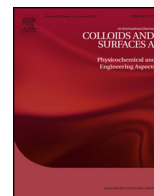




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The effect of cation type, ionic strength and temperature on the complexation between polyallylammonium cation and polystyrenesulfonate anion

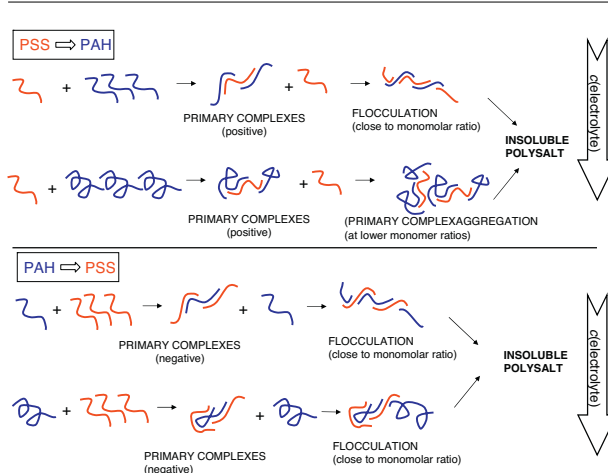
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HIGHLIGHTS

- Complexation between PAH and PSS was studied in various salt solutions.
- The influence of ionic strength, temperature and addition order was examined.
- At lower molar ratios primary polyelectrolyte complexes were formed, while close to equivalence the flocculation occurred.
- The complexation was predominantly entropically driven.
- A correlation between obtained reaction and cation hydration enthalpies was noticed.

GRAPHICAL ABSTRACT



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ABSTRACT

The reaction between polyallylammonium cation and polystyrenesulfonate anion was investigated in alkali-metal chloride (MCl, M = Li, Na, K, Rb, Cs), sodium perchlorate and tetraethylammonium chloride solutions by means of microcalorimetry, potentiometry, DLS and spectrophotometry. The influence of ionic strength, temperature and addition order on the course of interpolyelectrolyte neutralisation was examined. At lower molar ratios of positively to negatively charged monomers and at 25 °C primary polyelectrolyte complexes were formed. Close to equivalence their flocculation occurred. The complexation was predominantly entropically driven, however a correlation between obtained reaction and cation hydration enthalpies was noticed. The composition of the precipitates at equimolar monomer ratio in chloride salt solutions did not significantly depend on the addition order up to 1.0 mol dm⁻³ salt concentration. In contrast, the ratio of oppositely charged monomers in precipitates prepared in NaClO₄ (c/mol dm⁻³ ≥ 0.5) was affected by the addition order in a wide temperature range. The increase in electrolyte concentration and the decrease in temperature led to more pronounced asymmetric neutralisation. The equilibrium establishment in NaClO₄(aq) proceeded extremely slowly. Even at high perchlorate concentrations the final reaction product was virtually insoluble polysalt.

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1. Introduction

Recently we reported [1] on the remarkable effect of supporting simple electrolyte on the composition of the products formed by complexation of polyallylammonium cation (PAH) and polystyrenesulfonate anion (PSS) in aqueous solutions of various sodium salts (NaX, X = F, Cl, Br, I, NO₃, ClO₄) at 25 °C. At moderate electrolyte concentrations the interpolyelectrolyte neutralisation proceeded in the manner described by Fuoss and Sadek [2–4]. Charged polyelectrolyte complexes were formed at lower molar ratios of monomers, whereas their flocculation occurred close to equivalent monomolar ratio, above which no further pairing could be observed. The precipitates obtained at equivalence contained approximately equal amounts of oppositely charged functional groups. By contrast, at higher electrolyte concentrations and lower monomolar ratios the aggregation of positively charged complexes took place. The onset of aggregation was strongly anion specific, following the Hofmeister series [5–8]. Moreover, when the polycation was present in excess, the amount of positively charged monomers in the flocculate was higher than that of negatively charged, irrespectively of the polymer addition order. Quite the opposite, the aggregation of negatively charged complexes did not occur even at $c(\text{NaX}) = 3 \text{ mol dm}^{-3}$ and the interpolyelectrolyte neutralisation came to a halt once the surface of the product became coated with polystyrenesulfonate. Although part of described results, like the asymmetric incorporation of polyions into reaction products [9–11], or the aggregation of only one type (either positively or negatively charged) of polyelectrolyte complexes [12,13], have been occasionally reported, the influence of the counterion type on the course of interpolyelectrolyte neutralisation in solution was systematically explored for the first time. The energetics governing the PAH-PSS monomer pairing at variable ionic conditions (*i.e.* electrolyte type and concentration) was found to be particularly interesting. The enthalpies of complex and precipitate formation were virtually independent on the electrolyte concentration and were very weakly influenced by the counteranion type [1]. As it turned out, the reason for the observed influence of anion type on the aggregation of positive complexes, and the formation of products containing higher amounts of PAH monomers with respect to PSS, was related with the differences in anion distributions (the variable amount of directly and indirectly bound anions) around the polycation.

