Ionic strength and counteranion type influence on formation of PAH/PSS multilayers and correlation with polyelectrolyte complex formation in solution

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Introduction

The interest for studying the structure and physico-chemical properties of polylelectrolyte multilayers (PEMs) has been growing ever since their discovery in the early nineties. This is mainly due to their possible use in industry, medicine and, in particular, biotechnology. Some of these nano-assemblies have already been successfully used as biocompatible coatings preventing the formation of cloths in artificial blood vessels and stents[1,2] or as surfaces enabling the vascular cell growth around synthetic implants.[3] Still, there are many questions waiting to be answered. The most important one is the time scale on which metastable products of interpolyelectrolyte neutralisation at surfaces and in solution exist (*i.e* the time required for equilibrium establishment, especially at variable ionic conditions). The path towards the understanding of all the factors influencing the multilayer stability could be the detailed investigations of kinetics and thermodynamics governing the interpolyelectrolyte neutralisation in solution. Quite recently, we reported on the remarkable effect of electrolyte type and concentration on the composition of the products formed in the reaction involving poly(allylammonium) cation (PAH) and poly(styrenesulfonate) anion (PSS) in aqueous solutions of sodium salts (NaX, X = F, Cl, Br, I, NO_3, ClO_4).[4] At higher electrolyte concentrations the aggregation of positively charged complexes was observed and it was strongly anion specific. By contrast, at lower ionic strengths the anion specific effect could not be observed. The aim of the presented study was to explore in which measure the interpolyelectrolyte neutralisation in solution can be correlated with the formation of polyelectrolyte multilayers. For that purpose the PAH/PSS PEMs have been prepared in the presence of above mentioned salts at variable ionic strengths and studied by means of quartz crystal microbalance.

Materials and methods

- poly(sodium 4-styrenesulfonate), NaPSS, Mw ≈ 77 000 g/mol, degree of functionalisation f = 0,83, Aldrich
- poly(allylamine hydrochloride), PAHCl, Mw ≈ 15 000 g/mol, degree of functionalisation f = 0,89, Aldrich
- NaF, NaCl, NaBr, NaI, $NaNO_3$, $NaClO_4$

- quartz crystal microbalance with dissipation monitoring (QCM-D)

Results

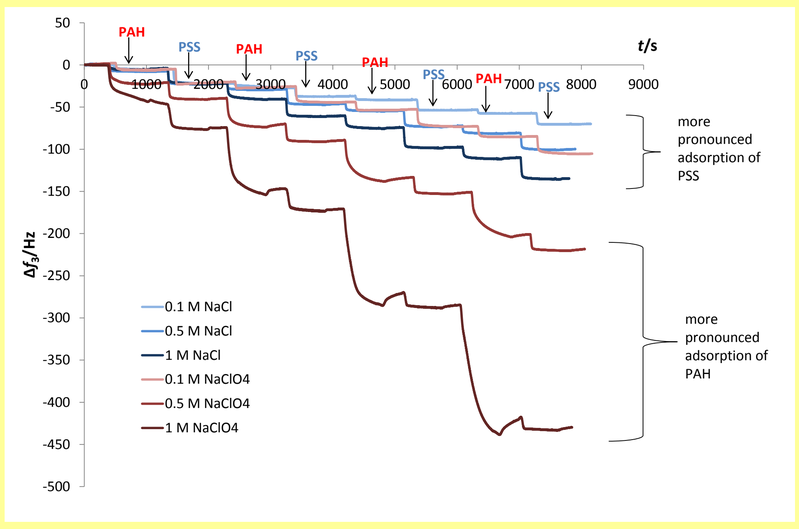

Fig. 1. The normalised frequency shift of the third harmonic during formation of PAH/PSS multilayer in solutions of NaCl and $NaClO_4$. ϑ = 25.0 °C, c_m(PAHCl) = c_m(NaPSS) = $1 \cdot 10^{-3}$ mol dm^{-3}, flow rate: 150 µL s^{-1}, adsorption step: 10 min, rinsing step: 5 min.

