Molecular mass dependence of adsorbed amount and hydrodynamic thickness of polyelectrolyte layers

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Highly charged polyelectrolytes adsorbed on oppositely charged colloidal particles are investigated by electrophoresis and dynamic light scattering. The dependence of the adsorbed amount and of the hydrodynamic layer thickness on the molecular mass and the salt level is analyzed. The adsorbed amount increases with increasing salt level and decreases with increasing molecular mass. The hydrodynamic layer thickness is independent of the molecular mass at low salt levels, but increases with the molecular mass as a power law with an exponent 0.10 ± 0.01 at high salt. The same behavior was observed for different polyelectrolytes and substrates and therefore is suspected to be generic. Due to semi-quantitative agreement with computer simulations carried out by Kong and Muthukumar in 1998, the observed behavior is interpreted with conformational changes of single adsorbed polyelectrolyte chains.

Polyelectrolytes are widely used to control stability and rheology of colloidal suspensions[1–3] and to create functional multi-layered surface coatings.[4–6] Only in the last few decades, however, researchers started to unravel the underlying structure of adsorbed polymeric layers experimentally and theoretically.[1,2,7–10] Adsorption of neutral polymers from good solvents is relatively well understood.[1,2,10–13] The layer thickness L of an adsorbed polymer obeys the scaling-law

EQ1

where M is the molecular mass and a an exponent. Hydrodynamic layer thickness obtained from dynamic light scattering (DLS) yields the exponent a C 0.6 reflecting Flory's exponent characterizing the size of a self-avoiding chain in a good solvent.[14,15] Ellipsometry,[12] neutron scattering,[13] or direct force measurements[16] yield a smaller exponent a C 0.4. De Gennes explained this discrepancy by pointing out that the adsorbed layer is rather diffuse and that different experimental methods probe different moments of the layer profile.[1,11] Other researchers have argued that the adsorbed amount G should follow a similar scaling-law[12,13]

EQ2

The experimentally observed dependence on the molecular mass is typically weak, and leads to exponents b between -0.05 and 0.2. Recently, attention shifted towards properties of adsorbed polyelectrolyte layers.[2,6,8–10,17,18] This complex problem is still far from being settled, as one must consider numerous parameters, such as the charge density of substrate and polymer, presence of inert salt, and the extent of specific ion binding.[19–23] The question can be narrowed down by focusing on the practically relevant situation of highly charged polyelectrolytes adsorbing on oppositely charged substrates. In this case, the polyelectrolyte adsorption initially leads to charge reversal (or overcharging), and subsequently to a saturated adsorption layer.[24–29] The saturated amount increases with the salt level, as the adsorption is limited by the lateral repulsion of the charged polyelectrolyte chains.[19,25,30] To our knowledge, basically no information on the general molecular mass dependence of saturated adsorbed polyelectrolyte films is currently available.

Here, we fill this gap by experimentally determining the adsorbed amount of polyelectrolytes on oppositely charged colloidal particles and the corresponding layer thickness as a function of the molecular mass. The saturated adsorbed mass was obtained by electrophoresis while hydrodynamic layer thickness by multi-angle DLS. A wide molecular mass range is spanned from 2.6 to 5600 kg mol^{-1} with polyanions poly(styrene sulfonate) (PSS) and poly(acrylic acid) (PAA), and the polycation linear poly(ethylene imine) (LPEI). Monodisperse polystyrene latex with cationic amidine or anionic sulfate or carboxyl surface groups are used as substrates. The influence of monovalent salt potassium chloride (KCl) is also investigated, as this parameter significantly alters the adsorption behavior of polyelectrolytes through electrostatic screening effects.[19,25,30]

The characteristic overcharging of a charged substrate upon addition of oppositely charged polyelectrolytes can be best followed by electrophoresis.[24,26,28] The mobility of positively charged amidine latex particles decreases upon increasing the dose of PSS and reverses its sign at the isoelectric point (IEP, Fig. 1). The mobility decreases further, and finally levels- off at a plateau. Such overcharging is most characteristic for oppositely charged polyelectrolyte/particle systems, and is related to charge correlation phenomena and the presence of additional non-electrostatic attractive forces (e.g., van der Waals, hydrophobic).[8,9,22–24,26,28] The polyelectrolyte adsorption is quantitative prior to the plateau and suggests a quasi-irreversible adsorption process. This point can be verified by the independence of the electrophoretic mobility on particle concentration (Fig. 1a).[31] Beyond the plateau, the adsorbed amount remains constant, and any excess polyelectrolyte remains dissolved in solution. One can accurately estimate the adsorbed amount at saturation from the transition point between these two regimes, whereby kinetic effects broaden the ideal cusp-like shape of the curve.[26]

