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Polyelectrolyte complexes IV. Interpolyelectrolyte complexes between some polycations with *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units and poly(sodium styrenesulfonate) in dilute aqueous solution

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Abstract

We report first on the interpolyelectrolyte complex formation (PEC) between one polycation of integral type having about 95 mol% of *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units in the backbone (PCA_5) and poly(sodium styrenesulfonate) (NaPSS), in dependence on the polyion concentrations and the mixing order. The PEC formation was qualitatively followed by viscometry, conductometry and UV-spectroscopy. Quasi-soluble PECs could be formed in the polyion concentration range of 0.1–1.0 unit mM. A complex stoichiometry close to 1:1 was found by both the qualitative measurements on the formation of quasi-soluble PEC in dilute aqueous solutions (when PCA_5 concentration was lower than the overlap concentration, $C < C^*$) and elemental analyses of the insoluble PEC formed at the high polycation concentration (50 unit mM, $C \gg C^*$). The influence of the ionic strength on the PECs stability was followed by the subsequent addition of NaCl up to an ionic strength of 3.5 M on the reaction mixture, after the PECs formation with three polycations different by both the content of quaternary ammonium salt groups in the backbone and the degree of branching (PCA_5, PCA_{20} and PCT_{20}). No dissociation of PECs into the original components was evidenced irrespective of the polycation structure and the mixing order. © 2001 Published by Elsevier Science Ltd.

Keywords: Polyelectrolyte complex; Poly(sodium styrenesulfonate); UV-spectroscopy

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1. Introduction

The interpolyelectrolyte complexes (PECs) between synthetic polyelectrolytes are still very intensively studied as simple models for the common phenomena occuring in biological systems and as new biocompatible materials [1–6]. Considerable attention has been also focused on the study of complexes formed by the interaction of synthetic polyions, especially polycations, with proteins and enzymes because they are involved as substrates in many bioseparations [7–11].

PECs with a high tendency of aggregation usually result when both polyions have strong ionic groups and a good match of charges (polysalts) [12–18]. The aggregation level in this case is mainly dependent on the concentration of each component. First detailed studies on the formation and properties of the poly(vinylbenzyltrimethyl ammonium)/poly(styrenesulfonate) polysalts, developed by Michaels et al. [12,13], were followed by a large diversity of polyion combinations in order to find new materials and new applications for PECs as semipermeable membranes [12,13,19,20], flocculants in water purification [21–24], separation and purification of biopolymers [25,26], enzyme immobilization [27,28] and so on. Water soluble PECs can be obtained when the complementary polyelectrolytes have significant different molecular weights, in non-stoichiometric systems and dilute aqueous solutions, the structural differences between opposite polyions also being effective [1,3,10,29–35].

In our previous studies we followed the PECs formation in dependence on the polyion structure and molecular weight taking into account polycations with different contents of *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units in the backbone and two hydrophilic polyanions, poly(sodium acrylate) (NaPA) [36,37] and poly(sodium 2-acrylamido-2-methylpropanesulfonate) (NaPAMPS) [38]. The aggregation level of these PECs was not dependent on the strength of the anionic charges, being higher in the case of NaPA than for NaPAMPS, but more