The spectrophotometric investigations in solutions containing higher concentrations of sodium perchlorate were a clear remainder of how slow the establishment of equilibrium in reactions involving oppositely charged polyelectrolytes can be [14]. As reported in the so far published research [14–17], the presence of simple electrolyte was a prerogative for the formation of equilibrium products. The PAH-PSS pair was no exception. Interestingly, when the polycation was present in excess, the increase in electrolyte concentration initially favoured the formation of metastable products. The structural rearrangements within such flocculates at room temperature proceeded extremely slowly. The reaction mixtures containing equimolar ratios of oppositely charged monomers that were prepared at 25 °C had to be heated ($\theta = 60 \text{ °C}$) in order to reach equilibrium.

The study presented in this paper is an extension of our previous work aiming to resolve some of the still open questions regarding the PAH-PSS interpolyelectrolyte neutralisation. The first of them is: Are there remarkable cation-specific effects as were observed previously in the case of examined anions? For that purpose the neutralisation was studied in solutions of alkali chlorides and tetraethylammonium chloride in a wide range of salt concentrations by means of different experimental techniques (microcalorimetry, DLS, potentiometry and spectrophotometry). The chloride was chosen as the counteranion in all cases since

the number of directly condensed Cl⁻ to PAH chains was found to be considerably lower than that of perchlorates and nitrates [1]. We also wanted to explore whether the increase in temperature leads to more efficient interpolyelectrolyte neutralisation and/or the more rapid equilibrium establishment. This is important from the fundamental (understanding the effect of temperature on the reaction kinetics and equilibrium), but also from the applicative point of view, as it opens a path for further modification of polyelectrolyte multilayer (PEM) properties. The answer was provided by spectrophotometric investigations of supernatants prepared in NaClO₄(aq) at elevated temperatures. The mentioned salt was used due to the fact that the formation of metastable product in $c(\text{NaClO}_4) \geq 0.5 \text{ mol dm}^{-3}$ could be easily confirmed from the UV spectra of supernatants, prepared by titrations ran in both directions up to 1:1 monomer ratio.

We also tried to investigate if the interpolyelectrolyte neutralisation after the onset of flocculation proceeded less efficiently than during the formation of primary complexes. This important issue was resolved by measuring the counterion activity during the titration of polyallylammonium chloride with sodium polystyrenesulfonate and *vice versa*. Namely, on the basis of the so far carried research we could only conclude that the overall number of paired monomers in the flocculate was high. (The spectra of supernatants at 1:1 monomolar ratio showed no traces of free PSS-chains). However, the neutralisation after the onset of flocculation could still be less efficient than during the formation of primary complexes. Moreover, it could even depend on the polymer addition order.

The herein presented study is also aiming to provide a deeper understanding of the factors which determine the composition of metastable PAH-PSS composites and which govern their conversion to equilibrium reaction products. Such data could be of importance in the context of recently introduced polyelectrolyte complex-based saltoplastics [18,19], whose properties are critically dependant on the preparation procedure, salt concentration and, most likely, salt type. In the end, it should be stated that the interest in the examined polyion pair is also due to their promising use in corresponding polyelectrolyte multilayers in biomedical technology. For instance, PAH/PSS polyelectrolyte multilayers have already been successfully used as stent and catheter coatings [20,21] and as surfaces supporting cell proliferation [22]. Since the multilayer thickness [23–25] and the asymmetric incorporation of polyions within layers [6,26,27] can be regulated by changing the type of supporting electrolyte and its concentration, the understanding of how the polyion-counterion preferences affect the formation of PAH/PSS PEMs is considerable.

2. Experimental

2.1. Materials

Polyallylamine hydrochloride, PAHCl ($M_w = 70\,000 \text{ g mol}^{-1}$) was purchased from Aldrich. The degree of monomer functionalisation (f) was determined by potentiometric titration with standardised sodium hydroxide solution. The value obtained was $f = 0.94$.

Polysodium 4-styrenesulfonate, NaPSS ($M_w = 77\,000 \text{ g mol}^{-1}$), analytical standard for GPC, was purchased from Aldrich and was used as received.

The chloride and perchlorate salts of monovalent anions (LiCl, NaCl, KCl, RbCl, CsCl, Et₄NCl, NaClO₄) were obtained from various manufacturers (Merck, Sigma, Aldrich) and were of analytical purity grade. The solutions were prepared by dissolving the polyelectrolytes and simple electrolytes in aqueous solution of hydrochloric acid ($c(\text{HCl})/\text{mol dm}^{-3} = 1 \times 10^{-4}$), in order to assure the complete protonation of the polycation [28].

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