Competitive solvation effects in polyelectrolyte solutions

Alexandros Chremos^{1, a)} and Jack F. Douglas^{1, b)}

Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899, USA

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An understanding of the solution properties and phase behavior of natural and synthetic polyelectrolytes requires an understanding of the competitive association of water ("hydration") and ion association to the polymer backbone and the consequences of large scale clustering of counter-ions around highly charged polymers and associated chain clustering due to the high polarizability of this diffuse counter-ion cloud. We investigate the influence of counter-ion affinity for polyelectrolyte segments on the conformational properties of individual highly charged flexible polyelectrolyte chain using molecular dynamics simulations that include both ions and an explicit solvent. We find that an increase in the affinity of the counter-ions. For a constant charge interaction defined by a fixed Bjerrum length and Debye screening length, this increase in the number of interfacial counter-ions with an increased strength in counter-ion affinity for the polyelectrolyte segments decreases the size of the polyelectrolyte chain and the average polyelectrolyte shape becomes less extended. We also calculate and quantify the distribution of counter-ions around solvated polyelectrolyte chains, where we find that a strong affinity of the counter-ions for the polyelectrolyte segments results in a decrease in the spatial extent of the diffuse counter-ion cloud around highly charged polymers.

I. INTRODUCTION

Polyelectrolytes are complex ionic molecules in which charged groups are distributed along the backbone of a polymer chain and counter-ions are released to varying degrees into highly dielectric solvents, such as water, normally resulting in good polymer solubility.^{1,2} Many biological molecules such as DNA, RNA, proteins, and synthetic polymers such as sulfonated polystyrene and polyacrylic acid are polyelectrolytes and due to their unique rheological and thermodynamic properties they are widely used as rheology modifiers, adsorbent materials, coatings, biomedical implant materials, encapsulating materials for pharmaceutical drug delivery systems.^{3–5} It is generally appreciated that this ionization process leads to a charged chain backbone in aqueous solution and results in long-range repulsive Coulomb interactions between the polymer segments that cause the polymer to swell. These interactions are greatly influenced by counter-ions that remain in the general proximity of the polyelectrolyte backbone and these interfacial counter-ions exchange with the counter-ions in the solution at a reasonably high rate so that the state of the bounded counter-ions is highly dynamic.⁶⁻⁸ It is these weakly bound counter-ions and their effect on chain conformation that make the modeling of polyelectrolytes challenging.^{6,7,9–12} Although it has long appreciated from the Manning model^{13,14} of polyelectrolyte solutions, and numerous experimental studies,^{6,7,9–12} that the counterions of highly charged polyelectrolytes tend to be localized near the chain backbone in which the average concentration is enriched, even though the ion-polymer association is highly dynamic. Conventional modeling of polyelectrolyte solutions^{15–21} does not address the solvation of ions within the chain backbone and the uncharged species of the polymer, a phenomenon that greatly influences thermodynamic and dynamic properties of ionic solutions^{22,23} and recent work has shown that counter-ion solvation can lead to long range attractive interactions between polyelectrolyte chains²⁴ that can also greatly influence thermodynamic and dynamic properties of polyelectrolyte solutions. In the present paper, we are concerned with the particular problem of how competitive association between ions and solvent influence conformational properties of charged polyelectrolyte chains in the limit of infinite polymer dilution where interchain coupling effects can be neglected.

Without hydration, highly charged polymer chains naturally adopt rod-like conformations as Manning assumed, but recent simulations have indicated that hydration makes even highly-charged polymers to adopt molecular conformations closer to that of a random coil and the persistent length is highly sensitive to the counter-ion valence²⁵ as observed experimentally.²⁶ We have found that these phenomena derive from a tendency of the solvated counter-ions to remain localized in a diffuse domain around the polyelectrolyte, in addition to being bound to the chain backbone as Manning's model suggests, and strong reduction of the persistence length is found to that is caused by the tendency of the polyelectrolyte to chains "wrap" around the higher valent counter-ions.^{25,27}

To highlight the significance of solvation in polyelectrolyte solutions, we first summarize the effects of solvation in the "simple" case of electrolyte solutions (with no polyelectrolyte chains). Electrolyte solutions having different salts exhibit a wide spectrum of variation in solution properties, such as the density, viscosity, and surface tension; these changes in solution properties are