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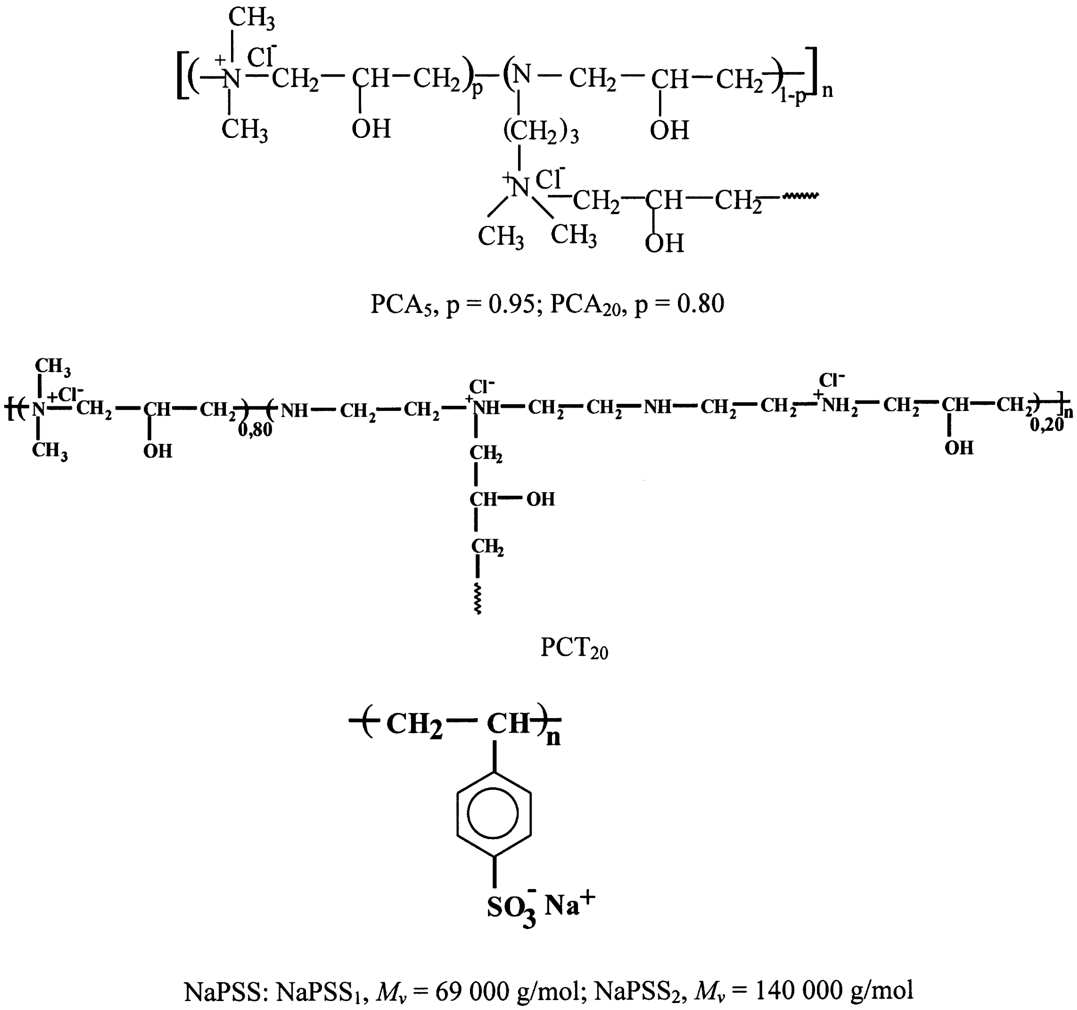

PCA_5, p = 0.95; PCA_{20}, p = 0.80

PCT_{20}

NaPSS: $NaPSS_1$, M_v = 69 000 g/mol; $NaPSS_2$, M_v = 140 000 g/mol

Scheme 1.

on the distance between anionic groups and the backbone. Poly(sodium styrenesulfonate) (NaPSS) was very often used as a strong polyanion in the multilayer buildup in order to get membranes with special properties or new materials for medical uses [12,13,39]. Successful materials can be obtained if the complex stoichiometry and the strength of the complementary polyion interactions in dependence on the environment ionic strength are well known. Therefore, the aim of the present paper is to follow: first the PEC formation between the polycation of integral type having about 95 mol% of *N*,*N*-dimethyl-2-hydroxypropylene-ammonium chloride units in the backbone (PCA_5) and NaPSS, in dilute aqueous solutions, and the aggregation level in dependence on the polyion concentrations, and second the response of the PECs already formed at the subsequent addition of NaCl, in dependence on the polycation structure (PCA_5, PCA_{20} and PCT_{20}) and the mixing order. Even if the linear charge density and the strength of the anionic groups in NaPSS are like in NaPAMPS, the chain hydrophobicity of NaPSS could induce particular aspects in these systems.

2. Experimental

2.1. Materials

Polycations of integral type with different contents of quaternary ammonium salt groups in the backbone were synthesized by the condensation polymerization of epichlorohydrin with dimethylamine and a polyfunctional amine such as *N*,*N*-dimethyl-1,3-diaminopropane (A) and triethylenetetramine (T), according to the method presented in detail elsewhere [40,41]. The chemical structures of the polyelectrolytes used in this work are shown in Scheme 1. The number in the polycation short name means mol % of the polyfunctional amine (A or T). The presence of the polyfunctional amines in different contents (PCA_5 and PCA_{20}) and different functionalities (PCA_{20} and PCT_{20}) allowed obtaining the polycations with different degrees of branching.

