Macromolecules **2007,** *40,* 731−738

Osmotic Coefficient Calculations for Dilute Solutions of Short Stiff-Chain Polyelectrolytes

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Received September 19, 2006; Revised Manuscript Received November 23, 2006

ABSTRACT: Osmotic properties of dilute salt-free solutions of stiff-chain polyelectrolytes are studied using computer simulations. A number of factors affecting the charge distribution around the macroions are analyzed quantitatively for parameters of an aqueous solution of a typical synthetic strongly charged rodlike polyelectrolyte. Departing from a mean-field treatment of an infinitely long linear charged rod, we significantly refine the model description. We found that incorporation of effects such as electrostatic correlations between counterions, chain flexibility, and addition of salt decreases the osmotic coefficient slightly. On the other hand, a model of a finite macroion with a noncentral charge distribution predicted significantly higher pressure. We quantify all these contributions separately and show what deviation one should expect from the prediction of the Poisson−Boltzmann solution of the infinite rod cell model. We further comment on the discrepancy between our simulation results and experimentally measured values.

I. Introduction

Strongly charged rodlike polyelectrolytes are an ideal model system to study the phenomenon of counterion condensation in dilute solutions. Unlike flexible-chain polyelectrolytes, they do not change their conformation upon changing the polymer concentration or adding salt. In a polar solvent, such macromolecules dissociate into highly charged rodlike macroions and oppositely charged counterions. If no salt is added, bulk properties of such solution directly depend on the distribution of the counterions which is defined by a delicate balance between electrostatic interactions and the translational entropy. While all counterions equally explore space, they can be hypothetically divided into two groups. Those counterions close to the macroion and localized by strong Coulombic forces are often considered as *condensed*,[1,2] whereas the others are *free* and osmotically active. This qualitatively explains why the experimentally measured osmotic pressure Π of such a system is far lower than the one predicted by assuming that all counterions are free. The reduced thermodynamic activity of the counterions can be expressed in terms of the osmotic coefficient

$$\phi = \frac{\Pi}{\Pi_{\mathrm{id}}} \tag{1}$$

where $\Pi_{\mathrm{id}} = c_c k_B T$ is the ideal gas pressure at given counterion concentration c_c and temperature T, and k_B is the Boltzmann constant. Experimental studies of strongly charged polyelectrolytes show that ϕ is a weak function of polymer concentration, and typically measured values are of the order of 0.2−0.3 for univalent counterions in the dilute regime; i.e., see references in ref 3. Similar values of the osmotic coefficient are also obtained within a Katchalsky cell model[4] by solving the Poisson−Boltzmann (PB) equation in cylindrical geometry.[5] Within this approach the counterion and polymer degrees of freedom in the solution are decoupled by considering only one fixed and completely rigid macroion confined together with its counterions in an electrically neutral cell. A further assumption, namely that the macroion is infinitely long, allows for an analytical solution of this system at zero salt.[6,7] Compared to a bulk polyelectrolyte solution, a mean-field (mf) assumption is employed twice in the standard PB approach: once, by decomposing the solution into a product of noninteracting cells, and posing only the problem of one macroion confined to a surrounding cell, and second, by employing the PB functional to find the counterion distribution within this cell. The first mf approximation can only be tested for finite-length charged rods, since in a solution all polyelectrolytes are of finite length. To this end we introduced recently an optimal cell model[8] showing that in this context the mf approximation works excellently from dilute up to semidilute conditions but that the differences induced by the *finiteness* can really become large for short rods. Recent theoretical and simulation studies of dilute polyelectrolytes also confirmed the validity of the cell model approximation provided an appropriate cell geometry is used.[9,10] The second mf assumption of applying the PB equation is known to be a good approximation only for a moderately charged rod in the presence of monovalent counterions (see references cited in refs 11 and 12).

If discrepancies are observed with either experiments or simulations, it is far from obvious to which degree they are due to the first and/or second mean-field approximation. Under experimental conditions there are a number of other factors that may affect the osmotic properties in various ways. These include electrostatic, excluded volume, and macroion−macroion correlations, residual salt, chain flexibility, backbone charge distribution, and nonelectrostatic interactions between the counterions and the backbone. It is one of the goals of this article to quantify the contribution of the above effects separately. In a previous study[5] we compared the influence of electrostatic correlations within the infinite-rod cell model and found them to only weakly influence the osmotic coefficient—they yielded a lower value on the order of a few percent. Experimentally measured values of the osmotic coefficient were still about 10% lower. This motivated us to investigate which variations of the

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10.1021/ma062179p CCC: $37.00

model are necessary to improve the comparison with the experiments.

The osmotic properties of a bulk polyelectrolyte solution can also be described by models that include many-body effects, for example those of refs 13−18. Using the idea of a "two state" model of condensed and free counterions and introducing additional approximations (random phase approximation, a Debye-Hückel approximation, etc.), such theories also have a limited scope of application. As a rule, there is no quantitative agreement when the experimental parameters are used within these theories. Similarly to the cell model, the predicted pressure is often higher than the experimental data. On the other hand, the agreement between the theoretical prediction and the simulation data seems to be better, which is yet another motivation to revise the simple models used before and to incorporate more details in order to describe the experimental systems better.

