PCCP

SUPPLEMENTARY INFORMATION

Ability of Poisson-Boltzmann Equation to Capture Molecular Dynamics Predicted Ion Distribution around Polyelectrolytes

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Finite size effects

The influence of the finite simulation box size, i.e. polyelectrolyte length was examined by comparing the ion distribution results of PGA decamers and icosamers. The decamer is referred to as PGA-10 and the icosamer as PGA. Figure S1 reveals that the counterion density distributions and fraction profiles for PGA-10 and PGA have the same form. Furthermore, the systems have negligible difference in their PB fitting and ion condensation parameters, see Table S1.

However, it is worth noting that the counterion density profiles differ slightly especially at distances corresponding to the r_0 and the PB fitting is better at longer distances, r > 1.5 nm, for the icosamer system. In conclusion, the ion distribution depends on slightly the system size at the level of the absolute density but the PB parameters are independent of the PE length at the decamer vs icosamer lengths. The results presented in the main article are based on icosameric PEs for the PEs with a medium-length monomers.

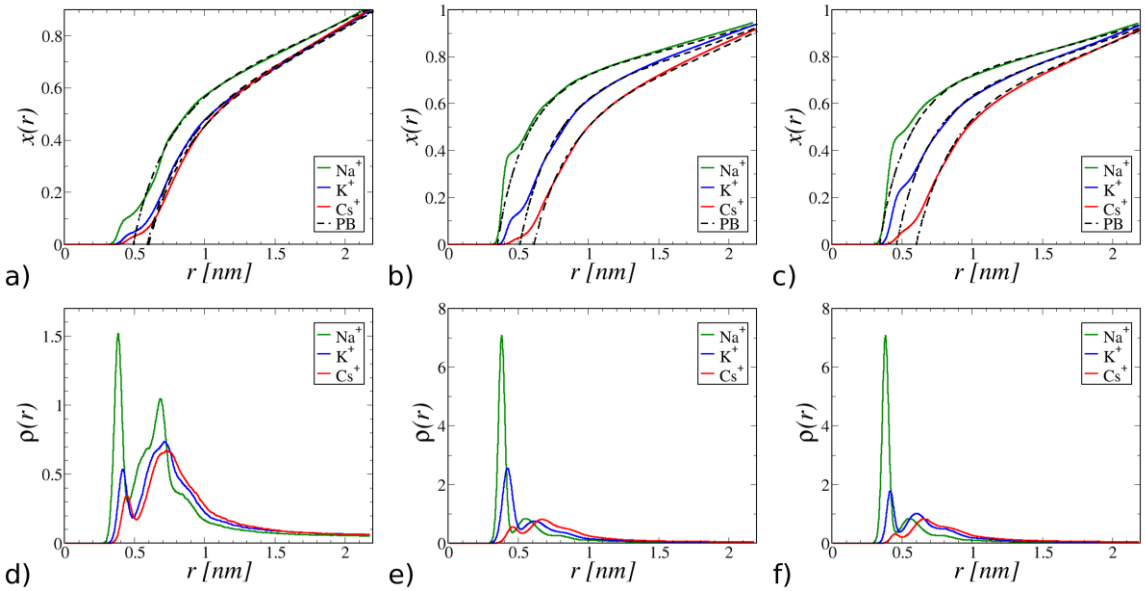

Figure S1. a)-c) The ion density and d)-f) the ion fraction profile for the PGA-10-Am (at left), PGA-10 (in the middle), and PGA systems (at right). The dashed lines denote the corresponding PB fitting.

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Force field dependency of the results

The force-field dependency of the molecular dynamics simulations was assessed by comparing the ion distribution around a PGA decamer system described by two different force fields. The force fields were Amber03 [1] and OPLSaa [2]. The Amber03 simulations employ the ion parameters by Dang [3] and the SPC/E water model [4] and are referred to as PGA-10-Am. The OPLSaa simulations PGA-10 and PGA use the OPLSaa standard ions with the TIP4P water model [5].

Figures S1d) and e) show that the fraction profiles differ somewhat by relative condensation peak intensities. This leads to small differences in the PB fitting parameters r_0 and V_0 and in counterion condensation parameters r_M and x_c. Table S1 presents the calculated parameters. The counter cations appear to condense more strongly and at shorter distance from the PE backbone with OPLSaa force field. The results suggest that the choice of the force field can influence significantly ion condensation specifics of MD simulations.

Additionally, Table S1 presents a comparison of our results with the findings of Heyda and Dzubiella [6] for the same system. Our results of ion condensation are consistent but vary in some parts slightly most likely due to differences in simulation software or protocol that could not be eliminated entirely.

Table S1. The calculated Poisson-Boltzmann parameters for PGA chains with different polymer lengths and description models. The table presents the effective radius of the PE r_0 (PB fitting parameter), the ion-specific interaction V_0 (fitting parameter), the Manning radius r_M, the fraction of condensed ions x_c, and the radius of the condensed layer r_{cl}. The values in the parentheses correspond to the error estimate of the fitting procedure. The square brackets contain the results of Heyda and Dzubiella [6] for the same system.

System	Ion	r_0 [nm]	V_0 [k_BT]	r_M [nm]	x_c	r_{cl} [nm]
PGA	Na^+	0.34	-1.8	1.28 (0.01)	0.78 (0.01)	0.94 (0.01)
	K^+	0.46	-1.4	1.39 (0.01)	0.75 (0.01)	0.93 (0.01)
	Cs^+	0.60	-1.2	1.52 (0.01)	0.73 (0.01)	0.92 (0.01)
PGA-10	Na^+	0.33	-1.9	1.29 (0.03)	0.78 (0.01)	0.96 (0.03)
	K^+	0.51	-1.5	1.44 (0.01)	0.76 (0.01)	0.93 (0.01)
	Cs^+	0.62	-1.0	1.51 (0.02)	0.72 (0.02)	0.89 (0.02)
PGA-10-Am	Na^+	0.48 [0.49]	-0.9 [-1.4]	1.36 (0.02) [1.35 (0.03)]	0.69 (0.01) [0.71 (0.02)]	0.88 (0.02)
	K^+	0.59 [0.58]	-0.6 [-1.0]	1.43 (0.02) [1.42 (0.02)]	0.66 (0.02) [0.66 (0.01)]	0.84 (0.02)
	Cs^+	0.61 [0.61]	-0.5 [-0.6]	1.43 (0.01) [1.36 (0.02)]	0.64 (0.02) [0.60 (0.01)]	0.82 (0.01)

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