Polycation samples were carefully purified by dialysis against distilled water until Cl^- ions were absent in the dialyzate (about three days). The dilute solutions were concentrated with a Rotations Vakuumverdampfer RVO-64, and then the polymer was precipitated with acetone and purified again by reprecipitation in methanol/acetone. Polycations were kept for several days in vacuum over P_2O_5 at room temperature and then characterized by elemental analyses (Cl_i — ionic chlorine, determined by potentiometric titration with 0.02N $AgNO_3$ and Cl_t — total chlorine, determined by the combustion method — Schöniger technique) and intrinsic viscosity in 1 M NaCl aqueous solution, at 25°C. Average molecular weights of the repeat unit were the followings: PCA_5, $M_u = 140.35$; PCA_{20}, $M_u = 148.90$; PCT_{20}, $M_u = 165.00$. PCA_5: Calcd: N 10.49; Cl_i 25,27. Found: N 11.00; Cl_t 23.58; Cl_i 23.22. PCA_{20}: Calcd: N 11.28; Cl_i 23.81. Found: N 10.85; Cl_t 23.22; Cl_i 22.92. PCT_{20}: Calcd: N 13.57; Cl_i 25.69. Found: N 12.11; Cl_t 23.83; Cl_i 23.81. The intrinsic viscosity values in 1 M NaCl, at 25°C were: PCA_5 $[\eta] = 0.368$ dl/g; PCA_{20} $[\eta] = 0.330$ dl/g; PCT_{20} $[\eta] = 0.340$ dl/g. NaPSS was prepared by polymerization of sodium 4-styrenesulfonate in water, using the ammonium persulfate–sodium metabisulfite system as initiator–activator. After dialysis against distilled water, the dilute solutions were concentrated and then NaPSS was precipitated with methanol and purified by reprecipitation with methanol from aqueous solution. Viscosity average molecular weight of NaPSS was measured in 0.5 M NaCl at 20°C [42]. Two samples of NaPSS were used: $NaPSS_1$ with $M_v = 69\,000$ g/mol and $NaPSS_2$ with $M_v = 140\,000$ g/mol. The polycation concentration was controlled by potentiometric titration of Cl^- counterions with 0.02 N $AgNO_3$. Three measurements were averaged. The concentration of NaPSS was controlled by UV-spectroscopy (characteristic absorbtion band at 225 nm), the Lambert–Beer law being checked up for concentrations between $10^{-5} - 2 \times 10^{-4}$ M.

2.2. PEC formation

Dilute aqueous solution of polycation and polyanion were used in the qualitative study of the PEC formation. The overlap concentration, C^*, for the PCA_5 used in this study is 0.097 g/dl. The PCA_5 concentrations in the starting solutions were always much lower than this value (0.1–1.0 unit mM, that is 0.0014–0.014 g/dl) and that one of the titrant was 10 times higher than the first one (1.0–10 unit mM), in order to minimize the changes of the reaction volume and stirring conditions during titrations. This range of concentrations led usually to quasi-soluble PECs on a colloidal level [43,44]. The formation of these PECs can be followed by viscometry and conductometry. The use of NaPSS as a polyanion allowed following the complex formation by UV-spectroscopy also. The aqueous solution of polyanion or polycation with a concentration of 1.0–10 unit mM was slowly dropped into 50 ml aqueous solution of the complementary polyion with a concentration of 0.1–1.0 unit mM, under a vigorous magnetic stirring, at room temperature (about 25°C), until a certain mixing ratio *R* was achieved. The mixing ratio *R* was defined as the ratio between the charged groups contained in the titrant and the oppositely charged groups in the starting solution. Both types of mixing order were used. The mixing was continued for 2 h to complete the complex formation. The time and the rate of stirring have a significant role in the release of counterions and thus in the complex formation. In our previous works we found that a stirring of 2 h is enough for the PECs formation when polycations type PCA and PCT were used as cationic components [36,37]. The PECs for gravimetric analyses were prepared by adding dropwise $NaPSS_1$ aqueous solution with a concentration of 100 or 50 unit mM to the PCA_5 aqueous solution with a concentration of 50 unit mM, at different mixing ratios *R*. PEC precipitates were isolated by filtration and washed repeatedly with bidistilled water until Cl^- ions were not present in filtrate. The PEC was dried to constant mass and analyzed to determine the complex composition.

2.3. Methods

Viscosities were measured with an Ubbelohde viscometer with internal dilution, at 25°C. Conductances were measured in a specific cell with platinum/platinum electrodes (Radiometer Copenhagen, type CDM 2d). UV absorption spectra of the reaction mixtures were recorded using a SPECORD M42 spectrophotometer (standard 1 cm quartz cell). Dilutions of three or 10 times were performed when NaPSS aqueous solutions with initial concentrations of 3 or 10 unit mM were used as titrant. The reaction stoichiometry between two polyions was checked comparing the supernatant characteristics with those of the control samples prepared, taking into account the composition expected for a stoichiometric reaction and a complete release of the NaCl. Thus, the control samples included the polycation in excess and NaCl corresponding to the mixing ratio *R*, on the left of the theoretical endpoint (1:1), and NaCl calculated for a stoichiometric reaction and the polyion in excess, on the right of the endpoint, respectively [36,37]). The response of PECs at the subsequent addition of NaCl into the reaction mixture up to a concentration of 3.5 M NaCl, after the PECs formation, was followed by UV-spectroscopy.

3. Results and discussion

3.1. Qualitative analysis of PEC formation

The PEC formation between PCA_5 and NaPSS in dependence on the molecular weight of NaPSS and the mixing order was first followed viscometrically. The variation of the specific viscosity, η_{sp}, in dependence on the mixing ratio *R* is shown in Fig. 1. The titrant concentration was 10 unit mM and that one of the starting solution was 1 unit mM in these experiments.

