND POLYELECTROLYTES

A NOTE ON DETERMINATION OF IONIC ACTIVITIES, WITH REFERENCE TO A MODIFIED POISSON-BOLTZMANN TREATMENT

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We compare the numerous available data on ionic activities, in the presence of polyelectrolytes, with evaluation of these quantities from a modified Poisson-Boltzmann equation in the framework of a cell model. This treatment gives an excellent description of the mean activity for various ions. The activity of counterions is well-predicted, that of co-ions is generally overestimated.

1. Introduction

Ions play a predominant role in numerous important biological processes. Thus, amine-induced DNA condensation depends markedly upon the presence of ions [1]. Likewise, interactions of ligands with nucleic acids are modulated by the concentrations of available univalent cations [2,3]. Another biological polyelectrolyte, heparin, exhibits anti-clotting activity deriving seemingly from its ability to bind divalent ions [4].

These few examples show the importance of a good understanding of the interactions between ions and polyions. A direct measure of such interactions is afforded by experimental determinations of activity coefficients of various ions in the presence of polyelectrolytes. Furthermore, we have devised a model which accounts well for results obtained by NMR observables for the counterion, i.e., depending mostly upon ionic concentrations in the immediate vicinity of the polymeric chain [5]. Since measured activities depend on ionic composition at the limits of the cell [6], a comparison between the observed and the calculated activities will provide a complementary test of our model. Furthermore, the recent spectrophotometric determinations of divalent ionic activities by Kwak et al. [7,8] provide extremely useful information about the average distribution of ions in the cell.

A large number of simplified models have been devised to reproduce, in more or less empirical manner, the activity of ions in the presence of a polyion. Among these, the most popular two-state model is assuredly Manning's [9,10], whose limitations we have already stressed [5,11].

More recently, Guéron and Weissbuch [12] have developed a newer two-state model based upon a derivation from the Poisson-Boltzmann equation. They attributed deviations between the results from their model and experimental determinations to polarization of the counterions.

At about the same time, we suggested intervention of site binding to explain discrepancy between the experimental results and a solution of the

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Poisson-Boltzmann equation [13]. However, such an interpretation is questionable, since it requires degrees of binding greater than 50%, i.e., much above their actual magnitude [11].

We have focussed our attention therefore on limitations intrinsic to the Poisson-Boltzmann approach, which completely neglects interionic correlations. By introducing a local activity correction proposed by Hill [14], we have obtained excellent agreement between experimental results and predictions from the Poisson-Boltzmann equation thus modified [11].

In this paper, we show how to simplify this formalism in order to increase its generality without sacrificing any of its quality.

We further improve the model by explicit consideration of excluded volume effects.

2. Data and treatment

2.1. Data from the literature

In order to draw significant conclusions from this study, we compare predictions from our model with measurements of ionic activity from experimental methods as diverse as potentiometry, osmometry, and spectrophotometry. We have also considered a great variety of polymers including polystyrene sulfonate (PSS) [15–17], pectates and pectinates [18], carboxymethylcellulose (CMC) [18,19], heparin [20,21] and dextran sulfate (DSS) [8]. Employing these polyelectrolytes we have calculated activities for the following ions: Na^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, and Cl^-.

2.2. Treatment

In the framework of our modified Poisson-Boltzmann treatment [5,11], and the cell model, we use an ionic distribution law of the form:

$$c_i(r) \propto \exp(-E_i(r)/kT) \tag{1}$$

and we write the energy of the i-th ion as:

$$E_i(r) = e_i(\psi(r) - \psi(R)) + kT \ln \gamma_i(r) \tag{2}$$

where R is the limiting radius of the cylindrical cell, and $\gamma_i(r)$ the ionic activity calculated from the local ionic strength (for justification of the use of $\gamma_i(r)$, see ref. 14).

The first term in eq. 2 describes the electrostatic interaction of an ion i, placed at a distance r from the polyelectrolyte, with the polymer and with the other ions present at distances other than r. The second term in eq. 2 expresses the interionic interactions for ions at the same radial distance r. Such an empirical correction improves considerably the classical Poisson-Boltzmann model [11].