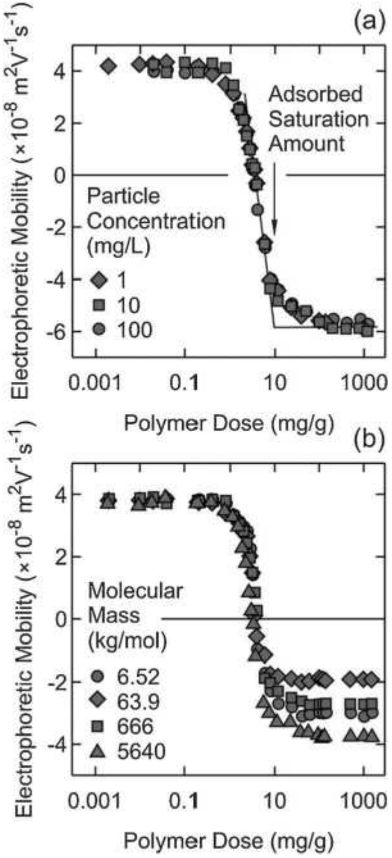

Fig. 1 Measurement of polyelectrolyte adsorption on oppositely charged colloidal particles by electrophoresis. Electrophoretic mobility of amidine latex particles upon addition of PSS (a) for different particle concentrations and (b) for different PSS molecular masses at an ionic strength of 10^{-4} M.

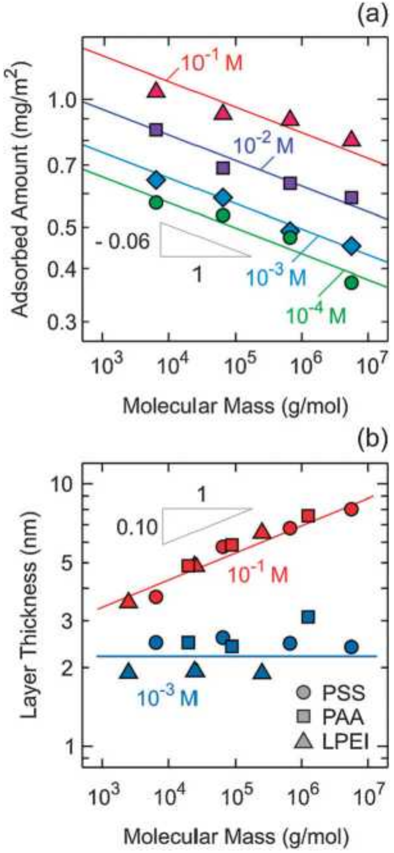

Fig. 2 Molecular mass dependence of the properties of adsorbed polyelectrolyte on oppositely charged particles in a doubly-logarithmic representation. (a) Adsorbed amount of PSS for different ionic strengths. (b) Hydrodynamic layer thickness for different polyelectrolytes at low and high ionic strength. Solid lines are fits with eqn (1) and (2). The respective exponents are indicated.

Adsorbed mass of PSS on amidine latex particles decreases with increasing molecular mass (Fig. 2a). While the adsorbed mass increases with the salt level, the molecular mass dependence can be always well described with eqn (2) with an exponent $b = —0.06 \pm 0.02$. Repeating the analogous experiments with three other polyelectrolyte/particle systems involving polyanions and polycations confirms that these conclusions are generic. While the adsorbed mass is system specific, the molecular mass follows a similar power-law with the exponent stated above. The observed weak molecular mass dependence is in line with theoretical predictions that the adsorbed amount of polyelectrolyte should be independent of molecular [19,20] mass.

Reliable measurements of the thickness of adsorbed polyelectrolyte layers can be obtained by time-resolved multi-angle DLS.[32] The layer thickness is obtained from the difference of the hydrodynamic radii of particles with and without adsorbed polyelectrolyte at high dilutions in the range of 0.05-0.1 mg L^{-1} to avoid any effects of particle interaction and aggregation. The multi-angle approach boosts the accuracy with respect to a classical single-angle technique further, which becomes crucial for polyelectrolyte layers with a thickness of only a few nanometres. The result of a typical multi-angle experiment shows that the hydrodynamic radii measured at different scattering angles differ by about ±5 nm (Fig. 3a). This variation of the hydrodynamic radii with the scattering angle is due to the small, but finite sample polydispersity, which leads to a different weighting of the diffusion coefficients by the respective form factors. However, the layer thickness obtained from the differences between the radii at the respective angles is highly reproducible and constant. Their average provides an excellent estimate of the layer thickness and is typically accurate to ±0.2 nm. The hydrodynamic thickness of PSS layers adsorbed on amidine latex particles increases with the salt level (Fig. 3b). At salt levels below 0.010 M, the polyelectrolyte layer has only a thickness of around 2 nm, and this thickness is independent of the molecular mass. The layer thickness increases with increasing salt level, and attains a plateau at salt levels above 0.1 M. At higher salt levels, the plateau layer thickness increases with the molecular mass. This increase can be well described with eqn (1) with an exponent $a = 0.10 \pm 0.01$ (Fig. 2b). We remark that a previous estimate of this exponent[24] was in error due to inaccurate thickness measurements of thin layers with single-angle DLS. Repeating similar experiments with three other polyelectrolyte/particle systems involving polyanions and polycations, we find these conclusions to be generic again. The crucial observation is that even at high salt levels the observed exponent is substantially smaller than for neutral polymers.

