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Shear induced changes in the streaming potential of polyelectrolyte multilayer films

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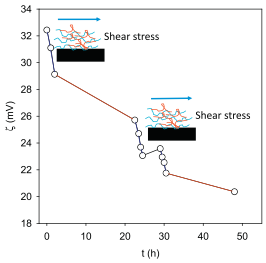
HIGHLIGHTS

- The zeta potential of multilayer films depend on measurement protocols.
- Shear stresses induce a decrease in the zeta potential.
- Higher stability of the zeta potential in the absence of flow.

GRAPHICAL ABSTRACT



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ABSTRACT

Streaming potential measurement is one of the most frequently used characterization methods of polyelectrolyte multilayer films. In most cases, the adsorption of a polyelectrolyte occurs up to an over-compensation of the surface charge. Herein, we generalize previous findings that the obtained streaming potential (transformed into a relative ζ potential) is dependent on the history of the measurement and in particular that shear stresses due to the flow of the solution induce a reduction in the absolute values of the ζ potential. These findings show that huge care should be taken when defining an experimental protocol aimed to measure the zeta potential of polyelectrolyte multilayer films using the streaming potential method. Ideally, to avoid the influence of shear induced desorption of polyelectrolytes on the zeta potential values, polyelectrolyte multilayer films made from different number of layers should be characterized independently under overall identical conditions.

1. Introduction

Polyelectrolyte multilayered (PEM) films obtained by the sequential deposition of oppositely charged species [1] are a popular surface functionalization method owing to their versatility: they can be deposited using either alternated dipping of the substrate in the polyelectrolyte solutions, alternated spraying [2] or alternated spin coating [3]. In addition it is possible to coat not only flat and macroscopic substrates but also colloids [4] and the pores of porous materials [4]. Twenty years after the boost of this field, there is still an astonishing contrast between the large variety of possible applications [5] and the rather poor understanding of the fundamental mechanisms allowing for the deposition of such coatings. It is still believed that the driving force allowing for the deposition of a polyelectrolyte oppositely charged to the last adsorbed one is due to charge reversal at the surface of the film, independently of the charge compensation mechanism in the

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bulk of the film [6]. Hence the electrokinetic potential of the PEM films is expected to alternate between positive and negative values after the adsorption of a polycation or a polyanion, respectively. Such an alternation of the electrokinetic potential of the PEM films has been found in many situations [7–11], but there are also some counterexamples [12,13]. In the case of the PEM films produced by alternated spraying from poly(allylamine) (PAH) and poly(sodium phosphate) (PSP) dissolved at 10^{-4} M (in monomer units) and in the presence of 0.15 M NaCl, the streaming potential was found to decrease monotonically as a function of the number of deposition steps m. In this case, the films were however island like and the measured streaming potential which was transformed in a ζ potential value by means of the Smoluchowski equation, may not reflect the accurate distribution of zeta potential. In addition, on island like deposits, the measured streaming potential may be strongly influenced by the hydrodynamic instabilities and the contribution of surface conductivity [14]. In addition it has been shown that the streaming potential of PEM films, may be unstable with time [11] due to either structural rearrangements [15,16] or to desorption phenomena. Indeed the shear forces underwent by the adsorbed polymers may be particularly strong upon an increase in pressure during the measurement. In the particular case of PEM films most investigators (our group included) use to characterize the streaming potential of PEM films after each deposition step and continue to build up the film (outside the streaming potential device) to an additional layer before further characterization, and so on up to the last deposition step. This method of determining the streaming potential versus m on a same film will be called method α in the following. It has the advantage to allow for the establishment of a zeta potential (proportional to the streaming potential in the framework of the Smoluchowski approximation) versus m on a single film. However, the streaming potential may be dependent on the history of the deposition–measurement steps. History dependencies on the structure of the film have been found when the films were dried before characterization [17]. One could also envision to use a PEM of a given composition and layering sequence and to measure its streaming potential before stopping the experiment, i.e. without additional deposition of polyelectrolytes. The streaming potential versus m curve will then be obtained on independently prepared films, and if the measurement protocol influences the value of the streaming potential, it will only affect the value for that film but not for the film obtained by continuing the alternated deposition process. This characterization method will be called method β. If shear forces indeed influence the streaming potential, the streaming potential curve versus the number of deposition steps should be different for methods α and β. It is the aim of this communication to show that this is indeed the case in at least two different systems of PEM films, namely for $(PAH\text{-}PSP)_n$ and for $(PAH\text{-}PSS)_n$ multilayer films. This finding will force to rethink, in addition to more theoretical considerations related to surface conductivity, the way to characterize the electrokinetic potential of PEM films.