We further improve upon this model by taking into account the finite size of the ions which preclude them from collapsing onto the polyelectrolyte. For this purpose, we set:

$$E_i(r) = \infty, \text{ when } r \leqslant a_i + a_p \tag{3a}$$

$$E_i(r) = e_i(\psi(r) - \psi(R)) + kT \ln \gamma_i(r), \text{ when } r > a_i + a_p \tag{3b}$$

where a_i is the ionic radius and a_p the polymer radius.

The model corresponding to eqs. 1 and 3 is a simplified version of the primitive model [22]. After normalization, one obtains:

$$\begin{aligned} c_i(r) &= Q_i^{-1} c_i^0 \exp(-E_i(r)/kT) \\ &= c_i(R)\gamma_i(R) \exp(-E_i(r)/kT) \end{aligned} \tag{4}$$

where

$$Q_i = V_T^{-1} \int_{V_T} \exp(-E_i(\vec{x})/kT) \cdot d\vec{x}$$

V_T being the cell volume.

We solve such a modified Poisson-Boltzmann equation by dividing the cell into a series of coaxial cylindrical crowns (or shells), in each of which the ionic concentration is constrained to remain constant. We substitute in this manner into the continuous Boltzmann distribution a sequence of step functions [11]. The activity coefficient $\gamma_i(r)$ had been formerly evaluated from the local ionic strength, at a distance r from the axis of the cylindrical polyion, according to the equations of Scatchard et al. [23]. These calculations of activity were dependent upon the type of ion considered and upon the nature of the sites on the polymer.

Such a correction demanded knowledge of the ionic composition at a radial distance r from the polymer axis, and there was a problem in the applicability of the equation used, since they are valid only for electrically neutral solutions [11]. Hence, we resort now, in order to calculate this term $\gamma_i(r)$, to the formalism by Sun et al. [24]:

$$\log \gamma_i(r) = -0.51 z_i^2 \left[\frac{\sqrt{I(r)}}{1 + 1.26\sqrt{I(r)}} - 0.15 I(r) \right] + 0.06 I(r) \tag{5}$$

where z_i is the valency of the ion considered. The numerical parameters in eq. 5 are those appropriate for inorganic salts [24]. Of course, the main term in eq. 5 is the Debye-Hückel factor, $\sqrt{I}/(1 + 1.26\sqrt{I})$. We have elected to use the formula of Sun et al. [24] because of its wide-ranging applicability. However, recourse to a pure Hückel formula leads to equally good results. We calculate the local ionic strength from:

$$I(r) = \tfrac{1}{2}\left[\sum_i z_i^2 c_i(r) + z_p^2 c_p \right] \tag{6}$$

where c_p denotes the concentration of the polyion sites, and $c_i(r)$ is the local concentration in ions of type i. Eq. 6 serves to calculate the local ionic strength, in order to maintain the total ionic strength of the solution:

$$\int_{V_T} I(\vec{x})\,\mathrm{d}\vec{x} = \frac{V_T}{2}\left(\sum_i z_i^2 c_i^0 + c_p z_p^2 \right) \tag{7}$$

where c_i^0 is the mean concentration in ions of type i within the solution.

The system constituted by eqs. 3–6 is applicable to any type of polyelectrolyte, in the presence or absence of added salts. It provides a useful generalization of the formalism previously used [11], while removing some empiricism from the evaluation of the corrector factor $\gamma_i(r)$.

3. Results and discussion

Calculated mean ionic activities in the presence of polymer are shown in fig. 1: the agreement is gratifying. A typical case, variation of the mean activity coefficients for NaCl and $CaCl_2$ in the presence of PSS, as a function of the mole fraction (x_{Na}) of Na^+, is presented in fig. 1 for a solution containing as many polymer sites as there are Cl^- ($X = 1$). Whatever the ionic composition of this solution, our model reproduces extremely well the variations of the activities of the two salts (fig. 1). For $X = 1$, the comparison with the more classical Poisson-Boltzmann treatment (eq. 3 without $\gamma_i(r)$) leads to approximately the same results as for NaCl but shows significant differences for $CaCl_2$. In each case (cf. fig. 2 of ref. 11) the new treatment provides a better agreement with experimental results than the classical Poisson-Boltzmann law.