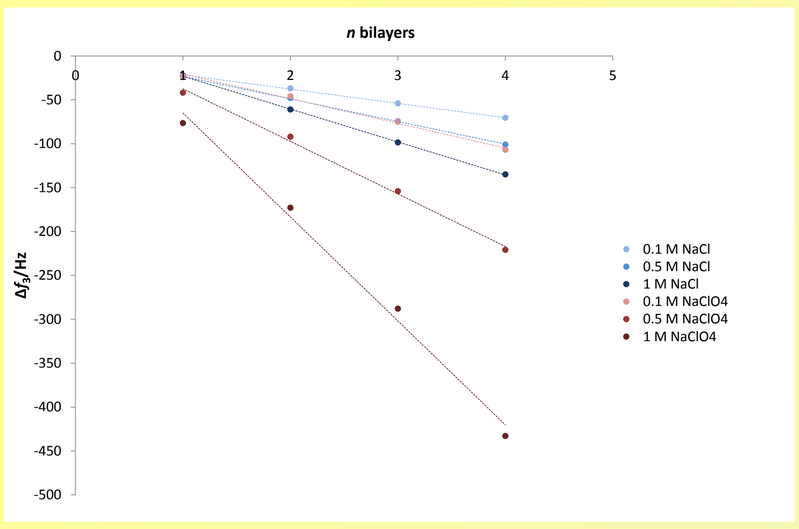

Fig. 2. The PAH/PSS multilayer growth in solutions of NaCl and $NaClO_4$. ϑ = 25.0 °C, c_m(PAHCl) = c_m(NaPSS) = $1 \cdot 10^{-3}$ mol dm^{-3}, flow rate: 150 µL s^{-1}, adsorption step: 10 min, rinsing step: 5 min.

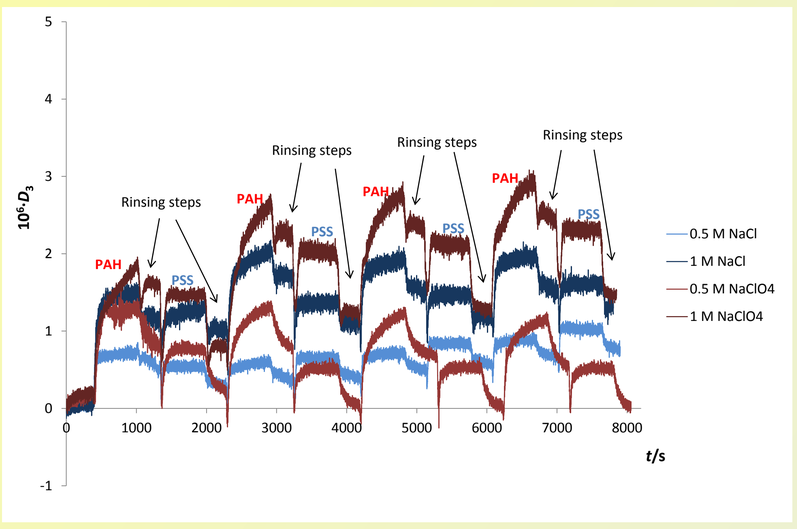

Fig. 3. The dissipation of the third harmonic during the formation of PAH/PSS multilayers in solutions of NaCl and $NaClO_4$. ϑ = 25.0 °C, c_m(PAHCl) = c_m(NaPSS) = $1 \cdot 10^{-3}$ mol dm^{-3}, flow rate: 150 µL s^{-1}, adsorption step: 10 min, rinsing step: 5 min.