One of the common arguments to explain the difference between the osmotic pressure measured experimentally and calculated theoretically is that the solvent cannot be taken as a uniform dielectric background. Solvent-mediated interactions have been extensively studied recently by computer simulation employing explicit solvent models.[19−21] For example, in a study on the potential of mean force between a simple Na−Cl electrolyte it has been shown that this assumption seems to be rather well justified[22,23] for the osmotic pressure. Some changes can be expected in regions where the ion concentration is high, i.e., close to the macroion. At such separations the solvent properties come into play on a molecular level and can lead to a lowering of the local relative dielectric constant[22] up to a factor of 2 if the salt concentration is of the order of 1 M or higher. Investigations in this direction are, however, out of the scope of the present study and hence will not be further considered here.

Not only simulations and theory face difficulties, but also experimental osmotic measurements by membrane osmometry have the drawback that they are affected by polydispersity, impurities, and the unavoidable presence of residual salt in the pure water cell, which makes the results difficult to compare to the simulation data, especially at low polymer concentrations. While the presence of salt can be taken into account theoretically by assuming a Donnan equilibrium, the quality of the sample and its solubility are crucial in osmotic measurements.

While the complexity of a real system makes it difficult to distinguish between different contributions to the experimentally observed osmotic coefficient, simulation allows us to assess the specific size of each contribution within a given model, and more important, we can make a direct comparison to the experimental data. In this paper we perform a systematic analysis of different effects influencing the counterion distribution in a polyelectrolyte solution by comparing results derived from different models. As a reference system we use a water solution of synthetic rodlike poly(*p*-phenylene) (PPP) polyelectrolyte which has been the subject of a number of investigations recently.[3,5,24,25] Unlike short DNA fragments which require a certain salt concentration to prevent their denaturation,[26,27] the conformation of PPP polyelectrolyte is not affected by the presence of salt. Its fully aromatic backbone exhibits an excellent chemical stability and retains its linear conformation when the polymer concentration is changed. A relatively high persistence length of ∼22 nm and excellent solubility in water make this system appealing for experimental study.

The remainder of this paper is organized as follows. Section II describes the different models which are used for predicting the osmotic properties of a polyelectrolyte solution and some of the employed methodology. The qualitative and quantitative effects of various modifications of the underlying model and inclusion or exclusion of different factors affecting osmotic properties are discussed in section III. This is followed by a general summary and conclusions in section IV.

II. Polyelectrolyte Models

The parameters of PPP polyelectrolytes are well-defined experimentally and can be used within a number of model systems to asses their applicability for the study of certain physical properties. Here we concentrate on how well different models of a polyelectrolyte solution can predict osmotic pressure, in particular its concentration dependence in the dilute regime.

A. Cell Model. Infinite Rod. Within a cell model approach the distribution of counterions around one macroion is considered to be independent of the presence of other macroions in the solution. This approximation should work well when the macroion−macroion correlations are weak and do not contribute significantly to such macroscopic properties as, for example, pressure. The cell boundaries are given by hard wall constraints which serve merely to impose the polyelectrolyte concentration. It is common practice to neglect the end effects and study an infinitely long macroion confined to a cylindrical cell of radius R, where the shape of the cell is fixed by symmetry considerations. This approach makes sense if the length of macroions is larger than the average distance between them, i.e., in the semidilute regime, but then macroion−macroion correlations might no longer be negligible. The first mf assumption of the cell model is best when the concentration is low, but then end effects can no longer be neglected. The situation improves greatly if some added salt is present in the solutions since then the associated screening diminishes both macroion−macroion correlations and end effects. The macroion is modeled as a cylinder of radius r_0 carrying a uniform linear charge λ. The strength of the electrostatic interactions is given by Bjerrum length

$$l_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T} \tag{2}$$

which sets the distance at which the interaction between two unit charges e is equal to the thermal energy k_BT. In the PB approximation the counterions are treated as an ideal gas interacting with a mean-field electrostatic potential $\psi(r)$. The counterion density, $\rho(r)$, depends only on cylindrical coordinate r and can be found from the PB equation

$$\left(\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr}\right)\psi(r) = -\frac{e}{\epsilon}\rho(R)\exp\left(-\frac{e\psi(r)}{k_BT}\right) \tag{3}$$

supplemented by the obvious boundary conditions for the electrostatic potential:

$$\left(\frac{d\psi(r)}{dr}\right)_{r=r_0} = -\frac{\lambda}{2\pi r_0\epsilon};\quad \left(\frac{d\psi(r)}{dr}\right)_{r=R} = 0 \tag{4}$$

Here ϵ is the dielectric constant of the solvent and $\psi(r)$ is assumed to be zero at the cell surface. It is convenient to introduce the dimensionless charge parameter $\xi = \lambda l_B/e$, also known as Manning parameter, which measures the number of elementary charges on the macroion per Bjerrum length. We shall only be interested in the case of strongly charged polyelectrolytes for which $\xi > 1$.

The osmotic pressure can be calculated by the contact theorem[28] as $\Pi = k_BT\rho(R)$, and the osmotic coefficient turns out to be given by

$$\phi = \frac{1+\gamma^2}{2\xi} \tag{5}$$

where γ is the numerical solution of the transcendental equation

$$\arctan\left(\frac{\xi-1}{\gamma}\right) + \arctan\left(\frac{1}{\gamma}\right) = \gamma \ln\left(\frac{R}{r_0}\right) \tag{6}$$

In the limit of infinite dilution, when R is much larger than r_0, γ is negligibly small, and the osmotic coefficient logarithmically approaches the Manning limit of $1/2\xi$.