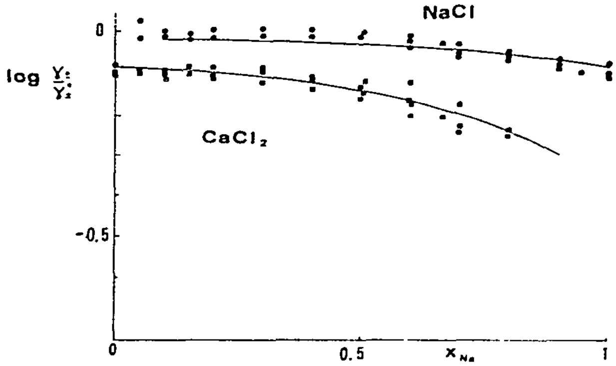

Fig. 1. Variation of the mean activity coefficients for NaCl (●) and $CaCl_2$ (■) in presence of NaPSS ($\xi = 2.80$) [15], as a function of the mole fraction x_{Na} in the solution, with $X = c_p/[Cl^-] = 1$. Curves display the results from the classical Poisson-Boltzmann treatment (······), and from the present modified Poisson-Boltzmann treatment (———).

Our method of calculation also provides a determination of ionic activities, as measured by potentiometry. However, the published experimental data use systematically the Wells correction [25] or, more frequently that by Iwasa and Kwak [26] which is based on the total ionic strength of the solution. In order to compare our calculated values and these experimental data, we have also applied the Iwasa-Kwak correction [26] to our numerical determinations. Since the experimental and the theoretical values undergo the same correction, the conclusions thus obtained are quite independent of the use of this correction.

In this manner, we obtain an excellent description of the mean activity of NaCl, not only in the presence of NaPSS, but also with many other polyelectrolytes such as pectates, pectinates and

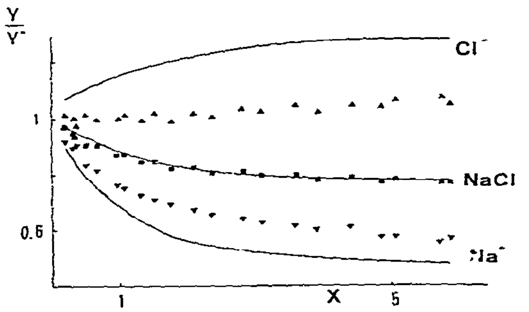

Fig. 2. Variation of the mean activity coefficient for NaCl (■) and for the activity coefficients of Na^+ (▲) and Cl^- (▼) in the presence of pectate ($\xi = 1.63$) [18] as a function of the concentration ratio X between the polymer concentration and the salt concentration. Comparison of the experimental results with our modified Poisson-Boltzmann treatment (———).

CMC (figs. 2–5). These results indicate how important it is to take into account interionic correlation, as we do by way of the activity correction (eqs. 3–5): this procedure provides a significant improvement of the Poisson-Boltzmann treatment.

Our calculations are performed with the following geometrical parameters: 4.8 Å for the radius of PSS [11] and 3 Å for the radius of the polysaccharides [5]. The distance H between adjacent polymeric sites is given by:

$$H = e^2/4\pi\epsilon_0\epsilon_r kT\xi \tag{8}$$

The dimension a_i is taken as the radius of the solvated counterions [27]. Our digitization procedure [11] uses 15–20 coaxial shells, and we have been careful to check that the results are invariant with respect to the total number of shells.

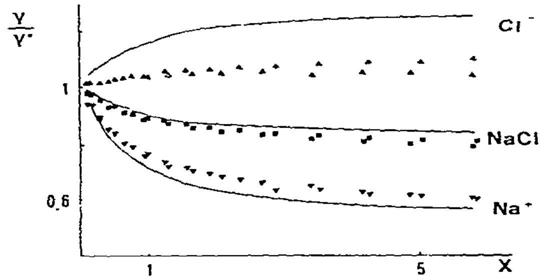

Fig. 3. Same as fig. 2 for pectinate ($\xi = 1.20$) [18].

