Supporting information for: Tuning the collapse transition of weakly charged polymers by ion-specific screening and adsorption

Richard Chudoba, *^{,†,‡,¶} Jan Heyda, ^{*,§} and Joachim Dzubiella^{*,‡,¶}

†Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, D-12489 Berlin, Germany

Physikalisches Institut, Albert-Ludwigs Universität Freiburg, Hermann-Herder-Straße 3, D-79104 Freiburg im Breisgau, Germany
 Research Group Simulations of Energy Materials, Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany
 Spepartment of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, CZ-16628 Praha, Czechia

E-mail: richard.chudoba@helmholtz-berlin.de; jan.heyda@vscht.cz; joachim.dzubiella@physik.uni-freiburg.de

1. NON-ELECTROSTATIC INTERACTIONS

The Lennard-Jones (LJ) potential is used to describe nonelectrostatic interactions both in the simulations and in the mean-field theory,

$$U_{\rm LJ}^{ij} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right]. \tag{1}$$

Parameters of the interactions are summarized in Table S1. Each interaction is also characterized by its second virial coefficient B_{2} ,

$$B_2^{ij} = -2\pi \int_0^\infty r^2 \left[\exp\left(-\beta U_{\rm LJ}^{ij}\right) - 1 \right] {\rm d}r, \qquad (2)$$

where $\beta = (k_B T)^{-1}$. The mean value \overline{B}_2 is computed for all salt types as an average of B_2 of the respective anion and the (universal) cation. A temperature T = 298 K is assumed when ε is evaluated numerically.

2. SIMULATION SETUP

The box size is chosen based on two criteria: (i) The amount of salt ions shall be in an excess compared to the number of monomers in the polymer chain. (ii) The polymer chain extended conformations shall accommodate into the box with a margin. A box with an edge length of 20.25 nm is used for simulations at low salt concentrations. The volume of the box is then 8300 nm^3 and thus 1 M salt concentration corresponds to 5000 anions and 5000 cations inserted into the box. The box is scaled down to one fourth of its original volume to reduce the number of particles contained in the system at high salt concentrations. The configurations used in simulations are summarized in Table S2.

Electrostatic interactions between charged particles are computed using the particle mesh Ewald (PME) method. The default parameters of the PME method in Gromacs 5.1 are well suited for atomistic simulations of a dense phase. For a sparse system in a large simulation box, however, too fine mesh limits the performance. To overcome the bottleneck we increase the spacing $d_{\rm grid}$ between the grid points simultaneously with a substantial increase in the real space cut-off distance $r_{\rm cut-off}$. The ratio between the grid spacing and the cut-off distance is kept approximately the same during the scaling. The optimal PME parameters for all systems simulated are shown in Table S2, as obtained by the gmx tune_pme command of the Gromacs package. ^{S1}

3. ADDITIONAL POLYMER CHARACTERIZATION

Salts having mean $\overline{B}_2 < 0$, e.g., $\varepsilon_{anion} = 1.1 k_B T$ in our setup, do not cross the isospheric point, as shown from simulations and the mean-field theory in Figure S1. The function $R_g(c)$ is shifted towards more collapsed states. The R_g corresponding to the isospheric point is reached at higher salt concentration.

Distributions of radius of gyration of the polymer chain are shown in Figure S2 for various salt concentrations. The most repulsive and attractive anions are chosen as examples in the top, and bottom panels, respectively. The probability of radius of gyration has a Gaussian distribution when the extended states are populated. As the polymer collapses to the globule at increased salt concentration, the distribution becomes more positively skewed. For highly charged polymers, no collapsed conformation (i.e., $R_g < R_g^{id} = 2.19$ nm) are present in the pure solvent which quality is determined by $\varepsilon_{mer} = 0.4 k_B T$.

Time evolution of the radii of gyration are shown in Figure S3 for fourteen simulations, which cover the whole range of ξ , c_{salt} , and ε_{mer} parameters employed in this work.

| interaction | $\sigma(nm)$ | $\varepsilon (k_{\rm B}T)$ | B_2 (nm ³) | $\bar{B}_2 (\mathrm{nm}^3)$ | interacting entities |
|-------------|--------------|----------------------------|--------------------------|-----------------------------|--|
| Α | 0.4787 | 0.1 | 0.1059 | | cation-monomer |
| В | 0.3385 | 0.1 | 0.0374 | 0.0717 | anion-monomer |
| С | 0.3385 | 0.3 | -0.0017 | 0.0521 | anion–monomer, ion–ion |
| D | 0.3385 | 0.4 | -0.0254 | | monomer–monomer (neutral or cationic polymer) |
| E | 0.3385 | 0.5 | -0.0510 | 0.0275 | anion–monomer, monomer–monomer (anionic polymer) |
| F | 0.3385 | 0.7 | -0.1075 | -0.0008 | anion-monomer |
| G | 0.3385 | 0.9 | -0.1713 | -0.0327 | anion-monomer |

Table S1: Parameters σ and ε in the LJ potential (eq 1) for the non-bonded interactions employed. The second virial coefficient B_2 of the interaction is computed at 298 K. The mean values \overline{B}_2 of respective salts are evaluated.