The PB method that can also be derived from a density free energy functional does not take into account counterion–counterion interactions. However, the counterions are charged, and their positions, especially in the dense region close to the macroion, are strongly correlated. It was shown previously[29] that one can add an extra term to the PB free energy expression[29] that can approximately account for these neglected correlations. The density profile can then be found by minimizing this modified functional. Other approaches for improved treatments are integral equations[30−33] and field theoretic strong coupling approaches.[34,35]

Alternatively, the effect of the counterion correlations can also be assessed directly in computer simulations. Explicit calculation of all interactions between the counterions, modeled as point charges or charged hard spheres, and simulation of a 1D periodic system analogous to the infinitely long cell will give the sought counterion distribution. For this purpose we used molecular dynamics simulations employing the MMM1D algorithm[36] included in the soft matter simulation package ESPResSo.[37]

B. Cell Model. Finite Rod. The end effects neglected within the usual PB treatment become important at low polymer concentrations and short polymer chain lengths. These criteria apply for PPP polyelectrolytes whose typical degree of polymerization used in experiments in ref 3 was about 40, and the osmometric data were taken at rather low concentrations. The volume of the cell is fixed by polymer concentration c_p at $1/c_p$, but its shape has to be defined through some assumptions, like symmetry or free energy considerations. In a very dilute solution, the cell might be assumed to be spherical[10] though, as the polymer concentration increases, this approach breaks down before reaching the semidilute regime. Nevertheless, a nice analytical solution for an infinite rod that is not completely neutralized by counterions can be employed to compute osmotic coefficients for effectively finite rods.[10] Recently, we proposed a cylindrical cell with adjustable geometry[8] which proved to predict osmotic properties of strong polyelectrolytes in a wide range of concentrations and even in the semidilute regime. Figure 1 illustrates such a cell whose aspect ratio is adjusted to provide a minimum free energy configuration. Analogous to the spherical cell, the pressure inside the cylindrical cell is given by

$$\Pi_{\mathrm{cell}} = \rho_S k_B T \tag{7}$$

where ρ_S is the average counterion density at the cell surface. There is no known analytical solution for either a spherical or a cylindrical cell containing a finite rodlike macroion, and the charge distribution has to be found either numerically by solving the PB equation with appropriate boundary conditions[38] or from direct computer simulations. The latter route is more favorable since it gives essentially the exact result and does not depend on a particular choice of the boundary conditions for the electrostatic potential.

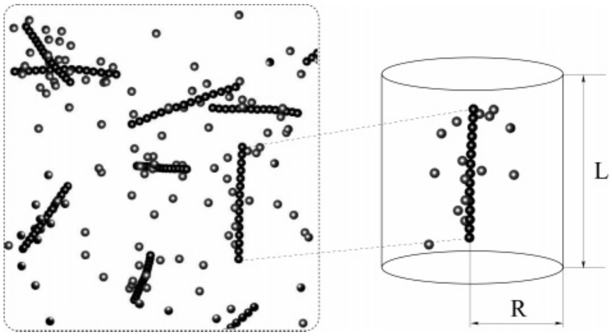

Figure 1. Dilute solution of stiff-chain polyelectrolyte. The snapshot on the left shows a typical bulk arrangement of rodlike macroions and small oppositely charged counterions. The sketch on the right illustrates the cylindrical cell model for a finite polymer chain.

C. Bulk Model. Since the cell model is based on the assumption of negligibly small polymer–polymer correlations, another model is needed to assess their impact on the osmotic pressure. A many chain bulk mesoscale system is the next step in incorporating system details into the model. Within this paper we do not go beyond a simple bead–spring polymer model, which is however already capable of addressing such phenomena as chain flexibility and correlations between the chains.

When the solvent is modeled as a uniform dielectric background of dielectric constant ϵ and there are no explicit interactions with solvent molecules, the total pressure Π calculated in such a system corresponds to the osmotic pressure measured in experiment. In our bulk simulations, the pressure was calculated as a sum of ideal gas contribution, the usual virial expression for short-range forces, and the electrostatic contribution proportional to the average electrostatic energy per unit volume:

$$\Pi = \frac{N_{\mathrm{tot}}k_BT}{V} + \left\langle \sum_{i<j}^{N_{\mathrm{tot}}} \frac{(\mathbf{r}_{ij}\cdot\mathbf{F}_{ij})}{6V} \right\rangle + \frac{\langle U_{\mathrm{el}}\rangle}{3V} \tag{8}$$

where N_{tot} is the total number of particles in the system and V is the system's volume. From the cell model point of view, the calculated bulk pressure can then be divided into two terms:

$$\Pi = \Pi_{\mathrm{m}} + \Pi_{\mathrm{c}} \tag{9}$$

where Π_{m} is the osmotic contribution of the macroions and Π_{c} is the pressure due to the counterions, which can be directly compared to the prediction of the cell model.

Under the assumption that electrostatic correlations between macroions are negligible, i.e., $\Pi_{\mathrm{m}} = c_{\mathrm{p}}k_BT$, the bulk osmotic coefficient exceeds that calculated in a cell by $c_{\mathrm{p}}/c_{\mathrm{c}} = 1/N$, where N is the number of counterions per polymer chain. This contribution should not be neglected for short-chain polymers since, for example, for $N \sim 40$ and $\phi = 0.25$ it can already be as much as 10% of the result.