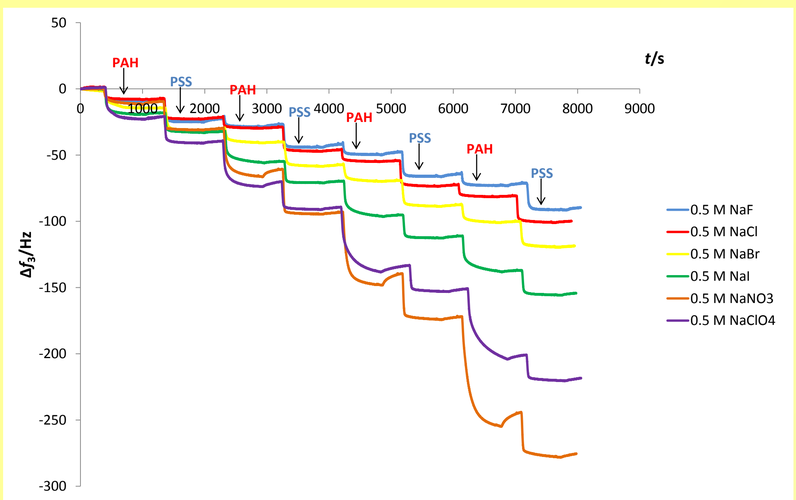

Fig. 4. Influence of the type of counteranion on normalised frequency shift of the third harmonic during formation of PAH/PSS multilayer obtained by QCM-D measurement at 25 °C, c_m(PAHCl) = c_m(NaPSS) = $1 \cdot 10^{-3}$ mol dm^{-3}, flow rate: 150 µL s^{-1}, adsorption step: 10 min, rinsing step: 5 min

Table 1. The enthalpies of colloid complex formation[4] and thickness of 8-layered PAH/PSS PEMs as a function of the counteranion type. c(NaX) = 0.1 mol dm^{-3} in calorimetric experiments, c(NaX) = 0.5 mol dm^{-3} in QCM-D experiments, SE – standard error of the average value, d^S – thickness calculated according to Sauerbrey equation, d^V – thickness calculated according to Voight model

Salt	$(\Delta_c H_{PAH \rightarrow PSS} \pm SE)$/kJ mol^{-1}	$(\Delta_c H_{PSS \rightarrow PAH} \pm SE)$/kJ mol^{-1}	d^S/nm	d^V/nm
NaF	-5.72 ± 0.06	- 5.60 ± 0.05	15.3	16.1
NaCl	- 1.74 ± 0.09	- 2.02 ± 0.02	17.1	17.3
NaBr	≈ 0	≈ 0	20.2	22.0
NaI	1.9 ± 0.1	≈ 0	26.3	26.2
$NaClO_4$	4.80 ± 0.07	2.07 ± 0.09	37.3	50.2
$NaNO_3$	2.73 ± 0.03	0.20 ± 0.06	47.3	37.0

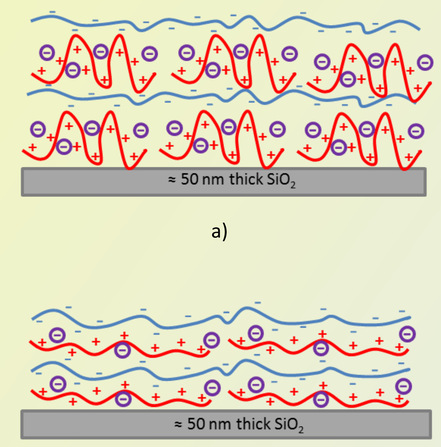

Fig. 5. Schematic representation of the PAH/PSS multilayers in solution of a) $NaClO_4$, b) NaCl. The Na^+ cations, counterbalancing the unpaired PSS monomers, are not shown for the sake of the scheme simplification.

Conclusions

The QCM-D measurements indicated that the increase in ionic strength resulted with larger thickness of deposited layers and the assymetric incorporation of polymers into nano-assemblies. At higher ionic strength the film thickness was found to be dependant on the type of anion counterbalancing the polycation charge. The largest amount of deposited material was obtained from polymer solution containing $NaClO_4$ and $NaNO_3$. This is in accordance with DLS and spectrophotometric experiments[4] in which anion specific aggregation of positive colloid complexes and the formation of precipitates with larger amount of PAH with respect to PSS was observed. The complexation enthalpies[4] could be correlated with the thickness of deposited films. The results can be explained by different counteranion distributions around polycation, caused by differences in the corresponding hydration enthalpies.

Acknowledgements

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