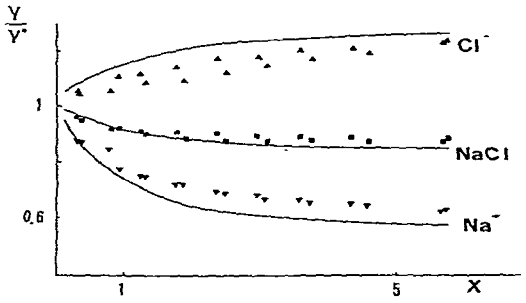

Fig. 4. Same as fig. 2 for CMC ($\xi = 1.19$) [18].

The calculated activities are slightly sensitive to the choices of different radii; a 10% change of the polymer radius modifies the Na^+ activity by only 0.1% while the activity of divalent ions varies around 1%. A 10% change of the radii of the counterions modifies the cationic activities by 1–2% while the co-ion activity remains constant.

We could have improved the quality of the results, for instance, those in fig. 3, by slight adjustments of the intersite distance, which could be due to conformational modifications with respect to the fully extended polymeric chain [28], which we nevertheless retain as a working hypothesis in the framework of the cell model.

Obviously, if we compare results from our model with the experimental data [18,19] (figs. 2–5), the activity of the Cl^- co-ions is systematically above the experimental value. Also, our calculations have a tendency to underestimate slightly the activity of the counterions. In the cases of sodium heparinate [20] and calcium heparinate [21], our computed

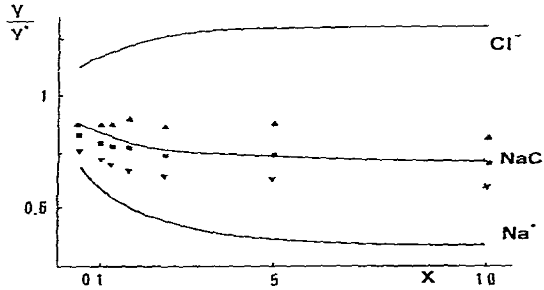

Fig. 5. Same as fig. 2 for CMC ($\xi = 1.38$) [19].

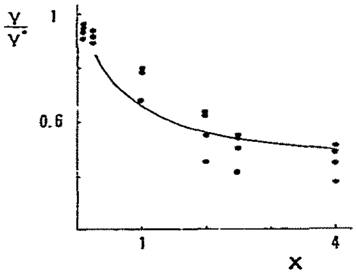

Fig. 6. Variation of the activity coefficients for Na^+ in the presence of heparin ($\xi = 1.66$) [20] as a function of the X ratio.

values are in agreement with the experimental determinations of the activities of the Na^+ and Ca^{2+} (figs. 6 and 7).

Furthermore, we cannot help noticing puzzling aspects in the experimental determinations. Thus, measurements performed by the same authors upon equivalent polymers (sodium pectinate $\xi = 1.20$ and Na CMC $\xi = 1.19$) are displayed in figs. 3 and 4: they show a completely different dependence of Cl^- activity upon X, probably due to some specific interactions in the case of Na CMC. For Na CMC, the measured Cl^- activity provides a better agreement with the predictions from our model.

Likewise, we show in figs. 4 and 5 the results for a single system (Na CMC $\xi = 1.19$; 1.38): again, there is some problem with the experimental values for the activity of Cl^-, since it drops from approx. 1.2 (fig. 4) to below unity (fig. 5). At the same time, the Na^+ activity measured by Rinaudo and Milas [19] is markedly greater than that obtained by Joshi and Kwak [18].

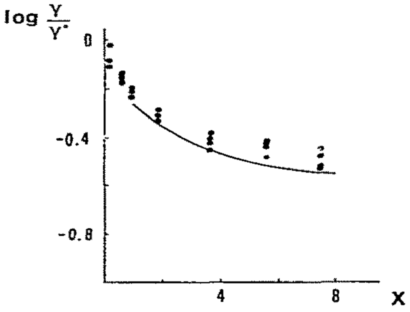

Fig. 7. Same as fig. 6, for Ca^{2+} [21].