^{a)}Electronic mail: <u>alexandros.chremos@nist.gov</u>

^{b)}Electronic mail: jack.douglas@nist.gov

typically classified in terms of the Hofmeister series. 28 Observations of Collins, 29,30 and theoretical arguments by Ninham et al.,³¹ suggest the importance of ion-size on the extent of ion-solvation and the dispersion interaction between ions and water, respectively, in understanding the trends of polymer solubility, i.e., the Hofmeister series. Indeed, the ion solvation energy effectively reflects a combination of Coulombic and dispersion interaction contributions between the ions and the solvent particles surrounding the ions.³² Motivated by these observations, we explored an explicit electrolyte solvent model in which the water-ion dispersion interaction parameter was determined by the ion solvation energy through the application of Born theory of ionic solvation.²² We found that molecular dynamics simulations utilizing this model captured semi-quantitatively observed changes in solution viscosity and water diffusion coefficient on ion type,²² an effect that classical coarse-grained pair-potential models fail to reproduce.³³ Recent calculations of the same model reveal that several other thermodynamic properties, including the density, isothermal compressibility, and surface tension, can be understood via the solvent-ion interactions, suggesting that the Hofmeister series is closely related to ion solvation.²³ Thus, if the solvent interactions with the ionic species plays such a crucial role in modulating the electrolyte solution properties, then it is logical to expect analogous effects in polyelectrolyte solutions.

The present paper explores the relatively large parameter space governing the competitive binding of solvent and counter-ions to the polymer backbone in the infinite polymer dilution limit. In particular, we calculate the average number of interfacial counter-ions with variation of the counter-ion affinity for the polyelectrolyte segments. These results are compared to different solvent affinities for the charged species in the polyelectrolyte solution. We also calculate the radius of gyration of the polyelectrolyte chain and its average molecular shape with variation of the strength of the different affinities. Finally, we calculate the charge distributions of the different ions surrounding the polyelectrolyte chain and we rationalize the resulting effects of the competitive solvation on the polyelectrolyte chain flexibility.

Our paper is organized as follows. Section II contains details of the model and simulation methods. Results of the conformational properties of the polyelectrolyte chain and the characterization of the spatial distribution of the counter-ions surrounding the polyelectrolyte chain are presented in Section III. Section IV concludes the paper.

II. MODEL AND METHODOLOGY

We employ a bead-spring model of Lennard-Jones (LJ) segments bound by stiff harmonic bonds suspended in explicit LJ solvent particles, some of which are charged to represent counter-ions.^{34–37} The system is composed of a

total of $N = 64\,000$ particles in a periodic cube of side L and volume V. The system includes a single polyelectrolyte chain having a molecular mass of $M_{\rm w} = 41$ and a total charge $-Z_{\rm p}e$ is distributed uniformly along the molecular structure, where e is the elementary charge. For the purposes of our investigation, we focus on systems having $Z_{\rm p}/M_{\rm w} = 1$. The bonds between polymer segments are connected via a stiff harmonic spring, $V_{\rm H}(r) = k(r-l_0)^2$, where $l_0 = \sigma$ is the equilibrium length of the spring, and $k = 1000 \varepsilon/\sigma^2$ is the spring constant. The system also includes N_{-} co-ions of charge -e and $N_{+} = N_{-} + Z_{\rm p}$ counter-ions of charge +e so that the system of interest has neutral total charge.

All macro-ion segments, dissolved ions, and solvent particles are assigned the same mass m, size σ , strength of interaction ε . We set ε and σ as the units of energy and length; the cutoff distance for LJ interaction potential is $r_{\rm c} = 2.5 \sigma$. The size and energy parameters between *i* and *j* particles are set as $\sigma_{ii} = \sigma_{jj} = \sigma_{ij} = \sigma$ and $\varepsilon_{ii} = \varepsilon_{jj} = \varepsilon_{ij} = \varepsilon$, except for three energy interaction parameters: the first interaction parameter is between the polyelectrolyte segments and the counter-ions $\varepsilon_{\rm pc}$, the second interaction parameter is between the solvent particles and the polyelectrolyte segments $\varepsilon_{\rm ps}$, and the third one is between the solvent particles and the positive ions $\varepsilon_{\rm cs}$. Variation of the interaction energy parameters between different types of particles reflect the degree of chemical incompatibility between the polymer repeating units.³⁸ The primary focus of this study is on influence of ε_{pc} parameter on the conformational properties of the poyelectrolyte chain, while the other two parameters have been studied previously³⁹ and used here as points of reference. All charged particles interact via Coulomb potential (with a cut-off distance 10σ) and a relatively short range Lennard-Jones potential of strength ε , and the particle-particle particle-mesh method is used.⁴⁰

