Interpolyelectrolyte interactions: relationship between formation of polyelectrolyte complexes in solution and polyelectrolyte multilayer build-up

Jasmina Salopek, Josip Požar and Davor Kovačević*

Division of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia

* davor.kovacevic@chem.pmf.hr

Interpolyelectrolyte interactions in solution and at surfaces lead to the formation of polyelectrolyte complexes (PECs) and polyelectrolyte multilayer (PEMs), respectively. Better knowledge of the relationship between the formation and properties of PEMs and PECs would enable the prediction and the control of deposition of a wide range of polyelectrolytes at various surfaces with important application possibilities. Therefore, we compared the results we obtained earlier [1,2] for the complexation of poly(allylammonium) chloride (PAH) and sodium poly(styrenesulfonate) (PSS) with the results obtained for PAH-PSS multilayer build-up. In order to do so, we studied the formation of PAH/PSS multilayers in aqueous solutions of various electrolytes by means of quartz crystal microbalance with dissipation monitoring (QCM-D) and atomic force microscopy (AFM). The QCM-D measurements indicated that the thickness of deposited layers depends on ionic strength and on the type of the type of salt used. The largest deposition of material was noticed in the case of nitrate and perchlorate anions. This is in accordance with the results obtained for PECs by means of DLS and spectrophotometric experiments which showed anion specific aggregation of positive complexes and the formation of precipitates containing larger amount of PAH with respect to PSS. The thickness of deposited films could be also correlated with the complexation enthalpies of used supporting electrolyte ions. The more enthalpically disfavourable complexation process in solution was, the larger was the amount of material deposited. The results can be explained by different counterion distributions around polyelectrolytes, caused by differences in the corresponding ion hydration enthalpies. The observed strong influence of counterion type on the composition of PAH/PSS nanoassemblies provides a path for the modification of multilayer properties simply be changing the type of salt during their preparation. Although the presented results were obtained solely on the system PAH/PSS, the conclusions could be also applied for various other combinations of polyelectrolytes.

- [1] J. Požar and D. Kovačević, Soft Matter, 2014, 10, 6530.
- [2] J. Požar, J. Salopek, M. Poldrugač and D. Kovačević, Colloids Surf. A, in press.