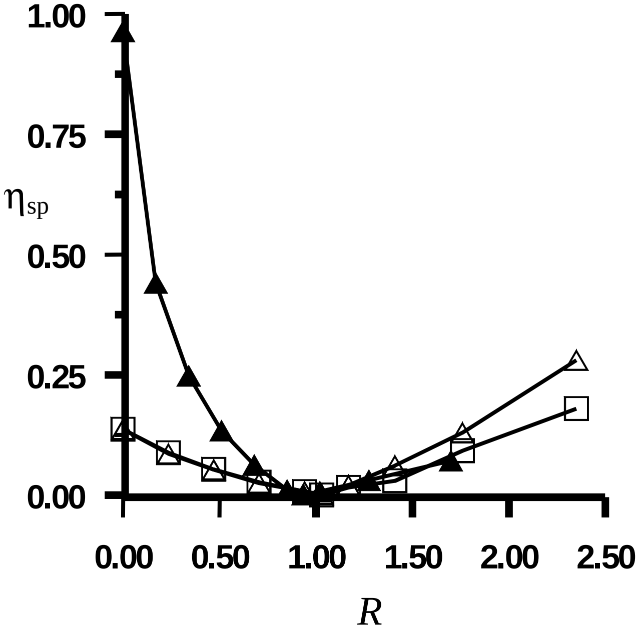

Fig. 1. Variation of the specific viscosity (η_{sp}) of the reaction mixture in dependence on the mixing ratio *R* for the PEC formation between PCA_5 and NaPSS: (△) $NaPSS_2$ (10 mM)/PCA_5 (1 mM); (□) $NaPSS_1$ (10 mM)/PCA_5 (1 mM); (▲) PCA_5 (10 mM)/$NaPSS_2$ (1 mM).

The continuous decrease of the η_{sp} before the equivalence of opposite charges was correlated to the decrease of the concentration of the component in excess and also to the increase of the NaCl concentration. For NaPSS/PCA_5 system, η_{sp} values were independent on the molecular weight of NaPSS, up to the endpoint. This is an evidence for the existence of the same macromolecular component, which is the polycation in excess, the PEC viscosity being not significant. $NaPSS_1$/PCA_5 and $NaPSS_2$/PCA_5 complexes separated from the continuous phase as small particles only at the endpoint and henceforth. The increase of η_{sp} after the endpoint depends on the molecular weight of NaPSS, being higher for $NaPSS_2$ than for $NaPSS_1$. The formation of these PECs is accompanied by the release of NaCl which was conductometrically followed (Fig. 2).

The conductance variation in dependence on the mixing ratio *R* evidenced the same stoichiometry of PECs (about l:1), as in Fig. 1. Little influence of the polyions mixing order on the conductance corresponding to a certain mixing ratio *R* was evidenced. The conductance values were a little higher after the endpoint when PCA_5 was used as a titrant. This could be caused by a less compact structure of the PEC formed when NaPSS was titrated with a flexible polycation with a concentration of 10 unit mM, which was the concentration of PCA_5 used as a titrant; in this case the concentration of PCA_5, C, was about 1.5 times higher than the critical overlap concentration, C^*.

The PEC formation and the microphase separation have been also followed by the UV spectroscopy in dependence on the polyion concentration, taking into account the characteristic absorbances of NaPSS which were evident at 225 and 260 nm. The value of the absorbance at 225 nm was independent of the molecular weight of NaPSS, at the same mixing ratio *R*. NaPSS added to PCA_5 led to a gradual increase of the maximum at 225 nm and a small variation of the maximum at 260 nm. As the component in excess was PCA_5, which has no absorbance in UV, the spectral changes before the stoichiometry could be correlated with the formation of the quasi-soluble PEC. The absorbance values at 225 nm in dependence on the polyion concentration and the mixing ratio *R* were collected in Fig. 3. A continuous increase of the absorbance at 225 nm was found until the endpoint, when the microphase separation took place and the absorbance values diminished abruptly, for the systems $NaPSS_2$ (10 unit mM)/PCA_5 (1 unit mM) and $NaPSS_2$ (3 unit mM)/PCA_5 (0.3 unit mM); this is an evidence for the absence of the quasi-soluble PEC and of the free NaPSS in the supernatant solution.

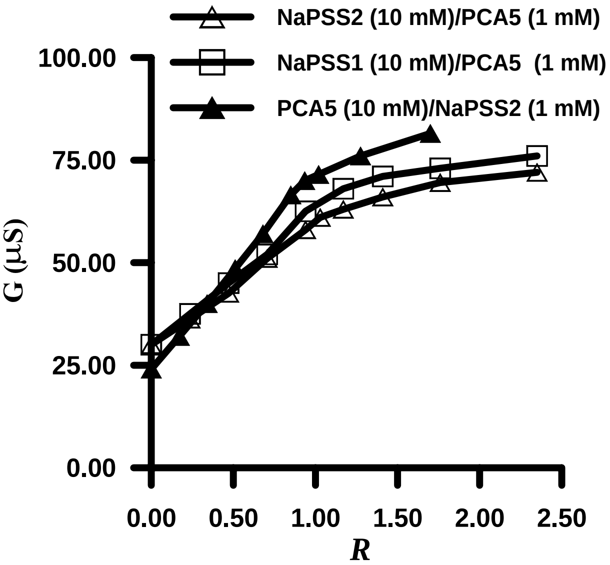

Fig. 2. Variation of the conductance (*G*) of the reaction mixture in dependence on the mixing ratio *R* for the PEC formation between PCA_5 and NaPSS.