2. Materials and methods

Poly(allylamine hydrochloride) (PAH, ref. 283215, number average molecular mass 15,000 g mol^{-1} as obtained by GPC), poly(sodium-4-styrene sulfonate) (PSS, ref. 24,305-1) and poly(sodium-phosphate) (PSP, Ref. 71600) were purchased from Sigma–Aldrich and used without further purification. They were dissolved at 1 mg mL^{-1} in a 20 mM NaCl solution, which was prepared from doubly distilled and deionized water (Milli Q+ system, Millipore, ρ = 18.2 MΩ cm). The polyelectrolyte solutions were freshly prepared before each film deposition experiment. The pH of the 20 mM NaCl electrolyte was equal to 6.2. The pH values of the PSP, PSS and PAH solutions were equal to 6.55, 6.8 and 4.34, respectively. No pH adjustment was performed during the deposition of the multilayered films, but the streaming potential measurements were systematically performed after intensive rinsing with the 20 NaCl electrolyte, hence at pH 6.20.

PSP having an average degree of polymerization of 23 [18] may not behave as a true polyelectrolyte and could also be considered as a multivalent anion.

The deposition of the $(PAH\text{-}PSP)_n$ and of the $(PAH\text{-}PSS)_n$ films was followed by means of quartz crystal microbalance with dissipation monitoring [19] (QCM-D, E1 device, QSense, Göteborg, Sweden). The adsorption substrates were silica coated quartz crystals (ref. QSX 303, QSense).

The glass slides (5 cm × 2 cm, 0.1 mm thick) used for the streaming potential measurements were polished on their edges to fit in the measurement cell.

All the adsorption substrates were cleaned in the same manner, namely by immersion in a 2% (v/v) Hellmanex solution (Hellma GmbH, Germany) during 30 min at ambient temperature, intensively rinsed with distilled water, immersed in a 0.1 M HCl solution during 10 min, and rinsed again with distilled water. The cleaning of the substrates was performed just before the beginning of the PEM deposition. In the case of the QCM-D experiments, these cleaning steps were performed in situ in the chamber of the QCM-D device.

The time required to reach steady state frequency changes of the quartz crystal upon exposure to the polyelectrolyte solutions was determined from the QCM-D response: the deposition process was considered to be finished when the reduced frequency changes were lower than 0.1 Hz, corresponding to 1.7 ng cm^{-2} of deposited mass (including the hydration water of the polyelectrolytes).

The streaming potential of the PEM films was measured in situ in a rectangular cell fitted to a ZetaCad device (CAD Instrumentation, Les Essarts-Le Roi, France). Two glass coverslips on which the PEM films were deposited were spaced by 0.5 mm with the aid of two Teflon spacers. The electrolyte solution was circulated in this cell between two connected reservoirs containing the 20 mM NaCl solution and the potential difference between the cell inlet and outlet was measured between two Ag/AgCl electrodes at both extremities of the cell. The potential difference between these electrodes was recorded with a Keitley 2700 multimeter. The pressure difference was varied from 0 to 300 mbar in a discontinuous manner by increments of 30 mbar for the $(PAH\text{-}PSP)_n$ films. In the case of $(PAH\text{-}PSS)_n$ multilayers, the pressure was increased up to 450 mbar. The conductivity λ of the electrolyte solution was measured simultaneously with the potential difference between the two electrodes. The temperature of the solutions was also recorded to allow for using the accurate value of the dynamic viscosity η. The zeta potential, ζ, was calculated from the streaming potential $\Delta V/\Delta P$ according to the Smoluchowski equation:

$$\zeta = \frac{\Delta V}{\Delta P} \cdot \frac{\eta \cdot \lambda}{\varepsilon \cdot \varepsilon_0} \quad (1)$$

ε_0 and ε being the dielectric constant of vacuum and the relative permittivity of water respectively. Herein, ζ was calculated from the measured streaming potential as is done in most of the investigations aiming to estimate the surface potential of films [9–13] assembled trough electrostatic interactions. However, the conductivity due the mobility of ions in highly hydrated films may play an important role [14,20] and Eq. (1) may hence be only a crude approximation.

The aim of this investigation was however not to provide accurate values of the ζ potential but to emphasize that different measurement protocols (method α versus β) yield different values of the streaming potential of PEM films.

AFM imaging, using a Nanoscope IV microscope (Veeco, Santa Barbara, CA) in air and in the contact mode, was performed on $(PAH\text{-}PSP)_{12}$ films dried under a stream of nitrogen. The 10 μm × 10 μm topographies were acquired at a scanning frequency of 0.5 Hz with