



The first step in layer-by-layer deposition: Electrostatics and/or non-electrostatics?

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ABSTRACT

A critical discussion is presented on the properties and prerequisites of adsorbed polyelectrolytes that have to function as substrates for further layer-by-layer deposition. The central theme is discriminating between the roles of electrostatic and non-electrostatic interactions. In order to emphasize this feature we refrain from discussing practical problems sometimes incurred in polyelectrolyte adsorption like freezing-in of non-equilibrium situations, patchwise attachment, unclear chemistry and only consider solid substrates. Although it is in principle ambiguous to discriminate between coulombic and non-coulombic or “chemical” interactions, it will be shown that, as a rule, non-coulombic contributions to the interactions cannot be neglected. They are responsible for the familiar overcharging. For obtaining more insight, it is recommended to consider electrometric techniques such as electrokinetics, conductometry and potentiometry, in combination with other analytical techniques applied to well-defined systems, for which various parameters can be modulated in a systematic way.

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1. Introduction

1.1. Dedication

This paper is a contribution to a special issue of the *Advances in Colloid and Interface Science*, dedicated to the memory of Nikolai (Kolya) V. Churaev, one of the outstanding Russian colloid scientists. He was nationally and internationally known as a capable and dedicated experimentalist with a broad expertise. In particular we appreciated him for his ability to conceive new experimental pathways for studying interfacial phenomena, often under adverse conditions. His expertise included electric double layers, electrokinetics, wetting layers and a variety of applied aspects of colloid science. Of special interest to the present theme was his study of polyelectrolyte adsorption in thin capillaries by electrokinetic methods [1–5]. Churaev and his team were able to prepare and characterize such capillaries with great precision. Many of the measurements were of an electrokinetic nature, and included electro-osmosis and surface conduction. A typical phenomenon is the reversal of the electrokinetic potential, ζ . As this reversal also plays a central role in the usual interpretation of layer-by-layer (LbL) deposition, it is expedient to consider these works systematically.

2. Literature anthology on LbL deposition

Nowadays LbL deposition is a well-known phenomenon [6,7]. The LbL concept refers to the building of polyelectrolyte multilayers by alternate deposition of oppositely charged polyelectrolytes. This technique has emerged as one of the most promising avenue for engineering new functional materials and sensors [8,9]. Although this technique has received tremendous research interest, the process remains not well understood. To obtain organized structures such as those observed in LbL molecular assemblies, a number of requirements can be formulated like irreversibility of the polyelectrolyte adsorption, and the propensity of adsorbed polyelectrolytes to overcharge. Irreversibility of polyelectrolytes adsorption as well as overcharging phenomena, have already been reported by several authors [10–17].

2.1. Basic enigma: electrostatics and/or non-electrostatics?

According to the usual interpretation, layer-by-layer deposition of polyelectrolytes is primarily an electrostatic phenomenon. See, for instance references [16,18,19]. After all, electrostatic interaction is strong, it has a long range and, between systems of opposite charges, it is attractive. However, this cannot be the complete story, because it cannot easily explain the generally observed reversal of ζ upon deposition of a layer of polyelectrolytes. At surface charge densities high enough to match those of the polyelectrolyte which requires a non-Coulombic attraction, had polyelectrolyte adsorption been purely electrostatically driven, the charge on the polyelectrolyte ought to exactly compensate the surface charge. Moreover, cases of residual

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Table 1
Observations from experimental studies building LbL films from strong polyelectrolytes.