D. Simulation Parameters. Here we take parameters of a typical synthetic stiff polyelectrolyte PPP which was already intensively studied[3,24,25] by means of different experimental techniques, including electric birefringence measurements, membrane osmometry, and X-ray scattering. At 40 °C this highly charged polyelectrolyte is characterized by a Manning parameter $\xi = 3.4$. The monomer length was taken to be 4.3 Å with two unit charges per monomer. The counterions were treated as point charges and could approach the backbone as close as $r_0 = 7.0$ Å. Three essentially different types of models were studied at these parameters: (a) an infinitely long rod, (b) one finite rod consisting of $N = 40$ monomers, and (c) a bulk system of 30 very stiff chains. The polymer chain length is $L = 17.2$ nm, which is less than the experimentally measured persistence length of 22 nm. All calculations were performed in the range of counterion concentrations $0.2 < c_c < 14$ mmol/L, for which experimental data are available.

III. Results and Discussion

The PPP system with the chosen parameters described in section IID has already been the subject of theoretical and numerical investigations.[5,11] Two effects were studied for a system of infinitely long rods: the effect of residual salt and the effect of electrostatic correlations. Below we summarize the findings in refs 5 and 11 and progress further by considering more realistic models of a polyelectrolyte solution.

A. Electrostatic Correlations and End Effects. The standard PB solution for the infinite-rod cell as a model for strongly charged polyelectrolyte solutions invokes two serious approximations. First, being a mean-field theory, it does not account for electrostatic correlations. Even for monovalent counterions the effect of ionic interactions might already be significant for our strongly charged polyelectrolytes at moderate concentrations,[8] as has been shown by comparison with explicit ion simulations for the infinite-rod cell model.

This effect was found to decrease the osmotic pressure by ~7% [5] at low concentrations for the polyelectrolytes we study here, and this could also be obtained by using the modified PB functional of ref 29. The second problem which both the original and modified PB theories have in common is that they are both applied to an infinitely long rod. This approximation works well for long polymer chains when the end effects are negligible, indeed. However, for short-chain polymers like the ones we are investigating here, this approach completely breaks down at low concentrations. The problem is that at infinite dilution a finite chain loses all its counterions, resulting in an osmotic coefficient of 1, whereas for an infinite rod it approaches the limiting value of $1/(2\xi)$. To assess how the finiteness of the chain affects the osmotic coefficient at a given polymer concentration, we performed a series of simulations for the parameter set described in section IID using a spherical and cylindrical cell model (section IIB) as well as bulk simulations (section IIC). Figure 2 summarizes the results of these simulations. The osmotic coefficients measured using the finite cell models are corrected by the $1/N$ term to obtain the bulk pressure, as discussed in section IIC.

All finite rod methods yield similar results which are significantly higher than both theoretical and simulation predictions of the osmotic coefficient for an infinite rod. The small deviation between the cylindrical and spherical cells at higher densities is due to the fact that application of the latter is limited to very low densities, when the polymer chain is considerably smaller than the cell diameter. The optimal cylindrical cell, on the contrary, can be successfully applied up to the semidilute regime.[8]

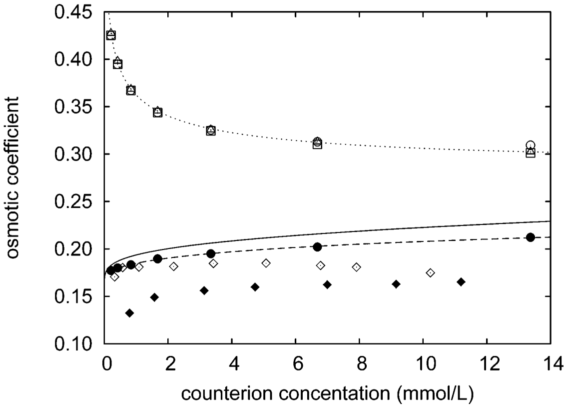

Figure 2. Osmotic coefficient calculated at different counterion concentrations using various models. The results for a finite rod calculated using the spherical cell model (empty circles), cylindrical cell with adjustable geometry (empty squares), and bulk system (empty triangles) are found in a very good agreement. The dotted line is a numerical fit to the bulk data drawn to guide the eye. The solid line is the prediction of the PB theory, and the dashed line fits the results obtained from MMM1D simulations for an infinitely long rod (filled circles). Experimentally measured osmotic coefficient for iodide (open diamonds) and chloride (filled diamonds) counterions[24] are also shown.

The prediction of the optimal cylindrical cell model in turn was found to be always below the measured bulk pressure. This effect, found to be of the order of 1%, was attributed to the weak polymer−polymer interactions present in bulk but not in the cell model. Because of these interactions, Π_m, the first pressure term in eq 9, should also include a virial term, in addition to the ideal gas contribution. For the current system parameters this virial term is about 4 times less than the ideal gas pressure, and it was found to be even smaller for shorter chains.

The simulation of a cylindrical cell periodic in one dimension made it possible to directly assess the counterion−counterion electrostatic correlations. Their effect was found to decrease the osmotic pressure compared with the mean-field PB prediction. This is in good qualitative and quantitative agreement with previous theoretical studies[5] and simulations[11] of strong polyelectrolyte solutions. Other kinds of electrostatic correlations which are present in the real experimental system but had not been included in our approach are the correlations between counterions and the charges on the polymer backbone. Since the charge distribution on the chain is nonuniform, the effective short-range attraction is expected to be stronger than that of a uniform linear charge.[39] This effect, however, is easily to be included in our model and was found to be 2 orders of magnitude smaller than the counterion−counterion electrostatic correlations and hence negligible.