The continuous increase of the absorbance at 225 nm after the endpoint reflects the increase of the free NaPSS concentration with the increase of the mixing ratio *R* and is also an evidence for the absence of the interaction between NaPSS and PEC particles, in pure water. A different behavior was evidenced in the system with the lowest polyion concentrations, NaPSS (1.0 unit mM)/PCA_5 (0.1 unit mM), (Fig. 3). The endpoint was also marked by the decrease of the absorbance at 225 nm, but the values were higher than those corresponding to the first systems. Much part of the PEC remained in the supernatant solution even at the endpoint and then. This suggests that the quasi-soluble PEC formed in the last system has the highest stability as regards the microphase separation.

Fig. 4a shows that the dynamic of spectral changes was

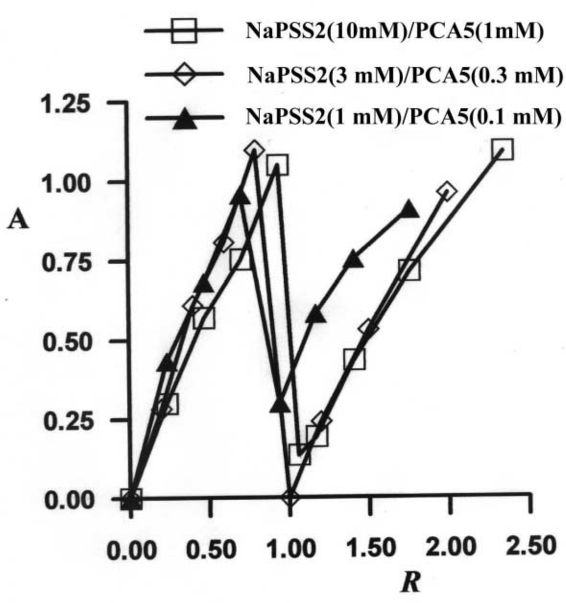

Fig. 3. Variation of the absorbance (A) at 225 nm vs. the mixing ratio *R* in the formation of the NaPSS/PCA$_5$ complexes at different polyion concentrations.

different when the polycation was added to NaPSS. Very small variations of the absorbance at 225 nm were evidenced in this case by the increase of the mixing ratio *R*. The spectra corresponding to different mixing ratios should be like in Fig. 4b, which includes the UV spectra for the control samples, if only the free NaPSS would absorb at this wavelength.

The differences between the UV spectra of the PEC samples and those of the control samples show that UV behavior of the quasi-soluble PEC formed in this case is similar with that of the PEC formed when NaPSS was used as a titrant and also with that of the free NaPSS.

3.2. Quantitative analysis of PEC formation

The complex stoichiometry and the yield in PEC, in dependence on the mixing ratio *R*, for the system NaPSS$_1$/PCA$_5$, were determined. Composition of insoluble PECs is very important when assesing their potential application as new polymeric materials. The calculated values of the elemental analyses were obtained by assuming that 1:1 stoichiometric reaction and total counterion release occurred (Table 1).

Yield in PEC was obtained as a ratio between the amount of PEC at a given mixing ratio and the amount of PEC expected for a complete stoichiometric reaction. In the range of the polyion concentration used for these series of experiments, the PEC aggregation started even at very low mixing ratios. PEC composition (contents of Cl, S, N) and the yield in PEC are closed to those expected for a 1:1 stoichiometry, irrespective of the mixing ratio.

