

Polyelectrolyte adsorption: theoretical predictions and ellipsometry measurements

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Refractive index calculation

The adsorbed amount (Γ) was calculated using Feijter's formula¹ (assuming isotropic media and planar interface):

$$\Gamma = c * d \quad (1)$$

where c and d denote polyelectrolyte concentration and average layer thickness, respectively. Furthermore,

$$n_s - n_0 = c \frac{dn}{dc} \quad (2)$$

where n_s is the refractive index of the adsorbed layer, whereas n_0 is the refractive index of the salt solution. the gradient, dn/dc , is the refractive index increment value for polyelectrolytes. This

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was measured by an Abbe refractometer. The value obtained for PVNP was $dn/dc = 0.176 \text{ cm}^3/\text{g}$, in the buffer solution. We also evaluated the salt concentration dependence of this quantity. The results, presented in Figure 1, show that this dependence is very weak. The measured values falls within the range of those typically reported (0.16-0.18) in the literature.

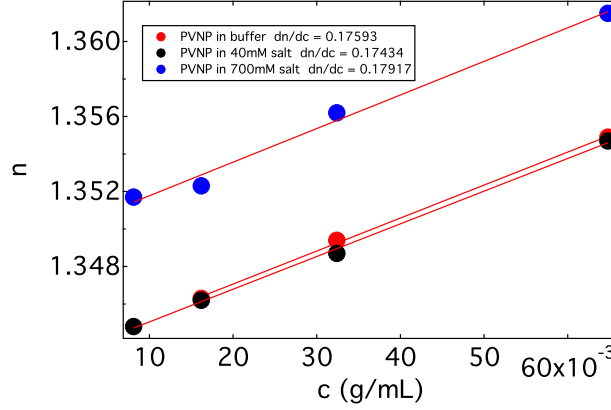


Figure 1: Refractive index increment of PVNP, at different salt concentrations.

Since the simple anion in PVNP is iodide, the dn/dc value $0.176 \text{ cm}^3/\text{g}$ would ideally reflect the adsorption of polyions and iodide. However, in reality, the concentration of I^- is presumably low, in the adsorbed layer. Thus, calculations directly based on this value would be incorrect. In other words, given the dominance of simple salt in the solutions, the gradient (dn/dc) value for polyion-chloride is more appropriate. We have used the Lorenz-Lorenz equation to evaluate this quantity (see below).

At a given wavelength (in our case 401.5 nm) and temperature (25°C), a useful relation is:

$$\frac{Q_{mixture}}{\rho_{mixture}} = \sum_i x_i \frac{Q_i}{\rho_i} \quad (3)$$

where the sum runs across all species i in the mixture. The weight fraction of species i is denoted x_i , whereas $\rho_{mixture}$ is the density of the studied mixture, while ρ_i is the density of a pure i -sample. $Q_{mixture}$ and Q_i are defined as:

$$Q = \frac{n^2(mixture, T, \lambda) - 1}{n^2(mixture, T, \lambda) + 2} \quad (4)$$

and

$$Q_i = \frac{n^2(\text{pure } i, T, \lambda) - 1}{n^2(\text{pure } i, T, \lambda) + 2} \quad (5)$$

where n is the refractive index, at temperature T , and wavelength λ .²

Thus, by combining these relations for a NaCl solution, a NaI solution, a polyion iodide (PI) solution, and a polyion chloride (PCI), we obtain a linear equation system:

$$\frac{Q_{\text{NaCl solution}}}{\rho_{\text{NaCl solution}}} = x_{\text{Na}^+} \frac{Q_{\text{Na}^+}}{\rho_{\text{Cl}^-}} + x_{\text{Cl}^-} \frac{Q_{\text{Cl}^-}}{\rho_{\text{Cl}^-}} + x_{\text{H}_2\text{O}} \frac{Q_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \quad (6)$$

$$\frac{Q_{\text{NaI solution}}}{\rho_{\text{NaI solution}}} = x_{\text{Na}^+} \frac{Q_{\text{Na}^+}}{\rho_{\text{I}^-}} + x_{\text{I}^-} \frac{Q_{\text{Cl}^-}}{\rho_{\text{I}^-}} + x_{\text{H}_2\text{O}} \frac{Q_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \quad (7)$$

$$\frac{Q_{\text{PI solution}}}{\rho_{\text{PI solution}}} = x_{\text{P}^+} \frac{Q_{\text{P}^+}}{\rho_{\text{I}^-}} + x_{\text{I}^-} \frac{Q_{\text{I}^-}}{\rho_{\text{I}^-}} + x_{\text{H}_2\text{O}} \frac{Q_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \quad (8)$$

$$\frac{Q_{\text{PCI solution}}}{\rho_{\text{PCI solution}}} = x_{\text{P}^+} \frac{Q_{\text{P}^+}}{\rho_{\text{Cl}^-}} + x_{\text{Cl}^-} \frac{Q_{\text{Cl}^-}}{\rho_{\text{Cl}^-}} + x_{\text{H}_2\text{O}} \frac{Q_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \quad (9)$$