The correlation effects discussed above are all small in comparison to the large difference between the pressure obtained for a finite and an infinite polymer chain. The finiteness of the chain therefore plays the leading role in the studied concentration range. The $\Pi(c_c)$ curve obtained for the finite macroion does not only decrease monotonically, as would indeed be expected at very low density, but also goes well above the curve obtained for an infinite rod. Compared to our previous findings,[5] we face the fact the we found now an even bigger difference between the simulation and the experimental data of ref 24 for finite rods. Other issues like chain flexibility, residual salt, charge distribution on the backbone, and specific interactions between the backbone and counterions will be investigated in the next sections as possible candidates to close the gap between calculated and measured data.

B. Flexible Macroions. The effect of chain flexibility was assessed at different counterion concentrations using a single polymer chain in a spherical cell. Replacing a stiff chain with a completely flexible one was found to reduce the osmotic pressure noticeably. Despite having repelling charges along the

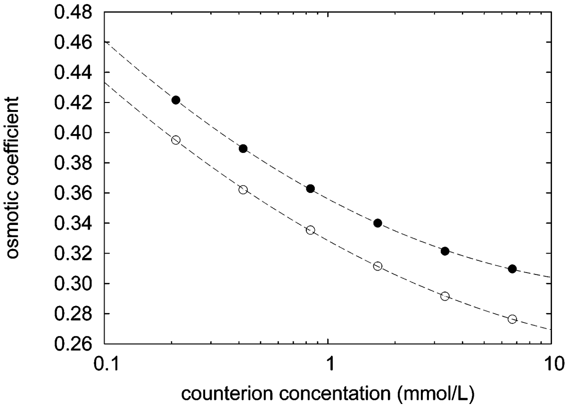

Figure 3. Osmotic coefficient of rigid (filled circles) and completely flexible (open circles) polymer chains at low counterion concentrations measured using a spherical cell model.

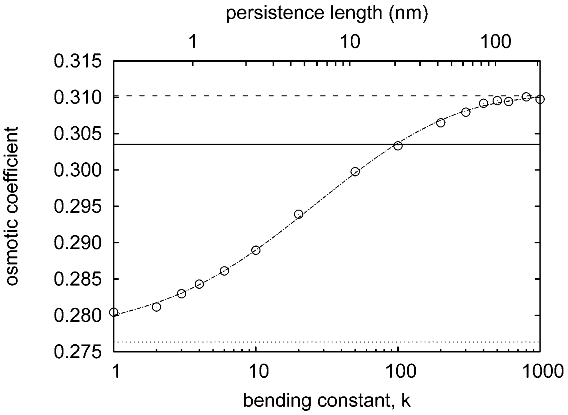

Figure 4. Osmotic coefficient at concentration $c_c = 6.7$ mmol/L as a function of chain stiffness k. The horizontal solid line corresponds to the persistence length of a PPP polyelectrolyte. The dotted and dashed lines give correspondingly the osmotic coefficient of a completely flexible and stiff polymer chain.

backbone, the flexible chain experiences an entropic contraction, its end-to-end distance decreases, and the effective linear charge increases. This drives two opposite processes: on the one hand, this increases the number of condensed counterions; on the other hand, a shorter chain loses more of its counterions. The overall effect was found to be in favor of the condensed counterions, confirming that flexible chains have fewer free counterions than stiff chains of the same contour length. The corresponding decrease of the osmotic coefficient was about 10−15%—less at low concentrations and more at high concentrations (see Figure 3). At a fixed concentration of $c_c = 6.7$ mmol/L we calculated the osmotic coefficient for chains with different stiffness ranging between completely flexible and very stiff. Here, we used a simple cosine form of the bond angle potential $U = k \cos(\theta - \pi)$ and varied the chain stiffness by investigating the range of $0 \leq k/(k_B T) \leq 1000$. Figure 4 shows how the osmotic coefficient increases with chain stiffness. For each stiffness, the persistence length was measured from the decay of the orientation correlation function along the chain.[40] The results are shown on the upper x-axis in Figure 4 (note that the scale deviates from logarithmic since the persistence length is not exactly proportional to k). The typical value of the persistence length for the experimental PPP system is 22 nm. For this value the finite chain stiffness causes a decrease of the osmotic coefficient by about 0.007, which amounts to about 2% of the result, which is surprisingly small.

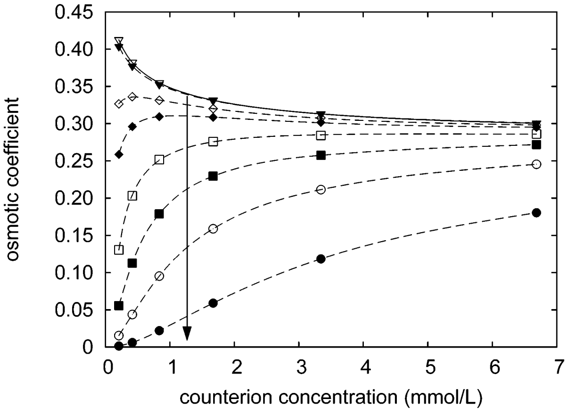

Figure 5. Osmotic coefficient as a function of polymer concentration measured at different salt content. The upper curve (open triangles) is the salt-free case. The salt concentration then increases along the shown arrow as follows: 1 μmol (filled triangles), 10 μmol (open diamonds), 20 μmol (filled diamonds), 50 μmol (open squares), 100 μmol (filled squares), 200 μmol (open circles), and 500 μmol (filled circles).