The systems were equilibrated at constant pressure and constant temperature conditions, i.e., reduced temperature $k_{\rm B}T/\varepsilon = 0.75$ (where $k_{\rm B}$ is Boltzmann's constant) and reduced pressure $\langle P \rangle \approx 0.02$, and the production run were performed at constant temperature constant volume, maintained by a Nosé-Hoover thermostat. The Bjerrum length was set equal to $l_{\rm B}$ = $e^2/(\epsilon_{\rm s}k_{\rm B}T) \approx 2.4\,\sigma$, where $\epsilon_{\rm s}$ is the dielectric constant of the medium. The Debye screening length: $\lambda_{\rm D} = [4\pi l_{\rm B} (\rho_+ + \rho_-)]^{-1/2} \approx 2.2$, where $\rho_{\pm} = N_{\pm}/L^3$ are the ion densities. Typical simulations equilibrate for 4000τ and data is accumulated over a $10\,000\,\tau$ interval, where $\tau = \sigma (m/\varepsilon)^{1/2}$ is the MD time unit and the time step $\delta t = 0.005 \tau$. Typical screenshots for different types of solvent affinities are presented in Fig. 1. For comparison, we also consider an implicit solvent model at the some volume and temperature as our explicit solvent model, except that there is no solvent and all LJ interactions are described by Weeks-Chandler-Andersen potential.



FIG. 1. (a) Schematic of the different energetic interactions between three species in polyelectrolyte solutions namely, the polyelectrolyte segments, the counter-ions, and the solvent. The parameters at the corners of the outer triangle correspond the self-interaction energy parameters and the parameters at the corners of the inner triangle correspond to the cross-energy interaction parameters. Screenshots of typical molecular conformations of the polyelectrolyte chains (beads in red color) surrounded by counter-ions (beads in blue color) and co-ions (beads in light orange color) are also presented. (b) Screenshots of the charged species in the simulation box with the solvent rendered invisible on the top and visible (beads having green color) on the bottom.

III. RESULTS & DISCUSSION

We initiate our discussion with the characterization of the interfacial layer around the polyelectrolyte backbone.

We set the interfacial layer based on an arbitrary distance criterion in which any counter-ion that is located at shorter distances than 1.1 σ are taken to be part of the interfacial region. This particular value, i.e., 1.1 σ , is chosen in order to discriminate between the counterions that are in contact with the polyelectrolyte from the remaining counter-ions. Based on our model, we find that the interfacial counter-ions exhibit a rich spectrum of behaviors for the different molecular topologies²⁷ and counter-ion valance.²⁵ Now that we have defined the interfacial region for our model based on a precise geometric picture, we calculate the time average number of interfacial counter-ions, $\langle n_{\text{inter}} \rangle$, for different values of $\varepsilon_{\rm pc}$. As seen in Fig. 2, $\langle n_{\rm inter} \rangle$ is significantly increases as $\varepsilon_{\rm pc}$ increases and quickly reaches a saturation point at about $\varepsilon_{\rm pc}/\varepsilon \approx 3.8$. This trend is in the opposite direction compared to the trends of other two interaction parameters ($\varepsilon_{\rm cs}$ and $\varepsilon_{\rm ps}$) since an increase in the affinity of the solvent particles for counter-ions or polyelectrolyte segments leads to "kicking out" the counter-ions from the polyelectrolyte backbone. Based on these observations. we find that an increased affinity of the counter-ions for the polyelectrolyte segments leads to "kicking out" the solvent particles from the polylectrolyte backbone.

Due to their close proximity to polyelectrolyte, these interfacial counter-ions screen a significant portion of the bare charge of the polyelectrolyte. We calculate the effective polyelectrolyte charge as $Q_{\text{macro}} = Z_{\text{p}} - \langle n_{\text{inter}} \rangle$. As seen at the inset of Fig. 2, the effective charge can change significantly over the range of $\varepsilon_{\text{pc}}/\varepsilon$ values, i.e., for small $\varepsilon_{\text{pc}}/\varepsilon$ values $Q_{\text{macro}} \approx Z_{\text{p}}$. However, as $\varepsilon_{\text{pc}}/\varepsilon$ increases Q_{macro} progressively decreases becomes nearly zero beyond the saturation point ($\varepsilon_{\text{pc}}/\varepsilon \gtrsim 3.8$).