Using standard equation subtractions, we find:

$$\frac{Q_{\text{PCI solution}}}{\rho_{\text{PCI solution}}} = \frac{Q_{\text{PI solution}}}{\rho_{\text{PI solution}}} + x_{\text{Cl}^-} \frac{Q_{\text{Cl}^-}}{\rho_{\text{Cl}^-}} - x_{\text{I}^-} \frac{Q_{\text{I}^-}}{\rho_{\text{I}^-}} \quad (10)$$

$$\frac{Q_{\text{NaCl solution}}}{\rho_{\text{NaCl solution}}} - \frac{Q_{\text{NaI solution}}}{\rho_{\text{NaI solution}}} = x_{\text{Cl}^-} \frac{Q_{\text{Cl}^-}}{\rho_{\text{Cl}^-}} - x_{\text{I}^-} \frac{Q_{\text{Cl}^-}}{\rho_{\text{I}^-}} \quad (11)$$

$$\frac{Q_{\text{PCI solution}}}{\rho_{\text{PCI solution}}} = \frac{Q_{\text{NaCl solution}}}{\rho_{\text{NaCl solution}}} + \frac{Q_{\text{PI solution}}}{\rho_{\text{PI solution}}} - \frac{Q_{\text{NaI solution}}}{\rho_{\text{NaI solution}}} \quad (12)$$

By using a constant anion concentration in the 4 solutions (NaCl, NaI, PI, and PCI solution), we can assume that, at least for dilute samples, the density is close to that of pure water. Thus, the water contribution to the refractive index is approximately constant, between the solutions. This allows us to arrive at the final relation for the refractive index of PCI solutions:

$$Q_{\text{PCI}} = Q_{\text{NaCl}} + Q_{\text{PI}} - Q_{\text{NaI}} \quad (13)$$

The refractive index of NaCl, PI and NaI solutions were measured at 1mM, 0.5mM and 0.25mM, respectively. The refractive index of a PCl solution, at these concentrations, was calculated by equation (13). The gradient, dn/dc was then obtained via a least-squares fit to an assumed linear relation between n and c . In Figure 2, we see that the relation indeed is approximately linear.

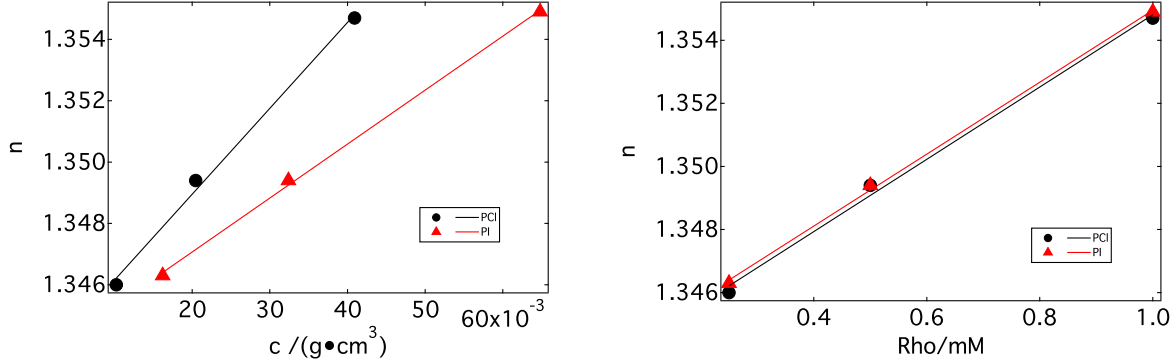


Figure 2: Refractive index of PCl and PI, as a function of concentration.
Left graph: concentration in units of g/cm^3 .
Right graph: *monomer* concentration in units of mM .

