

LIMITING LAWS AND COUNTERION CONDENSATION IN POLYELECTROLYTE SOLUTIONS V. FURTHER DEVELOPMENT OF THE CHEMICAL MODEL

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Counterion binding to polyelectrolyte chains is formulated as a chemical reaction $M^z(\text{free}) \rightarrow M^z(\text{bound})$. Expressions for the chemical potentials of free and bound counterions are set equal to obtain the reaction equilibrium. The results are equivalent to those in the previous paper of this series. An additional result obtained here is that a polyion holds its bound counterion layer with a strength on the order of 100 kcal/(mole cooperative unit). The method is then applied to the calculation of the polarizability along the chain due to the bound (condensed) counterions.

1. Introduction

In the previous paper of this series [1], hereafter referenced as IV, I developed a two-state theory for the problem of counterion binding in polyelectrolyte solutions. It represents a major advance over the earlier condensation theory, which essentially rested on one state for the counterions, the condensed state not having been treated at all. In a related approach, Iwasa, working independently, has pointed out that all the earlier results are recovered, while new applications have now become possible [2].

The purpose of this article is to recognize explicitly that the two-state model can be formulated as a chemical reaction,



where M^z is a z -valent counterion, the only counterion species present. The "bound" state is synonymous with the condensed state; it seems possible to use a more relaxed terminology now, both because the chemical model has eliminated the previously singular nature of the theory at non-zero concentrations and because a much larger segment than previously of the biophysical chemistry community has become

comfortable with the notion that a counterion can be bound to the polyion as a whole, in delocalized fashion, rather than necessarily being attached to discrete sites [1,3,4].

The problem will be analyzed as a special case of the modern thermodynamic theory of chemical reactions. An elegant presentation of the general theory may be found in the monograph by Kirkwood and Oppenheim [5]. Many familiar undergraduate textbooks of physical chemistry discuss chemical reactions from this point of view, and perhaps the present paper has been at least partially motivated by the desire to use a theory which I have often told my students is useful.

The system is identical to that treated in IV. In particular, I continue to assume the condition of excess simple salt. Conceived loosely, this condition means that the system under study is a single polyion immersed in a simple salt solution of molarity c_s . More precisely, $c_p \ll c_s$, where c_p is the equivalent polyion molarity. The limit $c_s \rightarrow 0$ is of central importance. In this context, it means that *both* c_p and c_s become small, with the former always remaining negligible compared to the latter. To understand fully the material in this paper, it will be necessary to have read IV previously.

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2. Chemical potentials of free and bound counterions

The reduced chemical potential of free M^z , that is, its chemical potential divided by RT , will be designated by μ_{free} ; the corresponding quantity for bound M^z , by μ_{bound} . One has

$$\mu_{\text{free}} = \ln(\nu c_s), \quad (2)$$

since simple salt of molarity c_s and ν moles of M^z ions per mole formula is present in excess ($\nu c_s \approx c_{M^z, \text{free}}$) and swamps out interaction of free M^z with the polyion. (More precisely, these interactions appear in μ_{free} only as higher-order terms in the small ratio c_p/c_s). I have departed from IV in setting the activity coefficient of free M^z equal to unity to be consistent with the neglect of analogous non-ideal effects for bound M^z ; similarly, the osmotic coefficient for the solution is taken here as unity.

The reduced chemical potential of bound M^z may be obtained by differentiating $\bar{g}_{\text{el}} + \bar{g}_a$ with respect to $|z|^{-1}r$, the number of moles of bound M^z per mole equivalent polyion. Recall that $1 - r$ is the charge fraction of the polyion, the fraction of its charge uncompensated by bound M^z . The symbol \bar{g} is the reduced Gibbs free energy per mole polyion equivalent; \bar{g}_{el} is the electrostatic free energy of the system, given by eq. (3) in IV, while \bar{g}_a is the ideal free energy of mixing of bound (associated) M^z and is given by eq. (11) in IV. The result is

$$\mu_{\text{bound}} = 1 + 2|z|\xi(1-r)\ln(1 - e^{-\kappa_s b}) + \ln(|z|^{-1}rV_p^{-1} \times 10^3), \quad (3)$$