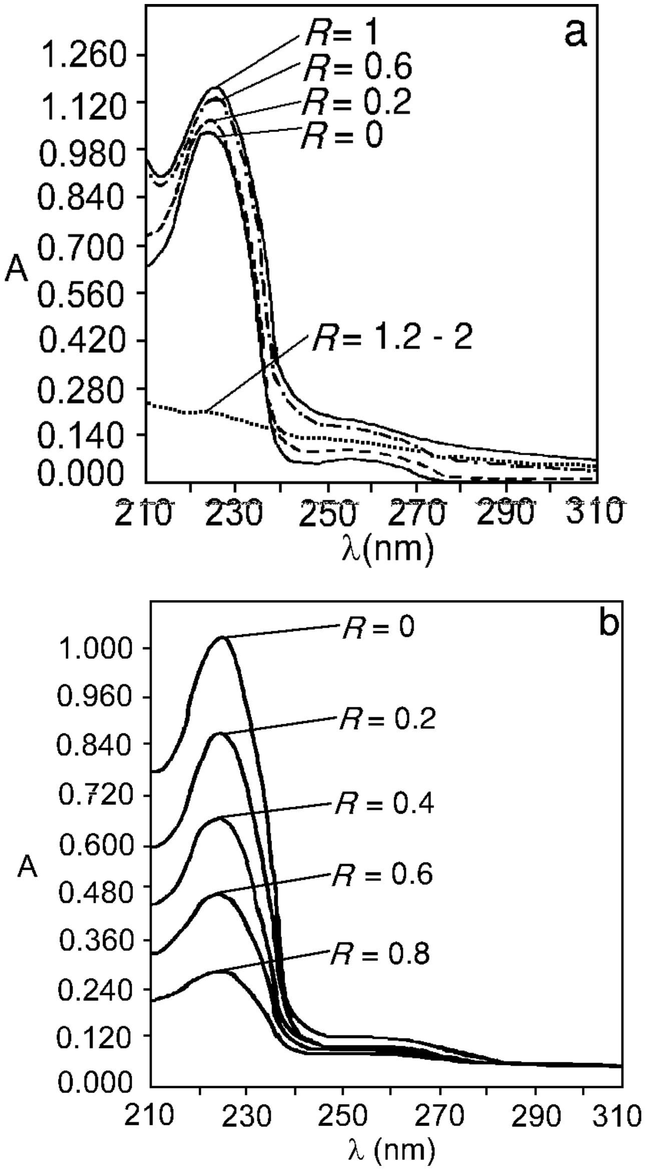

Fig. 4. Spectral changes for the system PCA$_5$/NaPSS$_1$ at different mixing ratios *R*: a. experimental samples; b. control samples.

The qualitative and quantitative results obtained when NaPSS was used as a titrant and the PCA$_5$ was the component in excess, at different mixing ratios, let us to suppose that the PEC formation takes place from the beginning by a cooperative mechanism leading to a more or less stoichiometric complex. Further amounts of NaPSS could generate another centers of complexation also with a definite structure. The particular aspect of this PEC is that the small particles have hydroxylic groups from the polycation on the surface that could keep them in solution in this range of concentration. This could explain why very small particles are distributed in the whole reaction mixture from the beginning of the reaction and why the microphase separation at low mixing ratios did not take place.

Table 1
Quantitative analyses of the PECs obtained in the system NaPSS$_1$/PCA$_5$ (R = ratio between the charged groups contained in the titrant and the oppositely charged groups in the starting solution)

PCA$_5$, unit mM	NaPSS$_1$, unit mM	R	Yield (%)	Cl (%)		S (%)		N (%)	
				Calcd	Found	Calcd	Found	Calcd	Found
50	100	0,2	–	0	0	11,1	10,1	5,83	–
		0,4	99,0	0	0,53	11,1	10,3	5,83	4,67
		0,6	88,5	0	0,89	11,1	10,3	5,83	4,92
		1	99,9	0	0	11,1	10,8	5,83	4,56
50	50	0,2	–	0	0	11,1	10,3	5,83	4,89
		0,4	–	0	0	11,1	10,2	5,83	5,02

3.3. Response of PECs at the subsequent addition of NaCl

A very important property of the PECs is their behavior in dependence on the nature and concentration of the low molecular weight salts. The critical ionic strength necessary for the dissociation of PECs into the original components or preventing the PECs formation depends on the chemical structure of the complementary polyelectrolytes [25,45–47], on the PEC structure [30–32] and on the neutral salts nature. By the NaCl subsequent addition to the PECs already formed we obtained information on their stability (the PECs dissociation into the original components), in dependence on the polycation structure and the mixing order, and on the interaction between the PECs particles and NaPSS in excess. The response of the PECs formed at the mixing ratio $R = 1.2$, using NaPSS as a titrant and three different polycations (PCA$_5$, PCA$_{20}$ and PCT$_{20}$) as starting solution, to the subsequent addition of NaCl was followed by UV-spectroscopy. Only stoichiometric PEC and some NaPSS in excess were present before the NaCl addition. The increase of the ionic strength up to 2.5 M NaCl had no significant influence on the UV spectrum of NaPSS in aqueous solutions with a concentration of 0.1 unit mM. The molar extinction coefficient remained about 10 000 l/mol cm, irrespective of the NaCl concentration. This behavior let us to assign all the spectral changes induced by the presence of NaCl to the interaction between PEC, NaCl and free NaPSS.

The UV spectra of the system NaPSS$_1$ (10 mM)/PCA$_5$ (1 mM), at the mixing ratio $R = 1.2$, in dependence on the NaCl concentration were collected in Fig. 5.