To better understand how the interfacial counter-ions organize along the polyelectrolyte backbone, we calculated the time average number of contacts these interfacial counter-ions have with the polyelectrolyte segments, $\langle n_{\rm cont} \rangle$, as can be seen in Fig. 3. If every interfacial counter-ion has exactly one polyelectrolyte segment contact then $n_{\text{inter}} = n_{\text{cont}}$, but as we have seen in pre-vious studies^{25,27,41} the polymer chain is more closely resembling a worm-like chain, meaning that the chain can "wrap" around counter-ions. This effect contributes to the inequality $\langle n_{\text{inter}} \rangle < n_{\text{cont}}$. Evidently, there is a substantial increase in the number of contacts per interfacial counter-ion as $\varepsilon_{\rm pc}$ increases. A similar trend is found with increasing the valence of the counter-ions from monovalent to trivalent. Specifically, in the case of the trivalent counter-ions the polyelectrolyte chain collapses by wrapping around the counter-ions. These close similarities mean one thing: the polyelectrolyte chain is coiling around the interfacial counter-ions even in the case of monovalent counter-ions provided the affinity of the counter-ions is stronger among the other competitive solvation interactions. This is also supported from the screenshots in Fig. 1 and by the calculations of polyelectrolyte size and shape, as we discuss below.

Having quantified the number of interfacial counter-



FIG. 2. Number of interfacial counter-ions n_{inter} as function of the cross energy interaction parameter between different species in polylectrolyte solutions. Specifically, ε_{pc} (circles), ε_{ps} (squares), and ε_{cs} (diamonds) correspond to the cross interaction energy between the polyelectrolyte segments and counter-ions, counter-ions and the solvent particles, and the polyelectrolyte segments and solvent the particles, respectively. The dashed line corresponds to the implicit solvant model. Inset: Effective polyelectrolyte charge, $Q_{\text{macro}} = Z_{\text{p}} - \langle n_{\text{inter}} \rangle$, as function of the strength of the cross energy interactions. The uncertainty estimates are smaller than the symbol size.



FIG. 3. Average number of contacts between the counterions and the polyelectrolyte segments, $\langle n_{\rm cont} \rangle$ as function of the strength of cross interaction parameters. Specifically, $\varepsilon_{\rm pc}$ (circles), $\varepsilon_{\rm ps}$ (squares), and $\varepsilon_{\rm cs}$ (diamonds) correspond to the cross interaction energy between the polyelectrolyte segments and counter-ions, counter-ions and the solvent particles, and the polyelectrolyte segments and solvent the particles, respectively. The dashed line corresponds to the implicit solvant model and the uncertainty estimates are smaller than the symbol size.



FIG. 4. Radius of gyration, $R_{\rm g}$, of a polyelectrolyte chain as function of the strength of cross interaction parameters. Specifically, $\varepsilon_{\rm pc}$, $\varepsilon_{\rm ps}$, and $\varepsilon_{\rm cs}$ correspond to the cross energy interaction between polyelectrolyte segments and counter-ions, counter-ions and solvent particles, and polyelectrolyte segments and solvent particles, respectively. The dashed line corresponds to the implicit solvant model and the error bars correspond to two-standard deviations.

ions along the polyelectrolyte backbone, we shift our focus on the conformational properties of the polymer. Specifically, we calculate the radius of gyration $R_{\rm g}$ of the polyelectrolyte chain for different values of ε_{pc} and the results are presented in Fig. 4. An increase in ε_{pc} leads to a significant decrease in $R_{\rm g}.$ In the case of higher valent counter-ions, the interfacial counter-ions tend to increase the flexibility of the polymer chain by bending the chain around the higher valence ions.²⁵ An increased number of interfacial counter-ions along the polyelectrolyte backbone evidently has effect as in the introduction of higher valent ions. Indeed, for $\varepsilon_{\rm pc}/\varepsilon > 2.7$ the polyelectrolyte chain has collapsed and the overall size of chain is similar to the size of a polyelectrolyte chain in similar conditions, but having trivalent counter-ions. The conditions at which the polyelectrolyte chain collapses seems coincide with the condition at which the saturation occurs for the number of interfacial counter-ions and the average number of segmental contacts per counter-ion compare Figs. 2 and 3 with Fig. 4. The contrast between the other types of cross energy interaction parameters is obvious. As $\varepsilon_{\rm cs}$ and $\varepsilon_{\rm ps}$ increase the interfacial counterions are "kicked-out" of the interfacial layer leading for the polyelectrolyte chain to maintain its extended wormlike polymer over a wide range of $\varepsilon_{\rm cs}$ and $\varepsilon_{\rm ps}$ values; see Fig. **4**.