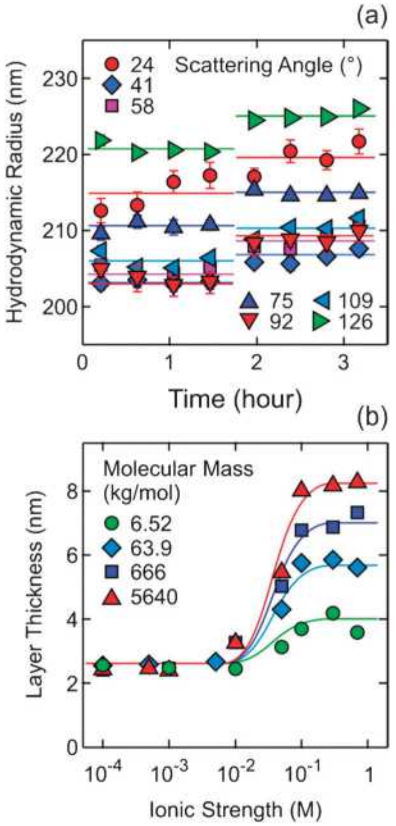

Fig. 3 Measurement of hydrodynamic thickness of adsorbed poly-electrolyte layers with multi-angle time-resolved DLS. (a) Time- dependence of the apparent hydrodynamic radius of amidine latex suspension before and after addition of the PSS with a molecular mass of 5640 kg mol ^{1} at an ionic strength of 0.3 M. (b) Hydrodynamic layer thickness in the same system as a function of ionic strength and for different molecular masses.

Our experimental layer thickness data are in striking agreement with earlier Monte Carlo simulation results of a single adsorbed polyelectrolyte chain by Kong and Muthukumar[21] (see Fig. 7a in their article). These authors predict that at low salt the thickness of an adsorbed polyelectrolyte is small and independent of its molecular mass. With increasing salt levels, the adsorbed polyelectrolyte swells, and its thickness reaches a plateau at high salt levels. This plateau value is predicted to increase with the molecular mass. All these features are in full accord with the present experimental data. However, by analyzing the published plateau values obtained from simulations, we find a C 0.66. This theoretical value is substantially larger than the presently reported experimental one. This discrepancy suggests that the simulation model is oversimplified as only electrostatic and hard-core interactions are being considered. We suspect that additional non-electrostatic attractive inter- actions between the polyelectrolyte and the substrate are present. Their importance is further corroborated by the fact that polyelectrolyte adsorption is present even at salt levels of 1 M. If only electrostatic forces would be operational, polyelectrolytes are expected not to adsorb as such high salt levels.[19,21]

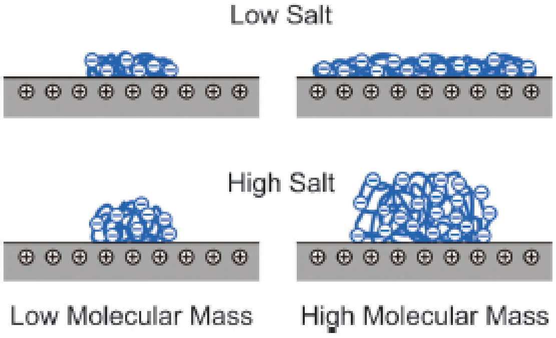

Fig. 4 Pictorial representations adsorbed polyelectrolyte chains.

Nevertheless, the semi-quantitative agreement between the present experimental data and the simulation results of single polyelectrolyte chains by Kong and Muthukumar[21] affirms that the adsorbed layer consists of isolated polyelectrolyte chains, and that the conformation of single polyelectrolyte chains determines the layer thickness. The corresponding mechanism is depicted in Fig. 4. At low salt, a polyelectrolyte chain adsorbs in a flat configuration. When its molecular mass is low, its lateral extensions remain comparable for low and high salt levels. When its molecular mass is high, however, its lateral extension is larger at low salt levels than at high ones. Therefore, the thickness of these layers increases with increasing molecular mass at high salt levels.

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