The increase of the NaCl concentration led to the continuous decrease of the absorbance at 225 nm this being an evidence for a possible interaction between the NaPSS in excess and the PEC particles and also for the stability of these PECs (the dissociation of PEC into the starting polyions should determine an increase of the absorbance at 225 nm). The UV spectra shown in Fig. 6 illustrate the PEC response at the NaCl addition for the system NaPSS$_1$ (10 mM)/PCA$_{20}$ (1 mM). A slight increase of the absorbance at 225 nm for the low NaCl concentrations (0.01 and 0.25 M) was first remarked, followed by an abrupt decrease at the NaCl concentrations higher than 1 M. The different behavior of this PEC comparative with the first one

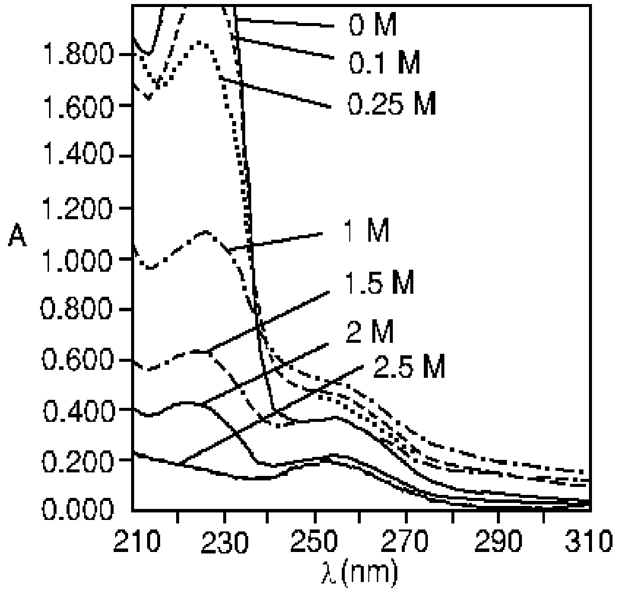

Fig. 5. Spectral changes of the system NaPSS$_1$ (10 mM)/PCA$_5$ (1 mM) at the mixing ratio $R = 1.2$, in dependence on the NaCl concentration.

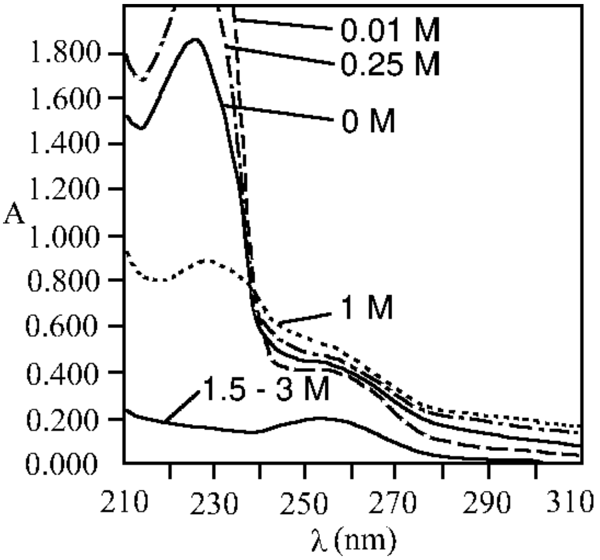

Fig. 6. Spectral changes of the system NaPSS$_1$ (10 mM)/PCA$_{20}$ (1 mM) at the mixing ratio $R = 1.2$, in dependence on the NaCl concentration.

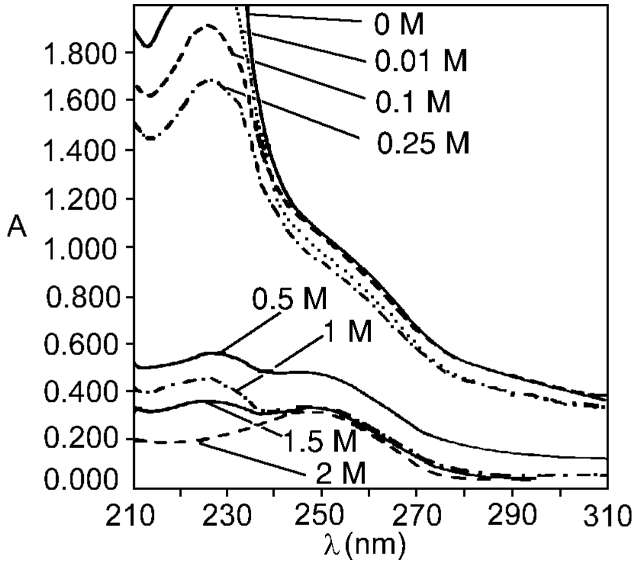

Fig. 7. Spectral changes of the system $NaPSS_1$ (10 mM)/PCT_{20} (1 mM) at the mixing ratio $R = 1.2$, in dependence on the NaCl concentration.