Recall from IV that V_p is the volume (cm^3/mole polyion equiv) of the "bound" region; therefore the local molarity of bound M^z is

$$c_{\text{bound}} = |z|^{-1}r/10^{-3} V_p \quad (4)$$

The quantity μ_{bound} can accordingly be rewritten in conventional form as

$$\mu_{\text{bound}} = \mu_{\text{bound}}^0 + \ln \gamma_{\text{bound}} c_{\text{bound}}, \quad (5)$$

where

$$\mu_{\text{bound}}^0 = 1 \quad (6)$$

and

$$\gamma_{\text{bound}} = (1 - e^{-\kappa_s b})^{2|z|\xi(1-r)}. \quad (7)$$

This separation of μ_{bound} into a "standard state"

and an "activity" term follows the convention that μ_i^0 contain only terms independent of concentrations, while the activity coefficient γ_i contain all concentration-dependent factors other than c_i itself. Note that $\gamma_{\text{bound}} < 1$, signifying an effectively attractive interaction.

Since $\kappa_s \sim \sqrt{c_s}$, γ_{bound} tends to small values with c_s (the limit being understood in the sense described above). Non-singular thermodynamics would require that the corresponding limiting value of the activity coefficient be unity. The singular limit obtained here has its origin in the excellent approximation of neglecting polymeric end effects in the calculation of \bar{g}_{el} in eq. (3) of IV [6].

In the above expressions for μ_{free} and μ_{bound} , terms corresponding to translational free energy and to interaction of an isolated M^z ion with pure solvent have been left out. These terms are assumed to be identical for both states and therefore cancel when the difference $\mu_{\text{bound}} - \mu_{\text{free}}$ is formed in the next section. The physical meaning of equality of the translational terms is that M^z in the bound state is delocalized in a three-dimensional region of volume. The equality of the solvent-interaction terms means that M^z in the bound state has not been "desolvated". See refs. [1,3] for discussions of the applicability of this model.

3. Differential free energy of reaction and reaction affinity

A general chemical reaction may be symbolized as

$$\sum_i \nu_i A_i = 0, \quad (8)$$

where A_i is a reacting species and, by convention, the stoichiometric coefficient ν_i is positive for products and negative for reactants. The progress variable λ (also called the extent of reaction or degree of advancement) is defined by the differential relation,

$$d\lambda = \nu_i dn_i, \quad (9)$$

where n_i is the number of moles of species i , and, because of the constraint imposed on the system by eq. (8), $\nu_i dn_i$ is independent of i . By convention λ is zero at the beginning of the reaction, so

$$\lambda = \nu_i(n_i - n_i^0) \quad (10)$$

where n_i^0 is the number of moles of species i present initially. Note that λ is an extensive quantity.

The differential Gibbs free energy of reaction is defined by $(\partial G/\partial \lambda)_{T,P}$, and it is easily proved that

$$(\partial G/\partial \lambda)_{T,P} = \sum_i \nu_i \mu_i, \quad (11)$$

where μ_i is the chemical potential of species i . If μ_i is a reduced quantity, that is, if it is expressed in units of RT , then G must be so expressed also. The reaction affinity is defined by the right-hand side of eq. (11),

$$\tilde{\Delta\mu} = \sum_i \nu_i \mu_i. \quad (12)$$

The reaction affinity is equal, not only to $(\partial G/\partial \lambda)_{T,P}$, but also to the λ -coefficients of every other thermodynamic potential with their "natural variables" held fixed. Hence, under any reaction conditions, if $\Delta\mu$ at a given stage of the reaction is negative, the reaction will proceed spontaneously forward to give products; whereas, if $\Delta\mu$ is positive, the reaction will proceed in the reverse direction. The equilibrium point corresponds to $\tilde{\Delta\mu} = 0$.

