

Electronic Supplementary Information

Theory and quantitative assessment of pH-responsive polyzwitterion-polyelectrolyte complexation

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1 Probabilities of zwitterion states derivation

Recalling the Helmholtz free energy expression $F = E - TS$, we will need the internal energy E and entropy S of the system. S is given by the Gibbs entropy formula, $S = -k_B \sum_i \mathbb{R}_i \ln \mathbb{R}_i$. The internal energy of each state is characterized by electrostatic interactions, and it follows that E is given by weighted sum of each state's internal energy E_i and probability \mathbb{R}_i , such that

$$\frac{F}{k_B T} = \sum_i \left[\frac{\mathbb{R}_i E_i}{k_B T} - \mathbb{R}_i \ln \mathbb{R}_i \right]. \quad (1.1)$$

In states B-D, there are no electrostatic interactions as they have at most one charge present. However, for state A, since two charges, one negative and one positive, are present, we can use Coulomb's law to determine the electrostatic interaction energy of two oppositely charged point charges separated by distance p_1 , the dipole length of the zwitterion, as

$$E_A = -\frac{e^2}{4\pi\epsilon_o\epsilon} \frac{1}{p_1}, \quad (1.2)$$

Recalling that E_B , E_C , and E_D are zero, and plugging in the corresponding values of E_A and S determined above, we see that

$$\frac{F}{k_B T} = -\mathbb{R}_A \frac{e^2}{4\pi\epsilon_o\epsilon} \frac{1}{k_B T} \frac{1}{p_1} + \mathbb{R}_A \ln \mathbb{R}_A + \mathbb{R}_B \ln \mathbb{R}_B + \mathbb{R}_C \ln \mathbb{R}_C + \mathbb{R}_D \ln \mathbb{R}_D. \quad (1.3)$$

Realizing that the first term in the above equation contains the definition for Bjerrum length, ℓ_B , the equation simplifies to

$$\frac{F}{k_B T} = -\mathbb{R}_A \frac{\ell_B}{p_1} + \mathbb{R}_A \ln \mathbb{R}_A + \mathbb{R}_B \ln \mathbb{R}_B + \mathbb{R}_C \ln \mathbb{R}_C + \mathbb{R}_D \ln \mathbb{R}_D. \quad (1.4)$$

To solve Eq. 1.4 in terms of \mathbb{R}_A , three additional constraints that relate the probabilities of each state to one another, and additionally, relate them to the parameters and conditions of our system, namely the pH. Thankfully, these additional constraints are not particularly challenging to derive. To

begin, we know that the sum of the probabilities must equal unity, since the zwitterion can only occupy one of these four states. Next, we know that all the positive charge associated with the zwitterion must be found in states A and C, and that the total fraction of positive charges on the zwitterion is defined by α_+ . Finally, using a similar argument, all the negative charges on the zwitterion must occupy either state A or B, and thus the probabilities \mathbb{R}_A and \mathbb{R}_B must add to $|\alpha_-|$. These constraints are summarized in Eq. 10 of the main text.

By rearranging and plugging in the above constraints to Eq. 1.4, we get

$$\begin{aligned} \frac{F}{k_B T} = & -\mathbb{R}_A \frac{\ell_B}{p_1} + \mathbb{R}_A \ln \mathbb{R}_A + (|\alpha_-| - \mathbb{R}_A) \ln(|\alpha_-| - \mathbb{R}_A) \\ & + (\alpha_+ - \mathbb{R}_A) \ln(\alpha_+ - \mathbb{R}_A) + (1 + \mathbb{R}_A - \alpha_+ - |\alpha_-|) \ln(1 + \mathbb{R}_A - \alpha_+ - |\alpha_-|). \end{aligned} \quad (1.5)$$

By minimizing the above expression with respects to \mathbb{R}_A , a closed-form expression for \mathbb{R}_A can be obtained,

$$\frac{1}{k_B T} \frac{\partial F}{\partial \mathbb{R}_A} = 0 = -\frac{\ell_B}{p_1} + \ln(\mathbb{R}_A) - \ln(|\alpha_-| - \mathbb{R}_A) - \ln(\alpha_+ - \mathbb{R}_A) + \ln(1 + \mathbb{R}_A - \alpha_+ - |\alpha_-|). \quad (1.6)$$

Rearranging, we see that

$$\frac{(\mathbb{R}_A)(1 + \mathbb{R}_A - \alpha_+ - |\alpha_-|)}{(\alpha_+ - \mathbb{R}_A)(|\alpha_-| - \mathbb{R}_A)} = e^{\ell_B/p_1}. \quad (1.7)$$

The expression above can be solved analytically to yield the closed-form expression for \mathbb{R}_A in terms of physically relevant parameters,

$$\begin{aligned} \mathbb{R}_A = & \frac{1}{2(e^{\ell_B/p_1})} \left[1 + (\alpha_+ + |\alpha_-|)(e^{\ell_B/p_1} - 1) \right. \\ & \left. - \sqrt{(1 + (\alpha_+ + |\alpha_-|)(e^{\ell_B/p_1} - 1))^2 - 4\alpha_+|\alpha_-|e^{\ell_B/p_1}(e^{\ell_B/p_1} - 1)} \right]. \end{aligned} \quad (1.8)$$

From here, the values for \mathbb{R}_B , \mathbb{R}_C , and \mathbb{R}_D can be solved using Eq. 10 of the main text.

