Polyelectrolyte adsorption kinetics under an applied electric potential: Strongly versus weakly charged polymers

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A B S T R A C T

Previous work has demonstrated adsorption of weakly basic polycations to a conducting substrate to be continuous, i.e. asymptotically linear in time over hours, under an applied anodic potential [A.P. Ngankam, P.R. Van Tassel, Proc. Natl. Acad. Sci. USA 104 (2007) 1140]. Adsorption without apparent saturation requires an interfacial charge regulation, which is possible for weakly charged polymers via segment deprotonation. We investigate here whether deprotonation is a necessary condition for continuous adsorption by comparing the behavior of a weakly and a strongly charged polyelectrolyte, the latter containing permanently charged segments incapable of deprotonation. We employ optical waveguide lightmode spectroscopy (OWLS) to measure adsorption of poly(N-vinyl imidazole) (PVI), a weakly basic polycation, and quaternized poly(N-vinyl imidazole) (QPVI), a structurally similar polymer with ca. 20% of its monomers containing a permanent positive charge, onto indium tin oxide (ITO). Under open circuit conditions, we observe both PVI and QPVI adsorption to reach a rapid saturation and be essentially irreversible. In contrast, at an ITO potential of 1.5 V (versus hydrogen) in a 0.1 M NaCl solution, we observe adsorption of both PVI and QPVI to be continuous and reversible. In salt free solution, we observe PVI but *not* QPVI to exhibit continuous adsorption at 1.5 V, and for both polymers to be essentially irreversibly attached. We propose interfacial charge regulation to occur via a deprotonation mechanism for PVI, and via a counterion condensation mechanism for QPVI. Continuous adsorption is therefore possible for a strongly charged polyelectrolyte, via a counterion condensation mechanism; this finding opens the door to nanofilms of controlled polymer content containing permanent charges.

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1. Introduction

Charged polymers, or polyelectrolytes, have a strong tendency to adsorb at the solid–liquid interface. Adsorbed polyelectrolyte layers have been used for years to separate minerals and suppress colloidal flocculation. More recently, adsorbed layers—or multilayers formed via the layer-by-layer (LbL) assembly of oppositely charged polymers [1,2]—are being developed as ion conducting membranes [3–6], bio- and chemical sensing substrates [7,8], and cell-contacting biomaterials [9–11].

Polyelectrolyte adsorption has been the subject of numerous experimental [12–25], theoretical [26–34], and simulation [35–42] studies. Due to the importance of electrostatic interactions, the focus is often on effects of solution pH and ionic strength, variables directly influencing charge–charge interactions. Substrate electric potential is another key variable, but its influence is much less

studied, in part owing to the challenge of measuring adsorption while applying a potential difference [43–50].

Recently, Ngankam and Van Tassel employed optical waveguide lightmode spectroscopy (OWLS) to investigate the adsorption kinetics of various amine side-chain containing polycations to a conducting indium tin oxide (ITO) substrate [51]. They found conditions under which adsorption becomes continuous, i.e. asymptotically linear (or nearly linear) in time over hours, upon the application of a modest anodic potential. This observation contrasts starkly with the typical case where polyelectrolyte adsorption saturates due to an accumulation of charge at the interface. The authors explain their finding in terms of a polymer–polymer binding mechanism, some details of which follow. Near a conducting surface, like-charged segments may approach one another due to suppressed electrostatic repulsion, driven either by image charge effects and/or enhanced correlations among charge screening species. Binding among like-charged segments may occur via short-range attractive interactions such as hydrogen bonding and van der Waals; such binding naturally promotes a loss of layer charge through a charge regulation process. X-ray photoelectron

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PVI:
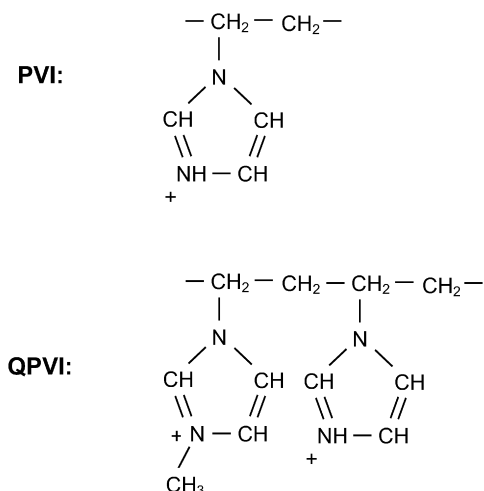
QPVI:

Fig. 1. Chemical structures of poly(N-vinyl imidazole) (PVI) and quaternized poly-(N-vinyl imidazole) (QPVI). The latter is a random copolymer of quaternized (left) and standard (right) N-vinyl imidazole monomers (degree of quaternization 20.7%). The quaternary amines are permanently charged, and the tertiary amines are weakly basic with pK_a ca. 7.

spectroscopy (XPS) analysis revealed a significantly lower degree of amine group protonation within adsorbed layers formed under an applied electric potential, compared to those formed under an open circuit potential, suggesting deprotonation of the charged segments to be the principal mechanism behind the observed loss of layer charge.