In the present case reaction (1) is supposed to begin when no M^z counterions are bound, so λ is equal to the number of moles of bound M^z , or,

$$\lambda = |z|^{-1} n_p, \quad (13)$$

where n_p is the fixed number of polyion equivalents. Moreover,

$$\tilde{\Delta\mu} = \mu_{\text{bound}} - \mu_{\text{free}}, \quad (14)$$

or

$$\tilde{\Delta\mu} = \ln[(10^3 e/V_p) |z|^{-1} \nu^{-1} c_s^{-1} \times r(1 - e^{-\kappa_s b})^{2|z|\xi(1-r)}]. \quad (15)$$

If $\tilde{\Delta\mu}$ is set equal to zero for the equilibrium state, eq. (12) in IV is recovered.

It is convenient to begin any analysis of a difference in chemical potentials by consideration of the low-concentration limit, since it is there that useful limiting laws (mass action, Henry's law, Van 't Hoff's law, etc.) are obtained. For the present case, analysis of the limit $c_s \rightarrow 0$ (see Introduction for the definition of this limit) determines a unique choice of V_p in eq. (15). Since $\kappa_s^2 \sim c_s$, it is clear from eq. (15) that for any fixed value of V_p and sufficiently small c_s , $\Delta\mu$ is

Table 1

Polyion charge compensation r as a fraction of ionic strength in 1:1 salt

c_s (M)	$\kappa_s b$	r	$\Delta(\%)$
0.0001	0.0082	0.656	0.2
0.001	0.026	0.657	0.3
0.01	0.082	0.661	0.9
0.1	0.26	0.682	4.1
0.2	0.37	0.700	6.9
0.5	0.58	0.747	14.0
1.0	0.83	0.820	25.2

negative for $r < 1 - |z|^{-1}\xi^{-1}$ and positive for $r > 1 - |z|^{-1}\xi^{-1}$. In order that an equilibrium state exist in the limit $c_s \rightarrow 0$, therefore, V_p must be chosen so that the expression in brackets in eq. (15) equals unity when r is set equal to $1 - |z|^{-1}\xi^{-1}$ and the limit $c_s \rightarrow 0$ is taken. Eq. (13) in IV may be used for κ_s . The result for V_p is

$$V_p = 4\pi eL|z'|v^{-1}(\nu + \nu')(\xi - |z|^{-1})b^3, \quad (16)$$

where primed quantities refer to the coion. This expression for V_p coincides with that for V_p^0 in IV. Henceforth, V_p in eq. (15) is understood to be represented by eq. (16), which defines the bound region at finite concentration. (I am indebted to Professor M. Mandel for suggesting that the presentation in IV could have been made clearer by fixation of V_p along these lines.)

Let us now consider $\tilde{\Delta\mu}$, not in the limit $c_s \rightarrow 0$, but for concentrations satisfying the constraint

$$\kappa_s b \ll 1 \quad (17)$$

so that the linear approximation

$$1 - e^{-\kappa_s b} \approx \kappa_s b \quad (18)$$

is valid. With V_p given by eq. (16), it is then easily verified from eq. (15) and the general expression for κ_s given in IV that the reaction equilibrium determined by $\Delta\mu = 0$ occurs at

$$r = 1 - |z|^{-1}\xi^{-1} \quad (19)$$

For a degree of binding less than this value, $\tilde{\Delta\mu}$ is negative and the reaction proceeds spontaneously toward greater binding; for a degree of binding greater than this value, $\tilde{\Delta\mu}$ is positive and the reaction proceeds spontaneously in the direction of release of bound M^z .