If the free energy of each state was identical, and thus equally energetically favorable, the probability distributions (w.r.t. pH) would be straightforwardly defined by α_+ and α_- like such

$$\begin{aligned} \mathbb{R}_{A,unweighted} &= \alpha_+|\alpha_-|, \\ \mathbb{R}_{B,unweighted} &= (1 - \alpha_+)|\alpha_-|, \\ \mathbb{R}_{C,unweighted} &= \alpha_+(1 - |\alpha_-|), \\ \mathbb{R}_{D,unweighted} &= (1 - \alpha_+)(1 - |\alpha_-|). \end{aligned} \quad (1.9)$$

It is useful to mention that our Boltzmann-weighted definitions for the zwitterion state probabilities decompose to Eq. 1.9 when all states are equally energetically favorable. Using a simple scenario in which $E_i = 0$ for all i , we see that the right-hand side of Eq. 1.7 becomes 1. Rearranging, it is apparent that we recover the limiting case in which \mathbb{R}_i is independent of the energetics of each state.

2 Derivation of the degrees of ionization

The definition for α_- can be determined by considering a general chemical equation for an acid, AH, and its conjugate base, A^- , in equilibrium and the Henderson-Hasselbalch equation,



The acid dissociation constant, K_a , can be estimated using

$$K_a = \frac{[A^-][H^+]}{[AH]}. \quad (2.2)$$

The fraction of available negatively charged groups to total number of negative moieties is the general definition for α_- ,

$$\alpha_- = \frac{[A^-]}{[A^-] + [AH]}. \quad (2.3)$$

Rearranging Eq. 2.2, substituting into Eq. 2.3, and taking H^+ as $10^{-\text{pH}}$, we arrive at

$$\alpha_- = \frac{1}{1 + 10^{\text{p}K_a - \text{pH}}}. \quad (2.4)$$

Considering α_- determines the negative charge density of the polyzwitterion, we prepend a negative sign to the above definition to reach our final equation (Eq. 11 of the main text).

The definition for α_+ can be reached by considering a general chemical equation for the condensation of a small negative salt ion onto the positively charged group of the zwitterion,



where N^+ is the positive moiety, R is the zwitterion in which N^+ inhabits, and X^- is a negative salt ion. K_{salt} is defined as

$$K_{\text{salt}} = \frac{[\text{NX}]}{[\text{N}^+][\text{X}^-]}. \quad (2.6)$$

It follows that α_+ , the fraction of available positively charged groups to the total number of positive moieties, can be generally described as

$$\alpha_+ = \frac{[\text{N}^+]}{[\text{N}^+] + [\text{NX}]}. \quad (2.7)$$

Rearranging Eq. 2.6, plugging it into Eq. 2.7, and taking X^- as $10^{-\text{pH}}$, since the only ions added to our system are in the form of a strong acid such as HCl, we arrive at our definition for α_+ ,

$$\alpha_+ = \frac{1}{1 + K_{\text{salt}} \times 10^{-\text{pH}}}. \quad (2.8)$$

3 Phase behavior constraint equations

The incompressibility condition for phase A is

$$\phi_{1,A} + \phi_{2,A} + \phi_{+,A} + \phi_{-,A} + \phi_{0,A} = 1. \quad (3.1)$$

where $\phi_{i,j}$ refers to the volume fraction of species i of phase j . Analogously, for phase B, the incompressibility constraint is

$$\phi_{1,B} + \phi_{2,B} + \phi_{+,B} + \phi_{-,B} + \phi_{0,B} = 1. \quad (3.2)$$

The electroneutrality condition for phase A is

$$\phi_{+,A} = \phi_{-,A}. \quad (3.3)$$

Finally, the four lever rules to solve the remaining variables are

$$\begin{aligned} \phi_{1,A} + (1-x)\phi_{1,B} &= \phi_1, \\ \phi_{2,A} + (1-x)\phi_{2,B} &= \phi_2, \\ \phi_{+,A} + (1-x)\phi_{+,B} &= \phi_+, \\ \phi_{-,A} + (1-x)\phi_{-,B} &= \phi_-. \end{aligned} \quad (3.4)$$