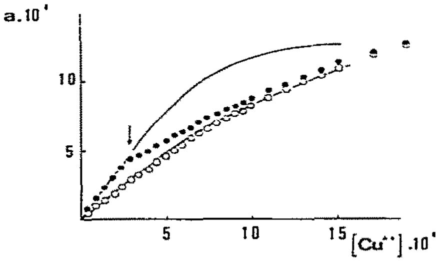

Fig. 8. Variations of the activities for Na^+ (●) and Cu^{2+} (○) upon addition of $CuSO_4$ to a 2 mM solution of NaPSS ($\xi = 2.80$) [16]. (●) $a_{Na^+} - a^0_{Na^+}$, where $a^0_{Na^+}$ is the activity of Na^+ in a solution containing only NaPSS. (○) $\Delta Cu^{2+} \equiv [Cu^{2+}] - a_{Cu^{2+}}$. (———) Calculated with our modified Poisson-Boltzmann model.

The experimental determination of ionic activities also seems to present difficulties. For instance, Miyamoto and Imai [16] have studied the variation in activities of Na^+ and Cu^{2+} upon addition of $CuSO_4$ to a solution of NaPSS. The plot showing the change in activity of Na^+ shows a break, above which our calculated values deviate substantially from their results, while we continue to reproduce extremely well the activity of the added Cu^{2+}.

Because of the above-stated problems, or possible deficiencies, in the potentiometric determina-

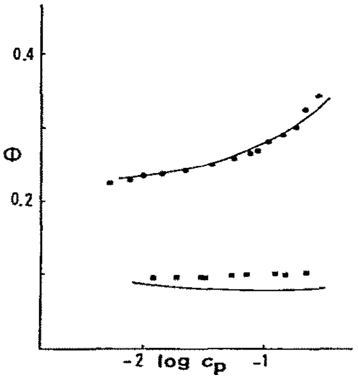

Fig. 9. Variation of the osmotic coefficient ϕ for solutions of NaPSS (●) and CaPSS (■) ($\xi = 2.80$) [16] as a function of polymer concentration. (———) Calculated with our modified Poisson-Boltzmann model; (· · · · · ·) corresponds to the classical Poisson-Boltzmann equation [17].

tions, we compare now our calculation of the ionic activity with measurements of the osmotic coefficient reported by Bratko and Vlachy [17] for solutions of NaPSS and CaPSS (fig. 9). Our calculations give an excellent fit for the Na^+ counterions; they underestimate slightly the activity of Ca^{2+}. For both systems (NaPSS, CaPSS), our model reproduces faithfully the variations with polymer concentration, which is certainly not the case for the classical Poisson-Boltzmann treatment [17].

A third comparison is provided by spectrophotometric methods [7,8]. They give information about ionic activities within the cell. We report here our results for Zn^{2+} in the presence of sodium dextran sulfate [8].

The spectrophotometric procedure relies upon introduction into the solution of a very small amount of a dye H^+D^- absorbing light at wavelength λ'. Upon complexation of divalent ions the dye forms an MD^+ species, absorbing at a new wavelength λ''. For the equilibrium:

$$\underset{(\lambda')}{D^-} + M^{2+} \overset{K}{\rightleftarrows} \underset{(\lambda'')}{MD^+} \qquad (9)$$

the apparent equilibrium constant for complex formation is $K_{app} = [MD^+]/[M^{2+}][D^-] = 8500$ in the present case [8]. The final value calculated for the mean activity $\langle a_{M^{2+}}(r)\rangle$ does not depend upon the particular choice for the constant K_{app}. The ratio of the absorbances at the two wavelengths λ' and λ'' provides the mean activity of M^{2+} in solution, according to:

$$\langle\phi(r)\rangle = \frac{\langle A(\lambda'')\rangle}{\langle A(\lambda')\rangle} = \frac{\epsilon_{D^-}(\lambda'') + \epsilon_{MD^+}(\lambda'')\langle a_{m^{2+}}(r)\rangle K_{th}}{\epsilon_{D^-}(\lambda') + \epsilon_{MD^+}(\lambda')\langle a_{M^{2+}}(r)\rangle K_{th}} \qquad (10)$$

where $\epsilon_i(\lambda)$ is the extinction coefficient for species i at wavelength λ, and K_{th} the thermodynamic equilibrium constant.