As explained in IV, inequality (17) is consistent with moderately high ionic strengths, since b is quite small for typical polyelectrolyte chains. In table 1 I have compiled equilibrium values of r as a function of c_s for a 1 : 1 salt (so that c_s equals the ionic strength) and a syndiotactic vinylic chain with $b = 2.5 \times 10^{-8}$ cm. The corresponding value of the reduced charge density parameter ξ (from eq. (2) in IV) is 2.9. The value of V_p is calculated from eq. (16) to be 1221 cm^3 . The equilibrium value of r for $c_s \rightarrow 0$ is $1 - \xi^{-1} = 0.655$. For non-zero values of c_s , the value of r for which $\tilde{\Delta\mu} = 0$ is determined from eq. (15) by iteration. The column Δ is computed from $[r(c_s) - r(0)]/r(0)$ and represents the departure of r from its limiting value when $c_s \rightarrow 0$. For values of $\kappa_s b < 0.1$, r departs by less than 1% from its low-concentration limit. Even for $\kappa_s b$ almost equal to 0.5, the departure is only 7%. Thus r remains substantially constant for ionic strengths up to about 0.1 M. The slight, but systematic, tendency of r to increase with ionic strength has obscure significance at present, since theoretical inconsistencies become substantial at the same concentrations at which the increase in r becomes important [1], and direct charge-fraction measurements to date have not revealed a variation of r with concentration [1,5].

4. Integral free energy of reaction

To obtain the Gibbs free energy difference between any two stages of a reaction, neither of which necessarily corresponds to the equilibrium point, it suffices to integrate the differential free energy of reaction over the corresponding range of values of the progress variable.

$$\Delta G = \int_{\lambda_1}^{\lambda_2} (\partial G / \partial \lambda)_{T,P} d\lambda = \int_{\lambda_1}^{\lambda_2} \tilde{\Delta\mu} d\lambda. \quad (20)$$

Suppose we wish to know the amount of free energy lost when a polyion, initially prevented from binding M^z by a hypothetical barrier impermeable to M^z and located at the outer surface of the "bound" region V_p , is allowed to combine with its full complement of condensed counterions by removal of the barrier. The answer is

$$\Delta G = \int_0^{|z|\Gamma^{-1}(1-|z|\Gamma^{-1}\xi^{-1})} n_p \tilde{\Delta\mu} d\lambda \quad (21)$$

Table 2
Numerical results from eq. (22)

c_s (M)	$\kappa_s b$	$\Delta\bar{g}$
0.001	0.018	-10.6
0.01	0.056	-7.9
0.1	0.177	-5.3

where eqs. (13) and (19) have been used for the upper limit of integration, and $\Delta\mu$ as a function of λ is obtained by substituting eq. (13) for r into eq. (15). Integration yields,

$$\Delta\bar{g} = |z|^{-1} (1 - |z|^{-1} \xi^{-1}) \ln[(10^{-3} \nu |z| V_p c_s)^{-1} \times (1 - |z|^{-1} \xi^{-1})(1 - e^{-\kappa_s b})^{1+|z|\xi}] \quad (22)$$

where $\Delta\bar{g} = \Delta G / n_p$.

In table 2 I have listed values of $\Delta\bar{g}$ corresponding to several values of the ionic strength c_s for a 1 : 1 salt. The parameter b has been chosen as 1.7×10^{-8} cm, the value appropriate to the structure of native DNA. Corresponding values of ξ and V_p are 4.2 and 646 cm^3 , respectively. To assess the meaning of these values of $\Delta\bar{g}$, recall first that ΔG was defined as a free energy reduced by division by RT . Hence, at 0.1 M ionic strength at 25°C the binding free energy for the condensed counterion layer is about 3.2 kcal/(mole DNA equiv). A segment of about 20 base pairs, or 40 phosphates, is needed to attain full polyelectrolyte properties [7]. Therefore, each polyionic segment of DNA holds its bound layer of counterions with a strength of about 130 kcal, a figure comparable to the hydration free energy of a small ion or to the strength of a covalent bond. The complex formed by a polyionic chain and a layer of mobile, hydrated counterions is highly stable!

5. Polarizability of condensed counterions

The present method can easily be applied to a long-standing problem in polyelectrolyte theory, the calculation of the contribution of counterions to the electric polarizability of polyionic chains [4,8-10]. I shall derive an expression for the contribution of condensed counterions to the low-field, static (equilibrium) polarizability α_i in the direction parallel to the axis of the linear array of charges that models the polyion.

