Thermodynamics of complexation of poly(styrene sulfonate) anion with poly(allylammonium) cation; the effect of ionic strength and electrolyte type

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Since the introduction of multilayers in the early nineties, polyelectrolyte complexes and polyelectrolyte multilayers have become the subject of numerous investigations. Although considerable progress in the field has been made, many fundamental questions considering both polyelectrolyte complexation and polyelectrolyte multilayer formation remained unexplained. Among them, the thermodynamic role of both the electrolyte concentration and electrolyte type (counterions present), should be particularly stressed.

We have therefore decided to study the complexation of poly(styrenesulfonate) anion (PSS; \( P_n \approx 300 \)) and poly(allylamonnium) cation (PAH; \( P_n \approx 700 \)) in the presence of simple sodium salts containing different monovalent anions (NaX; \( X = F, Cl, Br, NO_3, ClO_4 \)) by means of titration calorimetry. Additional information concerning the reversibility of complex formation, the structure and the composition of the products has been obtained from UV spectra, DLS experiments and vibrational Raman spectroscopy.

Our investigations have shown that the nanosized complexes of variable composition and size are formed before the equivalent amount of oppositely charged monomers present in solution. Their structure was dependant on the order of polyelectrolyte addition. At approximately equivalent amounts of oppositely charged monomers added, the nanosized complexes always precipitated in the form of insoluble polsalts, regardless of the initial polyelectrolyte concentrations.

The overall process of interpolyelectrolyte neutralization, resulting in insoluble products, was mainly entropically driven and, in some cases (NaNO_3, NaClO_4), entirely driven by the increase in entropy. The reaction enthalpy corresponding to formation of final products obtained at \( c(\text{NaX}) = 0.1 \ c^o \) was the most favorable in the case of NaF and the most unfavorable in the case of NaClO_4. At electrolyte concentrations equal or higher than \( c(\text{NaX}) = 0.5 \ c^o \) the intrinsic compensation of charge in the insoluble products was considerably shifted towards extrinsic charge compensation in the case of NaNO_3 or NaClO_4.