We found gradient values of $dn/dc = 0.28 \text{ cm}^3/\text{g}$ and $0.176 \text{ cm}^3/\text{g}$, for PCl and PI, respectively. Using monomer number concentrations, ρ , this corresponds to $dn/d\rho = 0.01140 \text{ L}/\text{mmol}$ and $0.01146 \text{ L}/\text{mmol}$, respectively. Adhereing to the use of monomer number concentrations, we can also calculate the adsorption amount, for PCl as:

$$\Gamma_{PCl} = \frac{n_s - n_0}{(dn/d\rho)_{PCl}} * d * M_{mon}(PCl) \quad (14)$$

where $M_{mon}(PCl)$ is the weight of a monomer-chloride pair in PCL. Analogously we find, for PI:

$$\Gamma_{PI} = \frac{n_s - n_0}{(dn/d\rho)_{PI}} * d * M_{mon}(PI) \quad (15)$$

Since $(dn/d\rho)_{PI}$ is similar to $(dn/d\rho)_{PCl}$, we arrive at:

$$\Gamma_{PCl} \approx \Gamma_{PI} \frac{M_{mon}(PCl)}{M_{mon}(PI)} \quad (16)$$

Note that the molar refractive index of Cl and I is 5.844 and 13.954, respectively. On the other hand, the atomic radii are about 99 pm , 133 pm Cl and I atoms. Thus, the refractive index contribution, per unit volume, becomes $5.844/(99^3) = 6.0 \times 10^{-6}/\text{pm}^3$ for Cl and $13.954/(133^3) = 6.0 \times 10^{-6}$ for I. In practice, this means that contributions to the refractive index of a typical monomer-chloride salt will be similar to that from monomer-iodide. This is the origin to the simple and practical relation, eq. (16).

Data from ellipsometry measurements

In this section, we have collected curves of measured adsorbed amount, at various salt concentrations, for the two different polyelectrolytes investigated. The green and black curves are two independent measurements for PVNP (as a check for reproducibility), while the blue and red curves represent PDADMAC.

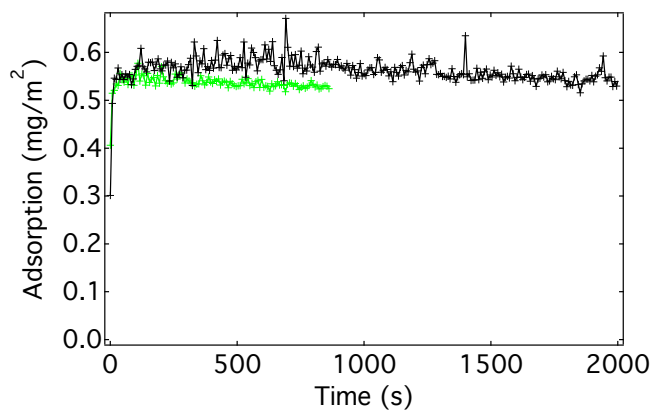


Figure 3: Adsorbed amount of PVNP and PDADMAC on a silica surface as a function of time, at a NaCl concentration of 40mM (pH = 9).

The PVNP employed in this study is relatively mono-dispersed. The polydispersity values tested by SEC (size exclusion chromatography) by a company (Innventia). They found values of are 1.224 and 1.229 (independent measurements). These values agree well with the one reported by the supplier (1.2). We also carried out an extra adsorption measurement on dialyzed PVNP, using the same dialysis procedure as for PDADMAC. The result is presented in Figure 8, and we

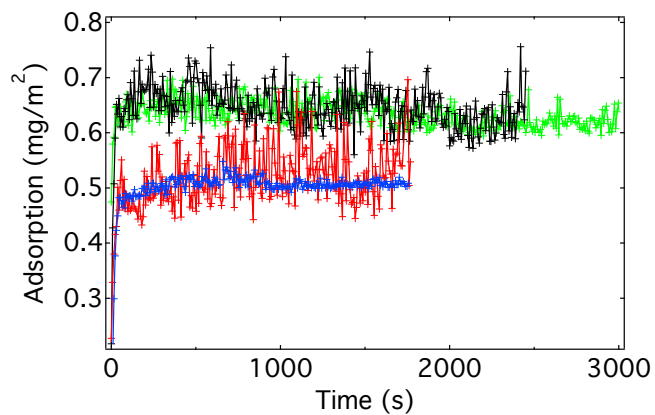


Figure 4: Adsorbed amount of PVNP and PDADMAC on a silica surface as a function of time, at a NaCl concentration of 160mM (pH = 9).