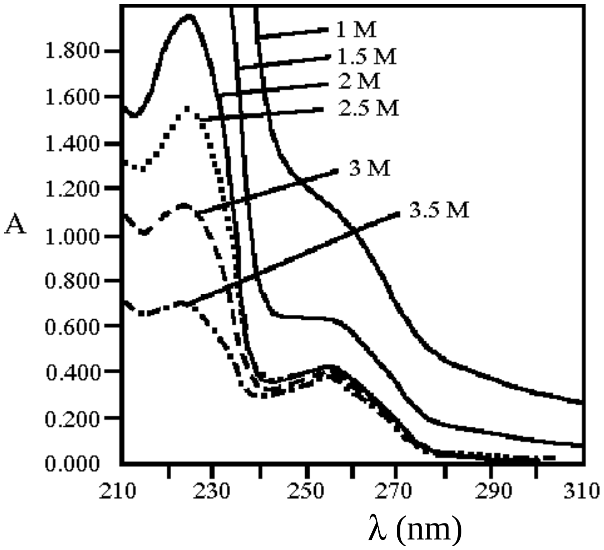

Fig. 8. Spectral changes of the system PCA_5 (10 mM)/$NaPSS_1$ (1 mM) at the mixing ratio $R = 0.6$, in dependence on the NaCl concentration.

could be caused by the higher branching degree of the polycation PCA_{20}. The higher the content of the polyfunctional amine (PCA_{20} has 20 mol% of amine A) the higher is the content of the quaternary ammonium salt groups in the side chains. The presence of a higher content of quaternary ammonium salt groups in the side chains of PCA_{20} comparative with PCA_5 has been already confirmed by its lower thermal stability [48]. The PEC formed in this case can include some NaPSS in a disorderly state to compensate the free positive charges in the side chains, the complex being not in a thermodynamic equilibrium. A small concentration of NaCl (0.01 and 0.25 M) can remove some NaPSS allowing the reorientation of the opposite polyions to a stable PEC. Further amounts of NaCl brought about the continuous decrease of the free NaPSS concentation in the supernatant solution.

The PEC response at the NaCl addition for the system $NaPSS_1$ (10 mM)/PCT_{20} (1 mM) is shown in Fig. 7. Even if the content of the quaternary ammonium salt groups in the backbone is about the same in PCT_{20} like in PCA_{20}, the influence of the polyfunctional amine nature is evident in the dynamic of spectral changes in this system comparative with the other one. The absorbance values at 225 nm decreased continuously starting from the first amounts of NaCl.

The influence of the NaCl subsequent addition on the PEC was also followed when PCA_5 was used as a titrant, the mixing ratio R between positive and negative charges being 0.6 (Fig. 8). Enough PEC was formed in this case and also a significant amount of NaPSS remained in excess. Before the addition of NaCl, the quasi-soluble PEC was in a colloidal state and could be evidenced by UV-spectroscopy besides the NaPSS in excess (like in Fig. 4a). The first effect of the ionic strength increase was the quasi-soluble PEC separation which started at an ionic strength of about 1.0 M NaCl. Only for high concentrations of NaCl (higher than 3.0 M) the microphase separation was complete and the supernatant was clear. The aspect of this PEC was different comparative with the PEC separated when NaPSS was used as a titrant, at the same mixing ratio, being much more hydrated. PEC with more structural defficiences, a less compact structure and a higher hydrophilicity can be formed at this concentration of polycation (see also the conductivities values for this system in Fig. 2). The absorbance value at 225 nm remained high enough even at 3.5 M NaCl, but the concentration of the free NaPSS decreased from 0.377 unit mM, corresponding to the initial reaction mixture, to 0.059 unit mM found at 3.5 M NaCl. NaPSS fractions with the highest molecular weight could be preferred for the thermodynamic stabilization process of the PEC at high ionic strength. A pronounced preference for the high molecular component was evidenced when poly(diallyldimethylammonium chloride) was added to NaPSS with different molecular weights, in the presence of high concentrations of NaCl [49,50].

4. Conclusions

In this paper we have investigated the main parameters which influence the formation of the interpolyelectrolyte complexes (PECs) between one polycation of integral type having about 95 mol% of *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units in the backbone (PCA_5) and poly(sodium styrenesulfonate) (NaPSS), in dilute aqueous solutions. Quasi-soluble PEC with a high stability as regards the microphase separation could be formed in the polyion concentration range of 0.1–1 unit mM. A PEC stoichiometry of about 1:1 was evidenced for both the quasi-soluble complex formed in dilute aqueous solutions and the insoluble PECs, isolated when the concentrations of the complementary polyelectrolytes were 50–100 mM.

UV-spectroscopy was used to get information on the stability of the quasi-soluble complexes in the presence of NaCl (as regards the microphase separation and PEC dissociation in the starting polyions) and on the interaction between these PECs and NaPSS in excess, in dependence on the polycation structure and on the mixing order of the complementary polyelectrolytes. The PECs response to the NaCl subsequent addition in the presence of some NaPSS in excess seems to be a specific process depending on the polycation structure. The higher the branching degree of the polycation the faster the adsorption process of NaPSS into the PECs, the absorbance values for the NaCl concentrations higher than 1 M being in the order: $PCA_5 > PCA_{20} > PCT_{20}$ (Figs. 5–7). A good stability of the PECs as regards the dissociation into the original components was found up to an ionic strength of 3.5 M.

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