Table S2: Simulation setups for various salt concentrations *c* in a cubic simulation box of an edge length *d*. Optimized parameters of the particle mesh Ewald method are provided in the last three columns.

| set | c (mм) | <i>n</i> ion pairs | d(nm) | $r_{\rm cut-off}({\rm nm})$ | grid points | $d_{\rm grid}/r_{\rm cut-off}$ |
|-----|--------|--------------------|-------|-----------------------------|-----------------|--------------------------------|
| A | 0 | 0 | 20.25 | 5.0 | 32 ³ | 0.127 |
| В | 100 | 500 | 20.25 | 5.0 | 32^{3} | 0.127 |
| С | 400 | 2000 | 20.25 | 3.8 | 42^{3} | 0.127 |
| D | 1000 | 1250 | 12.76 | 2.7 | 40 ³ | 0.118 |
| Ε | 2000 | 2500 | 12.76 | 2.5 | 42 ³ | 0.121 |



Figure S1: (a) Mean radius of gyration R_g obtained from the simulations of 200-mer bearing a charge fraction $\xi = 0.05$ as a function of salt concentration. Symbols in the plots indicate the various strength of the interaction between the anion and the polymer, ε_{anion} . Lines serve as a guide for the eye. Radius of gyration of an ideal chain R_g^{id} is indicated. (b) An effective radius of the polymer R_{pol} computed from the mean-field theory for the very same system.



Figure S2: Distribution of the radius of gyration R_g of 200-mer ($\varepsilon_{mer} = 0.4 k_B T$) in various systems. The fraction of cationic monomers, $\xi = 0.00, 0.05$ and 0.10, increases column wise from left to right. Panels in the top and bottom row depict the polymer chain in repulsive ($\varepsilon_{anion} = 0.1 k_B T$), and attractive ($\varepsilon_{anion} = 0.9 k_B T$) salt solutions, respectively. The salt concentrations are distinguished by line colors. For a neutral ideal chain the mean value $R_g^{id} = 2.19$ nm.



Figure S3: Time evolution of the radius of gyration R_g of 200-mer in selected simulations. The first 25 ns is considered as a part of equilibration and not included. Panels (a–d) show uncharged polymer, panels (e–j) weakly charged and panels (k–n) highly charged cationic polymer. Different colors indicate various salt concentrations; symbols are used to distinguish the salt type.

4. DONNAN POTENTIAL

The distribution of ions in the polymer phase creates a Donnan potential φ in a self-consistent manner. In the chemical equilibrium, the electrochemical potential of any ion inside the polymer phase $\bar{\mu}_i$ equals to its (electro)chemical potential in the reservoir $\mu_{i,\text{out}}$:

$$\mu_{+,\text{out}} = \bar{\mu}_{+} = \mu_{+} + z_{+}e\varphi \tag{3}$$

$$\mu_{-,\text{out}} = \bar{\mu}_{-} = \mu_{-} + z_{-}e\varphi,$$
 (4)

where z_{\pm} is the charge number of ions ($z_{\pm} = \pm 1$ in our case of a uni-univalent salt), and *e* is the elementary charge.

The chemical potential of ions in the reservoir as well as the chemical part of the electrochemical potential of ions in the polymer phase can be evaluated as

$$\mu_i = \left. \frac{\partial F}{\partial N_i} \right|_{N_i \neq i, V, T},\tag{5}$$

where F is the non-electrostatic part of the Helmholtz free energy of the respective phase (polymer or reservoir) and N_i the number of particular ions; N_j are the amounts of particles in the phase and V and T is the volume and temperature of the phase.

The chemical potential of cations and anions $\mu_{\pm,\text{out}}$ in the reservoir solely depends on the salt concentration ρ_{out} in our model:

$$\beta \mu_{\pm,\text{out}} = 2B_2^{\text{ion}} \rho_{\text{ion}} + \frac{2}{3} B_3 \rho_{\text{ion}}^2 + \frac{4}{3} B_4 \rho_{\text{ion}}^3 + \ln \rho_{\pm}, \quad (6)$$

where B_n are virial coefficients of the *n*-th order, $\rho_{\rm ion}$ is the overall concentration of ions in the reservoir and ρ_{\pm} is the concentration of cation, or anion, respectively. In the case of uni-univalent electrolyte, $\rho_{\rm ion} = 2\rho_{\rm out}$, and $\rho_{\pm} = \rho_{\rm out}$. The second virial coefficient between any ion pairs $B_2^{\rm ion} = 0$ in our model. The higher virial coefficients do not depend on the particle types in respective triplets and quadruplets in our model and are approximated by 2.00 σ^6 , and 2.64 σ^9 (hard spheres), respectively.