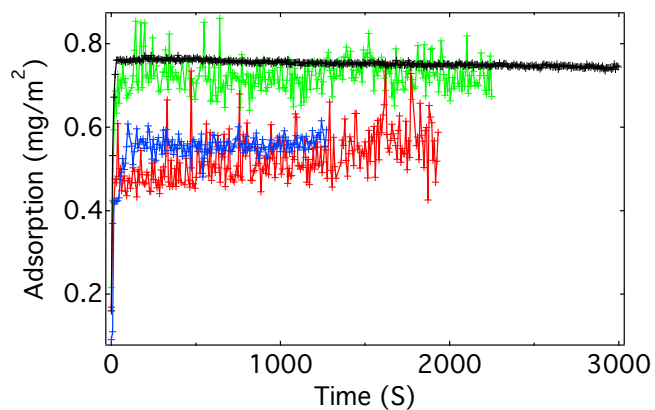


Figure 5: Adsorbed amount of PVNP and PDADMAC on a silica surface as a function of time, at a NaCl concentration of 200mM (pH = 9).

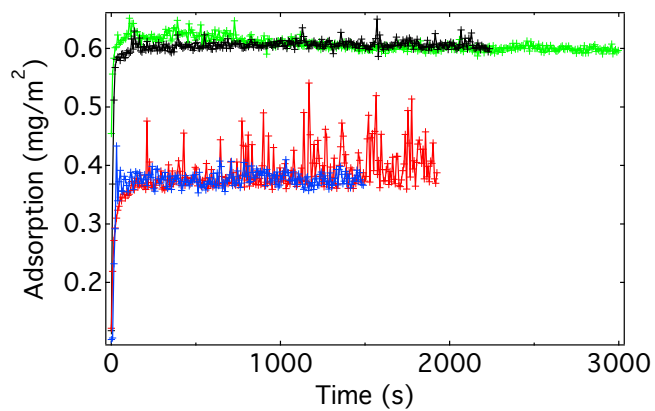


Figure 6: Adsorbed amount of PVNP and PDADMAC on a silica surface as a function of time, at a NaCl concentration of 300mM (pH = 9).

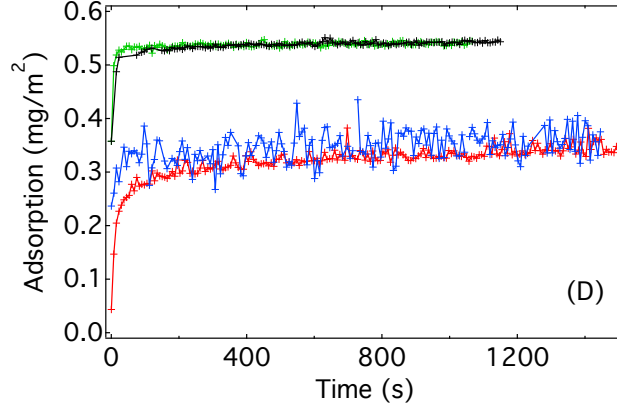


Figure 7: Adsorbed amount of PVNP and PDADMAC on a silica surface as a function of time, at a NaCl concentration of 700mM (pH = 9).

note that the dialysis procedure has no influence on the measured adsorption. This also indicates that the PVNP sample has a high purity.

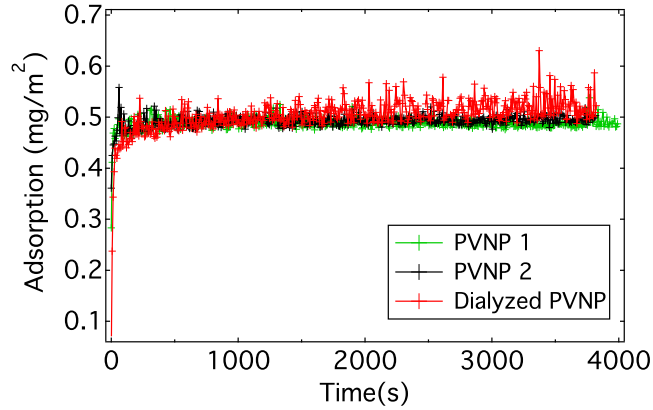


Figure 8: Comparison of adsorbed amounts, as measured with dialyzed and non-dialyzed PVNP, respectively, in 10mM salt. PVNP 1 and PVNP 2 are separate measurements, using non-dialyzed PVNP.

Charge position in “comb model”

Here we provide a brief comparison with our reference “comb polymer” model, where end bead in each side chain carries a unit charge, with a similar comb polymer, but with the charge placed on the second monomer, counted from the end. Theoretical predictions of the adsorbed amount, as found using either model under electrosorption conditions ($\beta w_s = 0$), are collected in Figure 9.