Suppose that an externally applied electric field E

is oriented parallel to the polyion axis. The reduced chemical potential of condensed counterions, as given by eq. (3), must be supplemented by a potential energy term $-zqEl/kT$, with q the protonic charge and l a distance coordinate along the polyion axis with respect to an arbitrary origin. The quantity r , a measure of the local concentration of bound counterions, now becomes dependent on l . At equilibrium, the chemical potential itself, however, must be independent of l ; hence, the total derivative of μ_{bound} with respect to l may be set equal to zero. The result of performing this operation is,

$$(dr/dl)[1 - 2|z|\xi r(l) \ln(1 - e^{-\kappa_s b})] = zqr(l)E/kT. \quad (23)$$

To get the linear response, it suffices to replace $r(l)$ in eq. (23) by its value r_0 at the origin $l = 0$, since departures of r from uniformity are $O(E)$. With this substitution and subsequent integration from $l = 0$ to an arbitrary value of l , eq. (23) yields,

$$r(l) = r_0 + (zqr_0El/kT)[1 - 2|z|\xi r_0 \ln(1 - e^{-\kappa_s b})]^{-1}. \quad (24)$$

Suppose now that the linear array of fixed charges has length L , where L is assumed to be sufficiently long to justify the neglect of end-effects implicit in eqs. (23) and (24). Let us consider the dipole moment m with respect to an origin chosen at the center of the array [10]. Being symmetrically disposed about this origin, the fixed charges themselves contribute nothing to the moment. In length dl at l , the charge contributed by condensed counterions is $zq|z|^{-1} \times rb^{-1}dl$, where b is the fixed-charge spacing. Therefore,

$$m = (zq/|z|b) \int_{-L/2}^{L/2} lr(l)dl. \quad (25)$$

Moreover, the polarizability is defined by

$$\alpha_{\parallel} = m/E. \quad (26)$$

Eqs. (24)–(26) then yield,

$$\alpha_{\parallel} = (|z|q^2r_0L^3/12kTb) \times [1 - 2|z|\xi r_0 \ln(1 - e^{-\kappa_s b})]^{-1}. \quad (27)$$

To use this formula, r_0 must be determined. This value of r characterizes the chemical potential of bound counterions in a segment dl centered on $l = 0$. Since the field has the effect of adding a term proportional to El to the r.h.s. of eq. (3), the chemical potential at $l = 0$ has the same form as the chemical potential for the field-free case. Therefore r_0 satisfies the condition $\Delta\mu = 0$, where $\Delta\mu$ is given by eq. (15). Table 1, with r replaced by r_0 , provides a numerical illustration for a special case. Since r_0 is the uniform value of r for the field-free case, it follows that

$$n = |z|^{-1}r_0b^{-1}L, \quad (28)$$

where n is the total number of counterions bound to the polyion at zero applied field. Substitution into eq. (27) yields,

$$\alpha_{\parallel} = (z^2q^2nL^2/12kT)[1 - 2|z|\xi r_0 \ln(1 - e^{-\kappa_s b})]^{-1}. \quad (29)$$

Eq. (29) has the same form as Mandel's classical result [8–10], but with two differences. Here, the number of bound counterions n is determined theoretically. Moreover, the factor in brackets, which contains an explicit ionic-strength dependence, does not appear in the Mandel formula. Note that the polarizability of the condensed counterions decreases as the ionic strength decreases, a behavior that reflects the increasing stability (resistance to distortion) of the field-free charge fraction as portrayed, for example, in table 2. If ineq. (17) is satisfied as is the case for many systems of practical interest, then r_0 satisfies eq. (19), the exponential can be linearized, and eq. (29) becomes

$$\alpha_{\parallel} = (z^2q^2nL^2/12kT)[1 - 2(|z|\xi - 1) \ln \kappa_s b]^{-1}, \quad (30)$$

where

$$n \approx |z|^{-1}(1 - |z|^{-1}\xi^{-1})b^{-1}L, \quad (31)$$

and b , for a real chain, is the axial length L divided by the total number of fixed-charge groups (phosphates for DNA).

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