| Phenomenon/ parameter monitored | Measurement/ method | System | Observations | References |
|---|--|---|--|---|
| Overcharging | Zeta potential in water, <i>without</i> added electrolyte | PSS/PAH (on <i>positively</i> charged particles, $\zeta = +35$ mV for uncoated particles; LbL built in NaCl 0.4–0.5 M, $t_{\text{ads}}^{\text{a}} = 20$ min) | ζ switching from -40 to $+33 \pm 10$ mV | [8] |
| | Zeta potential in water, <i>without</i> added electrolyte | PAH/PSS and PDADMAC (on <i>negatively</i> charged latex particles, LbL built in NaCl 0.25 M, $t_{\text{adss}}^{\text{a}} = 20$ min) | ζ switching from about $+50$ to -50 mV in both cases | [9] |
| | Current–voltage curves in KCl 0.1 M | PAH/PSS on <i>negatively</i> ($-\text{COO}^-$) charged nanopores (built from aqueous polymer solns ^b of 1 mg/ml, $t_{\text{adss}}^{\text{a}} = 2$ h) | Reported decrease in charge of the pore walls with increasing number of successive PAH/PSS bilayers | [26] |
| | Potential/silicon-on- insulator (SOI) based thin film resistor | P(DADMAC- <i>stat</i> -NMVA)/PSS on silicon oxide | No charge reversal | [27] |
| Effect of polymer charge density Strong PELs ^d | Potential/silicon-on- insulator | 5 mg/ml, in 10 mM Tris buffer at pH 7.5 containing 50 mM NaCl, $t_{\text{adss}}^{\text{a}} = 2$ min P(DADMAC- <i>stat</i> -NMVA)/PSS on silicon oxide | Full LbL only possible with PELs having more than 50% charged segments | [27] |
| | (SOI) based thin film resistor Thickness, roughness/ ellipsometry, AFM ^c | (5 mg/ml, in 10 mM Tris buffer at pH 7.5 containing 50 mM NaCl, $t_{\text{ads}}^{\text{a}} = 2$ min) PSS/P(DADMAC- <i>stat</i> -NMVA) (branched) $t_{\text{adss}}^{\text{a}} = 20$ min from solns ^b of 10^{-2} mole of monomer/L | Authors report stable films obtained at for degree of charge μ 68% | [28] |
| Effect of PEL charge density Involving one or two Weak PEL(s) ^d | Contact angles/FT-IR/dye staining/ellipsometry/ AFM | PAA/PAH on glass from solns ^b of 0.01 M with respect to MW of each repeat unit) $t_{\text{adss}}^{\text{a}} = 15$ min | LbL possible with about 30% degree of ionization This is pH-tunable (from 0.5 to 8 nm) Thickness is high at pH about 5, and low at pHs between 6 and 7.5 Layers highly interpenetrated | [29–31] |
| | Layer thickness/ ellipsometry/FT-IR | PAA/PDAC PVS/PAH SPS/PAH On silicon oxide (solns of 0.01 M with respect to MW of each repeat unit) $t_{\text{adss}}^{\text{a}} = 15$ min | Flat layers to thicker ones changing from fully charged to 70–90% charged units of the weak PELs | [32] |
| Effect of ionic strength | Neutron reflectometry | PSS/PAH on silicon wafer covered with a layer of 4-aminobutyltrimethylmethoxysilane (ABS) from 3 mM PELs ^d solns ^b (3 mM HCl) $t_{\text{adss}}^{\text{a}} = 20$ min | For $[\text{NaCl}] < 0.5$ M thickness varies with $[\text{NaCl}]^{1/2}$ $0.5 \text{ M} < [\text{NaCl}] < 1 \text{ M}$, thickness varies linearly with salt concentration $[\text{NaCl}] > 3 \text{ M}$, thickness increases slower Interdigitation | [33] |
| | Thickness, roughness/ ellipsometry, AFM | PSS/P(DADMAC- <i>stat</i> -NMVA) (branched) $t_{\text{adss}}^{\text{a}} = 20$ min from solns ^b of 10^{-2} mole of monomer/L | Increasing ionic strength leads to an increase in layer roughness. This effect is more significant at high degree of charge. | [28] |
| Effect of counterions | Counterion amount/XPS | PAH/PSS onto aluminium substrates from 10^{-2} M PELs aqueous solns $t_{\text{adss}}^{\text{a}} = 10$ min Various NaCl concentrations | Electrical charge in PAH (~80%) is constant, regardless the salt concentration. | [34] |
| | Thickness/ellipsometry | PSS/PDADMAC $[\text{XY}] = 0.1 \text{ M}$, X being the cation and Y the anion | Thickness increasing with ion size as $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ for X and $\text{F}^- < \text{Cl}^- < \text{Br}^-$ for Y | Refs. 38–40 according to [25] [35] |
| Hydration | Weight, water contents, thickness/QCM-D, ellipsometry | PHA/PSS on SiO_2 Grown from 1 mg/ml PELs solns in 0.5 M NaCl PDADMAC/PSS on SiO_2 | Linear growth of subsequent layers with constant water content Supralinear growth, hydration dependent on the previous PEL layer deposited | [36] |
| Effect of MW ^e | Thickness, diffusion/ ellipsometry, fluorescent labeling | HA/PLL PGA/PLL Spray procedure from 1.5 mM PELs ^d solns ^b in 0.15 M NaCl Using various PLL Mns ^e (21.5 to 362 kG/mole) | In the linear growth regime, the thickness is independent of MW PLL of MW [55 K diffuse into the whole HA/PLL LbL films, whatever the Mn of the PLL used | [36] |
| | Neutron reflectometry | PSS/PAH on silicon wafer covered with ABS from 3 mM PELs ^d solns ^b (3 mM HCl) Mn ^e of PSS investigated: 84 K, 184 K and 1070 K kg/mole $t_{\text{adss}}^{\text{a}} = 20$ min | Effect of MW was observed but found rather small. It was ionic strength-dependent (about twice more important for films built in 2 M NaCl compared to those obtained from 0.5 M NaCl solns) | [33] |
| | Thickness/ellipsometry | PA/PSS PA being adsorbed from acidic solns (pH 2.5) 0.4–2 mg/ml polymer onto surfaces coated with a first layer of PSS $t_{\text{adss}}^{\text{a}} = 15$ min Mn PA: unchanged Mn PSS: varying from 5 to 550 Kg/mole | No effect observed whatever the PSS Mn (bilayers averaging 41 Å) | [37] |

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