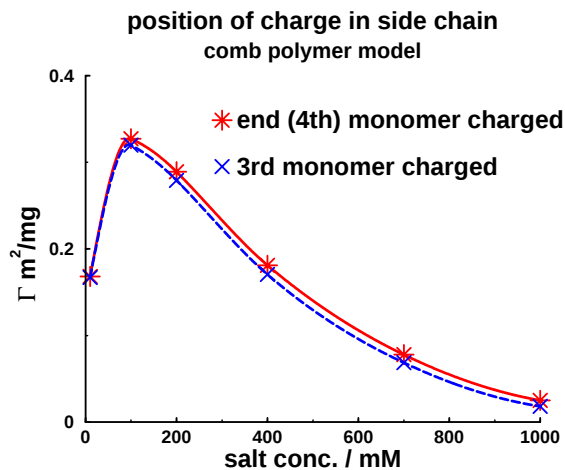


Figure 9: Adsorbed amount, as predicted by “comb models”, where the charge is at the end bead and second-to-end bead, respectively.

We note that the difference is negligible.

Chain length

Here we give some further support to the statement that the calculates adsorbed amount is virtually independent of polymer length, r , as long as r exceeds about 200. In Figure 10, we plot Γ versus r , at a concentration $c_s = 400mM$. Note that this is a salt concentration close to that where the chain length dependence is maximal. Nevertheless, while there is a substantial length dependence for $r < 100$, or so, the curve rapidly becomes flat (also in the presence on a non-electrostatic surface affinity). This flatness also explains why the predicted adsorbed amount is quite insensitive to the degree of polydispersity, unless the average polymer length is very small.

Effects of correlations

Finally, in Figure 11, we show results obtained without the correlation-correlation (pure mean-field), using model parameters identical to those adopted to reproduce the adsorption of PVNP on

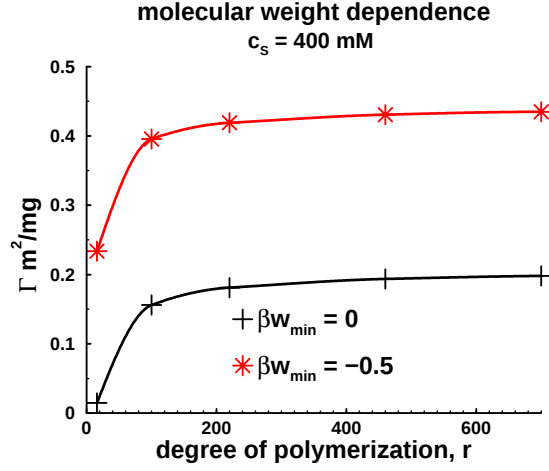


Figure 10: The dependence of adsorbed amount on the degree of polymerization (r), at $c_s = 400 \text{ mM}$. Our standard comb polymer model was utilized.

a silica surface (Figure 14 in the main paper). We note that the predicted adsorbed amounts are

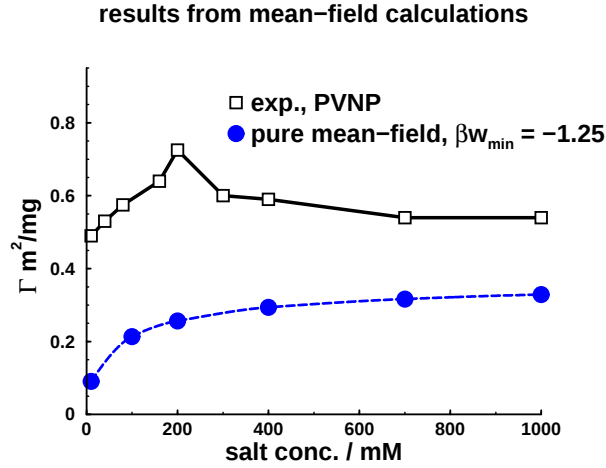


Figure 11: Predictions from DFT, in which the correlation-correction has been removed.

too low, but also that this cannot be compensated for by increasing the non-electrostatic surface affinity. In fact w_s is, under these circumstances, already so dominating that the predicted adsorbed amount increases monotonically with added salt, in qualitative disagreement with experimental data. Further, and more convincing, evidence on the shortcomings of the pure mean-field version

can be found in refs 5 and 19, in the main paper.

References

1. Feijter, J.; Benjamins, J.; Veer, F. Ellipsometry as a tool to study the adsorption behavior of synthetic and biopolymers at the air-water interface. *Biopolymers* **1978**, *17*, 1759–1772.
2. Tompkins, H.; McGahan, W. Spectroscopic Ellipsometry and Reflectometry. **1999**,