In order to address the question of whether polymer deprotonation is a necessary condition for continuous adsorption under an applied electric potential, we investigate here the adsorption kinetics of two structurally similar polyelectrolytes, poly(N-vinyl imidazole) (PVI) and quaternized poly(N-vinyl imidazole) (QPVI), onto indium tin oxide (ITO). PVI is a weak polycation in the sense that segment charge results from acid–base equilibria, and is thus sensitive to local environment. (All polyelectrolytes previously observed to exhibit continuous adsorption have also been weak polycations [51].) In contrast, QPVI is a strong polycation in the sense that some of its segments are permanently charged (due to the presence of a quaternary amine). (Chemical structures of PVI and QPVI are shown in Fig. 1.) If polymer deprotonation is indeed a necessary condition, then QPVI should not exhibit continuous adsorption. However, if QPVI exhibits continuous adsorption, then deprotonation is not necessary and other mechanisms are possible. As detailed in the remainder of the paper, we do indeed observe continuous adsorption under an applied potential for QPVI, and suggest a charge regulation mechanism involving counterion condensation to enable adsorption without apparent saturation for this strongly charged polyelectrolyte.

2. Materials and methods

2.1. Optical waveguide lightmode spectroscopy (OWLS)

OWLS is a highly sensitive method (precision ∼1 ng/cm^2) for measuring macromolecular adsorption kinetics at the solid–liquid interface [52–55]. Detection is based on excitation of guided modes via polarized laser light directed upon a grating coupler at the surface of an optical waveguide. Our OWLS instrument (MicroVacuum, Hungary) is composed of a parallel plate flow cell whose bottom surface is a OW 2400c Sensor Chip (MicroVacuum), consisting of a ca. 10 nm indium tin oxide (ITO) coating (In/Sn ratio 2.0 ± 0.1 as determined by XPS) on a ca. 200 nm planar silica–titania waveguiding film (Si/Ti ratio 3.0 ± 0.1, as given by the manufacturer), itself coated onto a glass substrate. Our recent modifications to

perform measurements under an applied potential include a flat Pt electrode at the flow cell ceiling, a power source and a voltmeter in series with the ITO and Pt electrodes (to provide voltage and measure current), and an electrometer in series with a Ag/AgCl reference electrode (to determine ITO potential in terms of a standard electrode) [45]. The voltage loss across the ITO portion of the circuit, based on the measured linear (hydrated) ITO layer resistance of 208 W/cm and a typical current of 0.2 mA, is of order 10^{-4} V. The voltage window available for study is about −0.2 V to 3.0 V relative to the standard hydrogen electrode; potentials below −0.2 V result in electrochemical reduction of ITO to metallic indium, and water hydrolysis becomes significant above 3.0 V.

2.2. Materials

Poly(N-vinyl imidazole) (PVI) and poly(N-vinyl imidazole) quaternized with CH$_3$I (QPVI) are obtained from Polymer Source, Inc. (Quebec). Chemical structures are shown in Fig. 1. The number averaged molecular weight M_n and the ratio of weight averaged to number averaged molecular weight M_w/M_n are, respectively, 12,700 and 3.38 for PVI and 16,500 and 1.5 for QPVI. 20.7% of QPVI segments contain quaternary amines (according to the manufacturer); the others contain tertiary amines.

10 mM Hepes is obtained from Sigma Chemical (St. Louis). All Hepes solutions are adjusted to pH 7.4 by addition of a small amount of 6 M NaOH or HCl. Addition of 0.1 g/L QPVI to 10 mM Hepes yields no measurable change in pH, suggesting the fraction of charged tertiary amines in QPVI at pH 7.4 to be no more than a few percent.

2.3. OWLS experiments

Prior to each experiment, the flow cell, tubing, and sensor chip are cleaned with 2% Hellmanex (Hellma, Mulheim, Germany). The sensor chip is then rinsed with deionized water, dried, and placed in a UV/O$_3$ chamber for 20 min. Deionized water is introduced into the OWLS system at flow rate corresponding to a shear rate of 1.3 s^{-1} at the adsorbing surface (this same shear rate is employed throughout). A mode spectrum yielding the effective refractive indices of the transverse electric (N_{TE}) and transverse magnetic (N_{TM}) modes are measured until stable values are reached. 10 mM Hepes buffer is then introduced until steady baseline N_{TE} and N_{TM} values are achieved. For experiments performed at an open circuit potential (0 V relative to the standard hydrogen electrode), a 0.1 g/L polymer solution is introduced and adsorption is detected through changes in N_{TE} and N_{TM}. After a certain period of time, pure Hepes solution is re-introduced to test for desorption. For other experiments, a potential of 1.5 V (relative to the standard hydrogen electrode) is applied and once steady values of N_{TE} and N_{TM} are obtained, a 0.1 g/L polymer solution is introduced. Following a given time, the polymer solution is replaced by the pure Hepes solution.

3. Results

In Fig. 2, we show the change in the effective refractive index of the transverse electric mode (ΔN_{TE}) versus time upon introduction of PVI and QPVI, in Hepes solution of pH 7.4 and 0.1 M NaCl, into the OWLS flow chamber at applied potentials of 0 and 1.5 V (relative to the standard hydrogen electrode). The observed increase in ΔN_{TE} is attributed to polymer adsorption onto the ITO coated OWLS sensor chip, and can be taken as roughly proportional to adsorbed mass [56]. At the lower (open circuit) potential, both PVI and QPVI rapidly reach a saturation, and no desorption is observed during a buffer rinse. The greater adsorbed amount of PVI relative to QPVI is likely due to its lower overall charge, leading to a