C. Residual Salt. A small amount of residual salt is known to be present even in deionized water, of the order of 1 μmol, depending on the experimental setup, and if the osmotic pressure is measured in a membrane osmometer against pure water, this will influence the resulting osmotic measurements. Salt results in a nonzero Donnan potential across the membrane separating the polymer solution from the pure water cell. The corresponding electric field affects the distribution of charged particles in the system,[5,41] resulting in a *decrease* of the measured osmotic pressure. For simplicity, we consider a PPP solution with a trace of a monovalent salt at bulk concentration c_b. Using the formalism of an electrically neutral spherical cell model with added positive and negative salt ions, we can write the condition of Donnan equilibrium in terms of charge balance at the cell boundary:

$$\rho_+(R)\,\rho_-(R) = {c_b}^2 \tag{10}$$

where $\rho_+(R)$ and $\rho_-(R)$ are the total boundary densities of positive and negative charges, respectively. Note that both counterions and salt anions contribute to $\rho_-(R)$. The resulting osmotic pressure is given by the difference between the osmotic pressures at the cell boundary acting from inside and from outside:

$$\Pi = (\rho_+(R) + \rho_-(R) - 2c_b)k_B T \tag{11}$$

The bulk salt concentration c_b cannot be set a priori in the cell simulation. However, the effects of the residual salt can still be incorporated by including a fixed amount of salt in the cell and then measuring the equilibrium values of the charge densities at the cell boundary. Then using eqs 10 and 11, both the bulk salt content and corresponding osmotic pressure can be calculated. Repeating this procedure for different amounts of salt at a fixed polymer concentration, we obtained $\Pi(c_b)$ curves at several polymer concentrations studied previously. The resultant values of the osmotic pressure as a function of both polymer and salt concentrations are summarized in Figure 5. As is expected, the effect of the residual salt is more pronounced at low polymer concentrations. It is the residual salt that is responsible for suppressing the asymptotic increase of the osmotic coefficient at lower polymer concentrations in experiments. However, as the polymer concentration is increased, this effect becomes relatively weak. Thus, to achieve an experimentally observed osmotic pressure at moderate polymer content, ~0.5 mmol/L of salt is needed. This is already 500 times higher than what is thought to be the usual residual salt

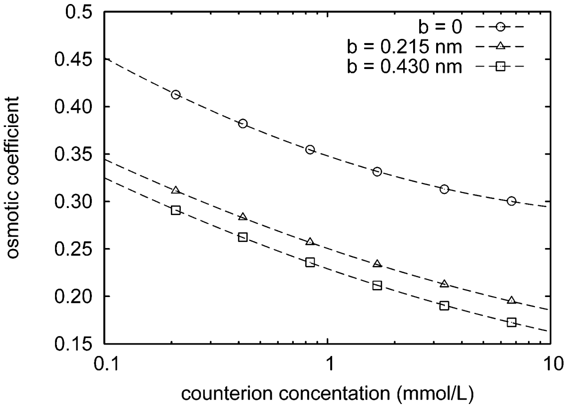

Figure 6. Osmotic coefficient measured in systems with binding energy $U_b = 4k_BT$ and different interaction range b as a function of counterion concentrations. Case $b = 0$ corresponds to the zero binding potential. As the range of this potential increases, the number of condensed concentrations also increases, resulting in lower osmotic pressure.

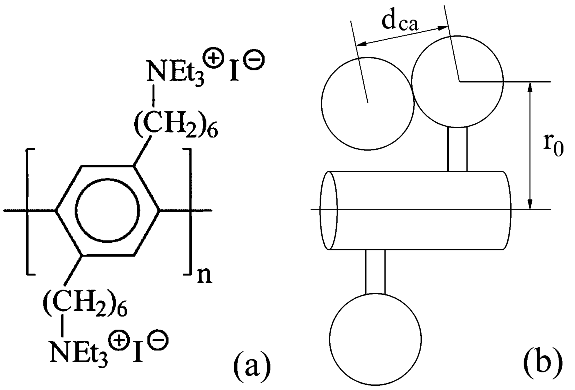

Figure 7. (a) Constitution formula for poly(p-phenylene) and (b) its model interpretation. It is normally assumed that ionic charges are centered on the central backbone axis and are not displaced off-center. However, the chemical structure of PPP shows that distance of closest approach d_{ca} and radius of the molecular cross section r_0 have different physical meaning.

concentration. Note that 0.5 mmol/L of univalent salt has a Debye length l_D, defined as

$$l_D = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{e^2 2c_b}} \tag{12}$$

of ~10 nm. This is much larger than the Bjerrum length (l_B = 7.31 Å for water at 40 °C), which indicates that screening only weakly affects the electrostatic interactions and the observed decrease in the osmotic coefficient is solely due to the Donnan potential. To summarize, for sufficiently low residual salt concentrations, one should observe experimentally the increase of the osmotic coefficient for short polyelectrolyte chains. In this case, upon lowering the concentration, the increase of the osmotic pressure due to the finiteness of the macroions might be seen before the residual salt brings it down to zero. Also, the experimentally data for iodide in Figure 2 seem to indicate this trend, and there is another paper on vinylic polyelectrolyte solutions[42] where the same behavior was observed.

