The osmotic coefficient of rod-like polyelectrolytes including counterion adsorption

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Abstract
To describe data for the osmotic coefficient of poly(p-phenylene), a rodlike polyelectrolyte, the Poisson-Boltzmann cell model has previously been used assuming that all counterions are released from the polyelectrolyte chains. Though the trend in the data could be reproduced, a quantitative fit was not achieved.

Here we argue that a quantitative fit can be achieved within the PB cell model when, instead of assuming that each monomer unit is fully charged, we consider that not all counterions desorb from the polymer chain (or equivalently, that counterions can re-adsorb). This aspect is included self-consistently using the well-known Langmuir type of adsorption isotherm that includes the energy of counterion adsorption, \( \Delta \mu_0 \), as well as the entropy related to the two states of the monomer. Using the “counterion adsorption theory” the fit to the data can be much improved, and for one data set (of the two in total) an exact description is even obtained.

Theory
Like in ref. 3 we use a cylindrical Poisson-Boltzmann (PB) cell model based on

\[
\frac{1}{r} \frac{d}{dr} \left( r \frac{dy}{dr} \right) = \kappa^2 \sinh y
\]

where the Debye length, \( \kappa^{-1} \), is given by

\[
\kappa^2 = \frac{2c_\infty e^2}{\varepsilon kT}
\]

where \( c_\infty \) is the ionic strength in m\(^{-3}\), which follows from the ionic strength in mM=mol/m\(^3\) times Avogadro’s number, \( N_{av} \). The ionic strength is defined in the polymer-free reference phase. We combine Eq. (1) with boundary conditions at the edge, \( E \), of the cell,

\[
\frac{dy}{dr} = 0
\]

and at the “surface” of the polyelectrolyte rod (\( r=R \))

\[
\frac{\lambda^* e}{2 \pi R} = \frac{\lambda \alpha e}{2 \pi R} = -\frac{e kT}{\varepsilon} \frac{dy}{dr}
\]

with \( \lambda^* \) the line charge density, which is \( \lambda \) times \( \alpha \), with \( \lambda \) the monomer line density (equal to \( 1/a \), with \( a \) the distance between monomer units along the polymer backbone) and \( \alpha \) the ionization degree of each monomer (the fraction of monomers that has released its counterion). Eq. (4) translates into

\[
\frac{2 \lambda \alpha}{R} \lambda_b = \frac{dy}{dr}.
\]
The ionization degree $\alpha$ can be related self-consistently to the dimensionless electrostatic potential at the polymer backbone (where $r=R$), $y_R$, following a classical derivation based on chemical equilibrium. We consider the chemical “reaction” between the positive polyelectrolyte groups, denoted by N, and the counterions, C (which are anions in our case), which together form a “surface complex”, NC. At equilibrium the chemical potential of the reactants equals that of the product:

$$\mu_N + \mu_C = \mu_{NC}$$

which, based on Langmuir entropy, and including electrostatic potentials, can be developed into

$$\mu_{N,0} + \ln \alpha + y_R + \mu_{C,0} + \ln c_{C,R} - y_R = \mu_{NC,0} + \ln(1-\alpha)$$

where $c_{C,R}$ is the concentration of counterions near the backbone (at $r=R$). Eq. (7) translates into

$$\ln \frac{\alpha}{1-\alpha} + \ln c_{C,R} = \mu_{NC,0} - \mu_{C,0} - \mu_{N,0} = \Delta \mu_{ads}$$

where $\Delta \mu_{ads}$ is the increase in energy when a counterion adsorbs (release when it desorbs).

In principle the problem can be solved self-consistently if we know the total number of all the ions in the system exactly, as well as the system size. However, when such information is absent, it is very useful to assume first of all a certain background ionic strength (just as in ref. 3), and secondly assume that all anions are the same, or at least have the same adsorption energy, $\Delta \mu_{ads}$. Then, the chemical potential of the counterion follows directly from the ionic strength, namely $\mu_C = \ln(c_\infty)$ and Eq. (8) becomes

$$\alpha = \frac{1}{1 + \exp\{y_R - \Delta \mu_{ads} + \ln c_\infty\}}.$$  

(9)