To determine to what degree a polyelectrolyte chain resembles a rod-like polymer or a random coil, we compare its shape to a chain with stiff bending potential and to other reference objects namely, a smooth sphere and selfavoiding walks. We use the ratio of the hydrodynamic radius over the radius of gyration, $R_{\rm h}/R_{\rm g}$, which is useful descriptor to quantify the shape of polymers^{42,43}; the calculation of $R_{\rm h}$ is based on the friction coefficient of an arbitrary shaped Brownian particle. The values of $R_{\rm h}/R_{\rm g}$ for a smooth sphere is 1.29, for a random walk is 0.79, and this ratio approaches to zero for infinite long rod-like objects.^{44,45} Unlike rigid rods, polymers exhibit coiled molecular conformation, meaning that we need to calculate the time average molecular shape, i.e., $\langle R_{\rm h} \rangle / \langle R_{\rm g} \rangle$. As we have shown in previous studies, ^{25,27} polyelectrolyte chains have a relatively stretched "worm-like" configuration somewhat stiffer than chains having no charges. Their shape is thus quite different from a rod.

The impact of a strong affinity between the monovalent counter-ions and the poyelectrolyte segments is presented in Fig. 5. An increase in $\varepsilon_{\rm pc}$ leads less coiled conformations, see also typical screenshots at Fig. 1a. For example, for counter-ion affinity for the polyelectrolyte segments $\varepsilon_{\rm pc}/\varepsilon \approx 2.6$ the resulting average molecular shape is approximately that of a random walk, meaning that there is a sufficient number of interfacial counterions that "screen" the repulsive electrostatic interactions between the polyelectrolyte segments, resulting in an average shape equivalent to that of polymer chains in θ solvent. For $\varepsilon_{\rm pc}/\varepsilon > 2.6$, the average molecular shape becomes more compact respect to a random coil in ideal conditions, but less symmetric than a sphere. However, we cannot characterize the molecular conformations as "collapsed", as this would indicate that the shape would be close to a smooth sphere when $R_{\rm g}/R_{\rm h} \approx 1.29$.

Why would the polyelectrolyte chain contract in size resulting in to a more compact molecular conformation for higher counter-ion affinity for the polyelectrolyte segments? While the propensity of the persistence length to be reduced by the counter-ion valence has been noted in previous theoretical work^{46,47} there is little understanding how the competitive van der Waals type of interactions between the different species in polyelectrolyte solutions influence the persistence length of the polyelectrolyte chains, since these effects are not captured by conventional theoretical frameworks.^{48,49} This phenomenon must be freshly addressed now that the importance of polymer and ion solvation effects on chain conformation have been established.

We now focus on the spatial distribution of counterions in relation to the position of the polyelectrolyte segments. Previously, we developed an approach for quantifying the spatial distribution of the counter-ions surrounding a polyelectrolyte chains and we briefly outline this approach.^{25,27} In particular, we calculate the average net charge q(r) as function of distance from the polyelectrolyte segments. As shown in Fig. 6a, q(r) is simply the difference of the counter-ion distribution $q_+(r)$ and the co-ion distribution $q_-(r)$, meaning that q(r) contains information for both the counter-ions that are located in the interfacial layer (defined as any particle being at a distance $r/\sigma \leq 1.1$ from any polyelectrolyte segment) as well as in the diffuse counter-ion cloud. This approach^{25,27} allows us to determine the size of the cloud of the diffuse