D. Interaction between the Backbone and Counterions. Within our model description the ions are treated as charged hard spheres, with a diameter that includes the hydration shell, moving in a dielectric continuum with a value ϵ related to the dielectric permittivity of water. There is no reason to believe that the long-range electrostatic interaction between the macroion and the counterions deviates from the Coulomb law. At short distances, however, effects of hydration shells and solvent mediated interactions might be seen. Since the pioneering works of Hofmeister in 1887, it is known that there exist some ion specific effects, known also as the Hofmeister effects (see for example a nice review by Kunz et al.[43]). The physics behind these effects is rather complex, and several mechanisms can be the cause of these ion specific forces, like hydration forces, hydrophobic forces, and polarization induced forces, to name just a few. In this case neither the bulk dielectric constant ϵ can be used nor can the interaction itself be described by the inverse distance law alone. Assuming that these solvent-mediated interactions are noticeable only at distances compared to the size of an ion, we included a short-range binding potential into our model to see its effect on the osmotic pressure. Here, an extra binding energy U_b was added to the ion−counterion potential if the separation between them was less then some interaction range b. For 2.15 Å ≤ b ≤ 4.30 Å, the binding energy required to bring the osmotic pressure down to the experimentally observed values was found to be in the range $3.8k_BT < U_b < 4.3k_BT$ depending on b. These calculations were performed at a counterion concentration of c_c = 6.7 mmol/L, which is a value at which the residual salt effects can be neglected. At lower concentrations the salt free models inevitably predict the increase of the osmotic coefficient upon decreasing the concentration, and the introduction of the binding energy only shifts the $\phi(c_c)$ curve down (Figure 6). Therefore, an additional short-range potential as considered above will not change the qualitative concentration behavior of the osmotic coefficient predicted for a finite rod.

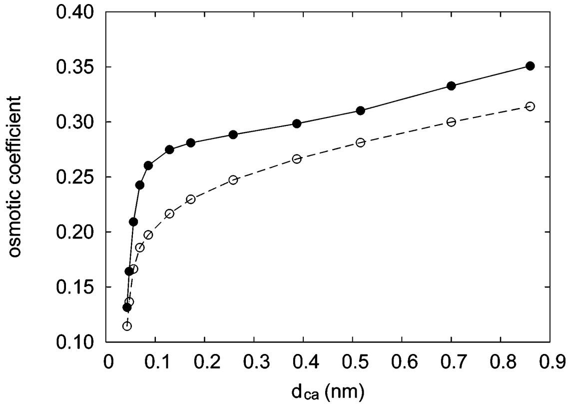

Figure 8. Osmotic coefficient at concentration c_c = 6.7 mmol/L as a function of distance of closest approach between ion and counterion d_{ca} calculated for r_0 = 0 nm (open circles) and r_0 = 0.7 nm (filled circles).

Until now, the macroion was modeled as a uniform linear charge or a linear set of equidistant charged spheres. To resemble the chemical structure of PPP, we propose to consider the ions to be attached to the backbone with a constant or harmonic bond of length r_0 (Figure 7). The polymer charges can freely rotate around the backbone but cannot move along it, so the linear charge is kept constant. In such a model the distance of closest approach d_{ca} between an ion and a counterion is introduced as a new parameter which controls ion−counterion interaction. It should be noted that d_{ca} defines neither ion nor counterion diameter but is the relevant electrostatic energy scale. As long as the distance of closest approach is kept constant, a system with point counterions and ions of diameter d_{ca} or a system with point ions and counterions of diameter d_{ca} gives similar osmotic pressure, as long as excluded volume interactions are negligible. The small difference of about 0.5% is attributed to the excluded volume correlations. An analogous pressure increase was also observed in our MMM1D simulations when point counterions

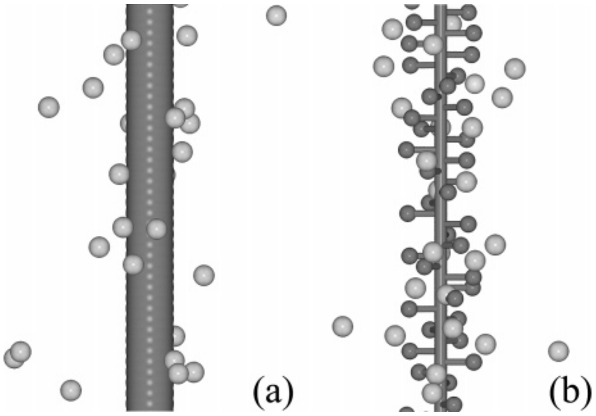

Figure 9. Simulation snapshots of two models of a PPP polyelectrolyte giving the same osmotic pressure. A linear arrangement of ions (a) gives the same osmotic coefficient of 0.3 for ion−counterion closest approach distance of $d_{ca} = 0.7$ nm, while the model with freely rotating ions gives the same pressure if d_{ca} is reduced down to 0.4 nm.