Calculation of the mean activity for Zn^{2+} in the cell demands simultaneous resolution of the modified Poisson-Boltzmann (eqs. 3–6) and of eq. 9, which expresses the local equilibrium between the ions D^-, Zn^{2+} and ZnD^+. For this purpose, we calculate first the thermodynamic equilibrium constant, in the Debye-Hückel approximation (eq. 5):

$$K_{th} = K_{app}\frac{\gamma_+(I_t)}{\gamma_-(I_t)\gamma_{2+}(I_t)} = K_{app}(\gamma_{2+}(I_t))^{-1} \qquad (11)$$

where I_t is the total ionic strength of the solution. Subsequently, we calculate anew the local equilibrium constant according to:

$$K(r) = K_{th}\gamma_{2+}(I(r)) \qquad (12)$$

where $I(r)$ is the local ionic strength (eq. 6).

We then resort to the following scheme: (α) we calculate the distribution of Na^+, Zn^{2+}, Cl^-, D^- and ZnD^+ from a numerical solution [11] of eqs. 3–6; (β) in each cylindrical crown we treat the local chemical equilibrium (eq. 9) with an equilibrium constant K as given by eq. 12. Calculation is repeated at step α until the difference between two consecutive results after step β becomes negligible. In practice, about five to ten iterations are sufficient to achieve self-consistency. Measurements are made for various Zn^{2+} concentrations at constant total ionic strength ($I_t = 5$ mM). The calculated curve of fig. 10 reproduces the experimental results for a dextran sulfate concentration of 1 mM extremely well.

One should note the deviation between the mean ionic activity for the divalent ion and its value at the edge of the cell. Indeed, any two-state model will lead to such overestimates of θ because such a treatment considers only noncondensed ions, i.e., ions which to all extents and purposes are equivalent to ions at the outer limit of the cell.

To sum up, our modification of the Poisson-Boltzmann equation can be generalized to any

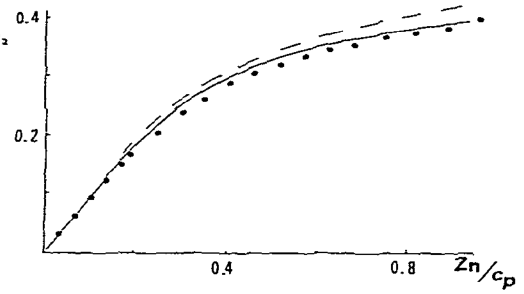

Fig. 10. Variation of Zn^{2+} activities in a solution of dextran sulfate ($\xi = 2.80$) [8] ($c_p = 1$ mM) as a function of the ratio $[Zn^{2+}]/c_p$ for a total ionic strength of $I_t = 5$ mM. ($\theta_2 = [Zn^{2+}]/c_p(1-(\gamma_{Zn^{2+}}/\gamma^0_{Zn}))$, where $\gamma^0_{Zn} = 0.745$). Comparison between our modified Poisson-Boltzmann model (———), and the experimental points. (·–·–·) Activity at the cell limit.

type of polyelectrolyte and it provides excellent determinations of the mean activities of various salts in the presence of a polyelectrolyte.

If the activity of counterions is compared according to various experimental methods, as discussed above, the overall agreement with our calculations is gratifying. Our model's major deficiency is the overestimate of the activity of the co-ion, which is greater than the experimental values. The Poisson-Boltzmann equation will always provide a co-ion activity higher than unity, due to electrostatic repulsion of that co-ion by the polyion. Perhaps it would be worthwhile in this respect to compare our empirical activity correction with other models which also incorporate interionic correlation [17,30], or interactions between polyions [31] neglected in the cell model.

Acknowledgments

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