FIG. 5. Ratio of the average hydrodynamic radius over the average radius of gyration $R_{\rm h}/R_{\rm g}$ as as function of the strength of cross interaction parameters. Specifically, $\varepsilon_{\rm pc}$, $\varepsilon_{\rm ps}$, and $\varepsilon_{\rm cs}$ correspond to the cross energy interaction between polyelectrolyte segments and counter-ions, counter-ions and solvent particles, and polyelectrolyte segments and solvent particles, respectively. The dot-dashed lines correspond to the reference values of reference objects, for a smooth sphere is 1.29 and self-avoiding walks in θ -solvent equals 0.79;^{44,45} we also include the value of $R_{\rm h}/R_{\rm g}$ for a finite size rod having the same molecular mass $M_{\rm w} = 41$ as for our polyelectrolyte chains, $R_{\rm h}/R_{\rm g} \approx 0.42$.²⁵ The error bars correspond to two-standard deviations. The dashed line corresponds to the implicit solvant model.

counter-ions (R_{cloud}) associated with the polyelectrolyte chain, since the boundary between this cloud and the bulk is at $q(r = R_{cloud}) = q_{+}(r) - q_{-}(r) = 0$. An example illustrating these charge distributions is presented in Fig. 6a. For a weak dispersion interaction strength, $\varepsilon_{\rm pc}/\varepsilon = \varepsilon_{\rm cs}/\varepsilon = \varepsilon_{\rm pc}/\varepsilon = 1$, a fraction of counter-ions have a small tendency to "condense" along the polyelectrolyte backbone. However, as we increase the counterion affinity for polyelectrolyte segments, we increase the number of interfacial counter-ions along the polyelectrolyte backbone along with the overall polyelectrolyte size and shape, thus significantly influencing the q(r)distribution, as illustrated in Fig. 6b. The difference in the impact with the other two cross energy interaction parameters is clear. Increasing $\varepsilon_{\rm cs}$ or $\varepsilon_{\rm ps}$ leads to the counter-ions to be dissolved and continue to interact with the polyelectrolyte chain at relative large distances $2 < r/\sigma < 10$, leading to an enrichment of the diffuse counter-ion cloud surrounding the polyelectrolyte chain. An increase in ε_{pc} , on the other hand, leads to a counterion enrichment at relative short distances $1 < r/\sigma < 5$.

We next consider the *cumulative net charge*, $Q(r) = \int_0^r q(x)dx$ at a distance r from polyelectrolyte segments to better quantify the net ionic distribution around a polyelectrolyte chain.^{25,27} Q(r) starts from 0 at short distances $r/\sigma < 1$ and progressively increases at long





FIG. 6. (a) Distribution of the ionic net charge, q(r), as well as the relevant distributions of the counter-ions $q_+(r)$ and co-ions $q_-(r)$, and the distribution of the polymeric segments, $q_{\rm pol}(r)$, as function of distance from the polyelectrolyte segments. (b) Distribution of the net charge q(r) for four different types of solvent affinity namely, no solvent affinity ($\varepsilon_{\rm cs}/\varepsilon = \varepsilon_{\rm ps}/\varepsilon = 1$), strong counter-ion solvent affinity ($\varepsilon_{\rm cs}/\varepsilon = 8$), strong polyelectrolyte solvent affinity ($\varepsilon_{\rm ps}/\varepsilon = 8$), and strong affinity between the polyelectrolyte segments and the counter-ions ($\varepsilon_{\rm pc}/\varepsilon = 8$). Results for different solvent affinities, namely (top) between the solvent and polyelectrolyte segments.

distances until it saturates, i.e., $Q(r)/Z_{\rm p} \approx 1$, see Fig. 8. The rate at which $Q(r)/Z_{\rm p}$ reaches unity follows the approximately universal functional form:

$$Q(r) = Z_{\rm p} \tanh^2 \left[(r - \mu) / \alpha \right], \qquad (1)$$

where α and μ are fitting parameters. The most important parameter is α , since it determines the overall size of the diffuse counter-ion cloud.

From previous studies, we know that the functional form of Eq. 1 holds for polyelectrolytes having different molecular architectures²⁷ and for different counter-ion valence,²⁵ suggesting that the rate of charge saturation is *coupled* to the structure of the polyelectrolyte chains and the charge carried by the counter-ions. Moreover,



FIG. 7. Net charge q(r) as function of distance from the polyelectrolyte segments. Results for different values of the cross energy interaction parameter between polyelectrolyte segments and counter-ions are also presented.