Table 1. Different Effects and Their Contribution to the Osmotic Coefficient Calculated for Parameters of PPP Polyelectrolyte at Counterion Concentration $c_c = 6.7$ mmol/L (See Text for Details)

effect	contribution
mean-field PB condensation	0.216
electrostatic correlations	−0.014
excluded volume correlations	+0.001
macroion−macroion correlations	+0.004
macroion osmotic contribution	+0.013
residual salt 1 μmol/L	−0.0003
finite chain length	+0.100
finite chain stiffness	−0.007
off-center ion distribution	+0.028

were substituted with hard spheres of diameter 4.3 Å. This demonstrates clearly that short-range repulsions between counterions make only a very small contribution to the osmotic pressure at the investigated concentrations.

We considered two extreme cases: the ions are fixed on the backbone ($r_0 = 0$), and the ions can freely move on the circle of radius $r_0 = 0.7$ nm. The difference between these two cases is informative of the effect of introducing an off-center charge distribution on the backbone. At the same time, in Figure 8, we show the effect of changing d_{ca} on the osmotic coefficient at a counterion concentration $c_c = 6.7$ mmol/L. It is evident that at any d_{ca} moving ions away from the backbone increases the osmotic pressure of about 10% compared to the central linear charge distribution. This shifts the osmotic coefficient even further away from the experimentally observed values.

The effect of having a mobile charge distribution 0.7 nm away from the backbone center can be compensated, in our example, by reducing the distance of closest approach from 0.7 to 0.4 nm. Figure 9 shows configurational snapshots of two systems having the same pressure. However, this demonstrates that changing d_{ca} in the range of physical parameters results in relatively small changes of the osmotic pressure. The distance of closest approach for a large counterion like iodine is expected to be in the range 3−5 Å, which includes its hydration layer. The hydration layer actually is responsible for a rather unique ionic size of this order for a large variety of ions.[44] One would need to adjust d_{ca} to ∼0.5 Å to bring the model prediction down to a value of 0.18, but ion separations of this order are surely not physical. The ion size will surely have some influence on the pressure, but within reasonable sizes it should not matter so much, which is quite opposite to extreme cases in very dense solutions, see, i.e., some refs 45−49.

IV. Conclusions

In this paper we investigated a number of interactions and modifications that go beyond the treatment of a dilute solution of strong polyelectrolytes with a simple PB treatment of the infinite-rod cell model and calculated their contribution to the osmotic coefficient. For a stiff-chain PPP polyelectrolyte with well-defined parameters we found that the finiteness of the macroion plays the most important role in the range of experimental concentrations. Not only the macroion itself contributes to the total osmotic pressure but it also has a distinctively lower fraction of condensed counterions compared to an infinite chain. Both effects therefore increase the pressure in the system. The contribution of macroion−macroion correlations to the pressure was found to be positive but small, which means that an appropriate cell model containing a single macroion and its counterions is a good tool to predict the pressure. From the analysis of varying the flexibility of the PE backbone it was concluded that finite chain stiffness has a small effect on the osmotic properties, but higher flexibility reduces the pressure. Another effect that was found to reduce the pressure slightly was the effect of electrostatic correlations, which is basically the difference between the PB solution and the simulation results. Ion specificity was considered as a generic short-range nonelectrostatic attraction of the counterion to the backbone with a high binding energy. Depending on the range and depths of this short-range attraction, this results in a decrease of the osmotic coefficient by simply shifting the $\Pi(\rho_c)$ curve be a nearly constant amount. Again, a nonphysical high binding needs to be postulated to retain the counterions in the condensed state and to lower the osmotic coefficient close to the experimental values. We do not know of any physical reason that would yield such a high binding affinity.

The osmotic coefficient was also found to be sensitive to the backbone ion distribution on the macroion—it increased if the ions were allowed to move around the backbone at certain radii, instead of being fixed on its central axis. Also, excluded volume correlations were found to increase the pressure slightly but were found to be negligible at the investigated concentrations, as could be expected.

Table 1 gives an approximate contribution of each effect studied. If all effects are incorporated into the simple cell model to make it resemble the experimental system more closely, the resultant osmotic coefficient almost twice exceeds the experimentally observed value of $\phi_{exp} \approx 0.18$.[24] It is not clear what the reason for this discrepancy is. It might be that the experimental system did not have such an ideal composition as was assumed and that some larger aggregates might have been present. Another experimental data set on small stiff polyelectrolytes in a salt-free environment would be desirable to test our results or to give further hints on what the difference between our computer model and the experimental system might be.

All the model systems considered in this paper were based on the assumption of pure Coulomb interactions in a uniform dielectric background. We do not believe, however, that this is the main cause of the mismatch to the experimental results. In light of our recent tests of the dielectric continuum model vs a simulation with an explicit water solvent,[22,23] the explicit water simulations might show a lowering due to the decrease of the local relative dielectric constant near the macroion, but probably only on the order of a few percent.

Summarizing again, we used simple geometric arguments to improve the model system from a single infinitely long rod to a solution of finite semiflexible polyelectrolyte macromolecules.

The latter, however, gives the osmotic pressure about twice higher than that predicted by experiment. We hope that our results will stimulate more experimental studies and computer simulations with explicit solvent to address this issue.

Acknowledgment. We thank M. Ballauff and M. Deserno for useful discussions and the German Science Foundation (DFG) for financial support through SFB 625, TR6, and Ho-1108/11-2.

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MA062179P