Similar expressions for the chemical potential can be derived also for the polymer phase within our model,

$$\beta \mu_{+} = 2B_{2}^{\text{ion}} \rho_{\text{ion}} + 2B_{2}^{+} \rho_{\text{mer}} + \frac{2}{3}B_{3}\rho_{\text{all}}^{2} + \frac{4}{3}B_{4}\rho_{\text{all}}^{3} + \ln \rho_{+}, (7)$$

$$\beta \mu_{-} = 2B_{2}^{\text{ion}} \rho_{\text{ion}} + 2B_{2}^{-} \rho_{\text{mer}} + \frac{2}{3}B_{3}\rho_{\text{all}}^{2} + \frac{4}{3}B_{4}\rho_{\text{all}}^{3} + \ln \rho_{-}, (8)$$

where B_2^{\pm} stands for the second virial coefficient of monomercation, or monomer-anion interaction, respectively, $\rho_{\rm ion} = \rho_+ + \rho_-$ is the overall concentration of ions in the polymer phase, $\rho_{\rm mer} = N/V_{\rm pol}$ is the density of monomers, and $\rho_{\rm all} = \rho_{\rm ion} + \rho_{\rm mer}$ is the total density of particles.

The Donnan potential φ can be evaluated from either eqs 3 and 4 directly, or by considering $\mu_{\pm,\text{out}} = \bar{\mu}_+ = \bar{\mu}_-$,

$$(z_{+}-z_{-})\,e\varphi=\mu_{-}-\mu_{+}.$$
(9)

Values of the Donnan potential φ are depicted in Figure S4 as functions of salt concentration and type. The cation is more

repulsive than the anion in all evaluated salts, thus the Donnan potential is negative in the uncharged polymer (panel a). In the case of cationic polymers (panels b, c), the Donnan potential is positive at low salt concentration. This can be explained as a compensation of the entropic penalty caused by the presence of negatively charged counterions to maintain the electroneutrality. The less the counterion is attracted to the polymer the lower the rate of the potential decrease with salt concentration.

5. ISOSPHERIC POINT

We have computed the concentration of various salt types when the effective volumes of the polymer are the same for the selected salt pair. Such concentrations as a function of polymer charge fraction ξ are shown in Figure S5.

We define an isospheric point as the salt concentration where the effective volume of the polymer is the same regardless of a salt type. The value of the isospheric point was found to be linearly dependent on the polymer's charge fraction ξ , providing the charge fraction is low ($\lesssim 0.05$). As the polymer's charge fraction increases, the isospheric point is gradually smeared out to the range of concentration and deviated from the original linear trend.

Salts with a highly attractive anion ($\varepsilon_{anion} \gtrsim 1.1 k_B T$) do not exhibit the isospheric point, as shown in Figure S5. This observation is consistent with the simulation data for the polymer chain having the charge fraction $\xi = 0.05$, see Figure S1 (a). Very weakly hydrated ions, such as perchlorate ClO₄⁻, are experimentally known to deviate in a similar manner.^{S2,S3}

REFERENCES

- (S1) Abraham, M. J.; Murtola, T.; Schulz, R.; Páll, S.; Smith, J. C.; Hess, B.; Lindahl, E. GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. *SoftwareX* 2015, 1-2, 19–25, DOI: 10.1016/j.softx.2015.06.001.
- (S2) Cho, Y. Thermodynamics and Applications of Elastin-like Polypeptides. Dissertation, Texas A&M University, USA, 2009.
- (S3) Okur, H. I.; Hladílková, J.; Rembert, K. B.; Cho, Y.; Heyda, J.; Dzubiella, J.; Cremer, P. S.; Jungwirth, P. Beyond the Hofmeister Series: Ion-Specific Effects on Proteins and Their Biological Functions. *J. Phys. Chem. B* 2017, 121, 1997–2014, DOI: 10.1021/acs.jpcb.6b10797.



Figure S4: Values of the Donnan potential φ between the polymer phase and the reservoir as a function of salt concentration and type, computed using the mean-field theory. The polymer phase is formed by a 200-mer chain. The uncharged polymer is shown in panel (a), while panels (b) and (c) depict cationic polymer consisting of charged monomers in a fraction $\xi = 0.05$, and 0.10, respectively.



Figure S5: The isospheric point of a 200-mer as a function of its charge fraction ξ . Each line corresponds to a pair of salts. The isospheric point is determined as a salt concentration where the effective volumes of the polymer phase coincide in both salt solutions.