FIG. 8. Cumulative net charge Q(r) normalized by the total bare charge of the polyelectrolyte chain $Z_{\rm p}$ as function of distance from the polyelectrolyte segments. Results for different values of the cross energy interaction parameter between polyelectrolyte segments and counter-ions are also presented.

for monovalent counter-ions, the size of ionic cloud is directly coupled to the size of the polyelectrolyte chain, as quantified by the radius of gyration, $R_{\rm g}$.²⁷ However, deviations from the monovalent counter-ion behavior were found for divalent and trivalent counter-ions, where the trend was amplified due to the stronger coupling between the counter-ions with the conformational properties of the polyelectrolyte chain, leading to a non-trivial dependence between the size of the ionic cloud and $R_{\rm g}$.²⁵ Here, we extend this type of calculation to polyelectrolyte chains having different degrees of counter-ion affinity for the polyelectrolyte segments. By plotting the parame-



FIG. 9. Size of the counter-ion cloud, α , surrounding the polyelectrolyte chain as function of the radius of gyration, $R_{\rm g}$. Each data point corresponds to different strength of cross energy interaction parameter between the counter-ions and the polyelectrolyte segments, $\varepsilon_{\rm pc}$; see also Fig. 4 for comparison. The error bars correspond to two-standard deviations.

ter $R_{\rm g}$ as function of α , we find that the average size of the polyelctrolyte chain is again found to scale with the α -parameter as we vary with the solvent affinity for the ionic species; see Fig. 9. This finding agrees with our observations from our previous studies where we examined the role of molecular architecture on the size of the counter-ion cloud²⁷ and for different solvent affinities,³⁹ i.e., $\varepsilon_{\rm cs}$ and $\varepsilon_{\rm cs}$. We emphasize this simple relation between α and $R_{\rm g}$ only exists for monovalent counter-ions.²⁵

Here we see that Eq. 1 only holds when the polyelectrolyte chain is sufficiently swollen, $\varepsilon_{\rm pc}/\varepsilon \lesssim 3.5$, $Q(r)/Z_{\rm p}$ starts from zero at short distances and progressively reaches saturation $Q(r)/Z_{\rm p} = 1$ at longer distances. In the case of a strong affinity $\varepsilon_{\rm pc}/\varepsilon \gtrsim 3.5$, Q(r) exhibits a maximum $(Q(r)/Z_{\rm p} > 1)$ at an intermediate scale and then progressively decreases $(Q(r)/Z_p = 1)$ at longer distances. The maximum occurs near to the minimum observed in q(r) distributions, see Fig. 7. This feature is associated with the formation of negatively charged layer of co-ions. A similar behavior was observed for the trivalent counter-ions,²⁵ suggesting that the formation of a maximum in the Q(r) curves is an indication of a charge inversion and collapse. Equivalent behavior has been observed in experiments of aqueous polyaspartate with multivalent cations.⁵⁰ Evidently, the solvation layer around different charged species exhibits a non-universal dependence on the relative strength of these competing interactions.

IV. CONCLUSIONS

In summary, we have investigated the conformational structure of an isolated polyelectrolyte chain and counter-ion distribution based on molecular dynamics simulations that include both ions and an explicit solvent. We particularly focus on the influence of the counter-ion affinity for the polyelectrolyte segments on the chain conformational properties. We find that an enhancement of the counter-ion affinity for polyelectrolyte segments results in significant increase of the average number of interfacial counter-ions. Moreover, the polyelectrolyte chains contract in size by "wrapping" around the interfacial counter-ions, thus greatly increasing the average number of the segmental contacts of the interfacial counter-ions. The contraction of the polymer size also makes the overall molecular shape of the polyelectrolyte chain more compact compared to a random coil. We also examined the net ionic distribution around the polyelectrolyte chain with variation of the counter-ion affinity for the polyelectrolyte chain and thus quantify the size of the diffuse counter-ion cloud surrounding the polyelectrolyte chain. The results are compared with two type of solvent affinities for the charged species, i.e., counter-ions and polyelectrolyte segments, where the trends in the conformational properties occur in opposite direction of the counter-ion affinity for the polyelectrolyte segments. We conclude that the competitive solvation of the polyelectrolyte backbone by solvent and counter-ions leads to a range of distinct polymer conformational behaviors in solution, underlying the need to include an explicit solvent in the modeling of polyelectrolyte solution properties.

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