Because $c_\infty$ will be treated as a constant for each data set (just as in ref. 3), we can combine it with $\Delta \mu_{ads}$, resulting in the effective ion adsorption energy, $\Delta$. The following simple relation between effective charge per monomer, $\alpha$, and the potential at the polyelectrolyte backbone, $y_R$, then results,

$$\alpha = \frac{1}{1 + e^{-\Delta}}.$$  

(10)

Note that though Eq. (10) looks simple, it contains the energy of counterion adsorption, as well as the entropy related to the two possible states of the Et$_3$N$^+$-monomer (charged, and uncharged). Note also that the reduction in polymer charge considered in Eq. (10) is not Manning condensation (which we include by using the full PB-equation), but binding due to a chemical affinity of an ion to the polymer backbone (combined with an entropy effect related to the two states of the surface groups).

Finally, we must consider that in the cell model, the cell outer radius, $E$, is given by

$$E = \frac{R}{\sqrt{c_m v_m}}$$

(11)

with $c_m$ the concentration of monomers and $v_m$ the monomer volume.

The osmotic coefficient $\phi$ is given by $\Pi/\Pi_0$ which is

$$\phi = \frac{\Pi}{\Pi_0} = \frac{2c_\infty}{\Pi_0} \frac{\cosh y_E - 1}{c_m}$$

with $y_E$ the dimensionless electrostatic potential at the edge of the cell, and $\Pi_0$ based on the entropy of the counterions, assuming a full dissociation of the polyelectrolyte; thus it equals $c_m$. 

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Results and Discussion

Like in ref. 3 we describe the poly(p-phenylene) polyelectrolyte as linear rods of radius $R=0.7$ nm (which includes the closest approach distance of the ions). The Bjerrum length is $\lambda_B=0.731$ nm (at 40 °C) and the monomer length (along the stretched backbone) is $a=0.215$ nm, which translates into $\lambda=4.65$ nm$^{-1}$. The volume per monomer is $V_m = \lambda^{-1} \cdot \pi \cdot R^2 = 0.215 \cdot \pi \cdot 0.7^2 = 0.33$ nm$^3$.

For a fully dissociated backbone (no ion adsorption), when $\alpha=1$, the present cell model calculations exactly match those of Fig. 2 of ref. 3 (where results are presented for an ionic strength of 2 µM which corresponds to a Debye length of $\kappa^{-1}=213$ nm; and for 20 µM which corresponds to $\kappa^{-1}=67.25$ nm), see Figure 1 (dashed lines).

Use of the ion re-adsorption model, Eq. (10), gives a much improved fit to the data, especially for chlorine (open circles), see Figure 1. For the data with iodine as counterion (full circles), we use the same value for $\kappa^{-1}$ as assumed in ref. 3. By adjusting $\Delta$, the fit to the data can be improved significantly, but a quantitative fit is not obtained. Under these conditions, the ionization degree is of the order of $\alpha=0.40$ (dependent on the polyelectrolyte concentration, $c_m$). For the data with chlorine as counterion, a quantitative fit can be obtained by using a somewhat higher Debye length than used in ref. 3 (namely, $\kappa^{-1}=80$ nm, which corresponds to $c_\infty=14.1$ µM). In this case, the ionization degree is about $\alpha=0.30$.

Conclusions

The PB-cell model can be adjusted to include the possibility of counterion adsorption. A simplified expression is presented to account for that, with only a single free parameter, the ion adsorption strength.

The concept of ion re-adsorption is different from Manning condensation which is only a simplification of the PB-equation. Instead, ion re-adsorption is due to the entropy related to the two states of the monomers (charged, uncharged) as well as to the energy related with ion adsorption.

Using the cell model including ion re-adsorption, the fit to the data for the linear rod-like polyelectrolyte poly(p-phenylene)$^{1,3}$ can be much improved. In case of the chlorine as counterion, a quantitative fit can even be obtained.
References


Figure 1. Osmotic pressure coefficient, $\phi$, vs. polyelectrolyte monomer concentration, $c_m$. Data points from ref. 3 (full circles: iodine as counterion; open circles: chlorine). Dashed lines: cylindrical Poisson-Boltzmann cell model without ion re-adsorption, thus $\alpha=1$, see ref. 3. Solid lines include ion re-adsorption. Ionic strength, $c_\infty$, is given with dimension $\mu$M; $\Delta$ is the adsorption energy, see Eq. (10).