FORMATION AND COLLOIDAL STABILITY OF SOME POLYELECTROLYTE COMPLEX DISPERSIONS BASED ON RANDOM COPOLYMERS OF AMPS

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The formation of some interpolyelectrolyte complexes between two random copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) and *t*-butyl acrylamide (TBA) and two strong polycations of integral type as a function of the ratio between opposite charges and the concentration of polyion pairs was followed in this work. Formation of the complex colloidal dispersion was followed via the optical density at 500 nm (OD_{500}) and the viscometric titration in salt-free aqueous solutions. Colloidal stability of the complex dispersions up to a ratio between charges of 1.8 was emphasized comparing the OD_{500} values measured after 24 h from the preparation with values found after one week of storage. The storage stability of the nonstoichiometric interpolyelectrolyte complexes as colloidal dispersions, with a ratio between charges of 0.6, as a function of polyion concentration (between 0.15 and 7.5 mmol/L), was followed by turbidimetric measurements after 24h and one week from preparation.

INTRODUCTION

The interaction between synthetic complementary polyelectrolytes is frequently involved either in the preparation of new materials, or in many solid-liquid separation processes. Numerous interpolyelectrolyte complexes (IPECs) have been reported, their structures and properties being controlled by some main parameters such as: polyion structure and charge density, polyion molar mass, polyion concentration, ionic strength and salt nature, polyions mixing ratio, and many other parameters that can be varied.[1-28] The known IPECs can be divided in three main types, according to their physical properties: insoluble and amorphous precipitates (polysalts),[1-9] soluble IPECs,[10-17] and IPECs as stable colloidal dispersions.[18-28] Nonstoichiometric IPECs (NIPECs) as colloidal dispersions, bearing positive or negative charges in excess, have already attracted the interest for different practical applications, such as: flocculants for cellulose, clay dispersions and low molecular organic compounds from the waste waters,[18,24] surface modification of different substrates,[22,23] etc. The most important characteristics of NIPECs as colloidal dispersions are their concentration in macromolecular components (as

high as possible) as well as the storage colloidal stability of the complex aggregates. In salt-free aqueous solutions, these characteristics can be monitored by the polyion structure, the mixing molar ratio and the addition rate of the titrant.[26-28] In our previous investigations, NIPECs with positive charges in excess corresponding to a molar ratio between charges, n^-/n^+, of 0.7 have been prepared with NaPAMPS as added polyion,[26] and their flocculation efficiency in the removal of monodisperse silica nanoparticles, comparative with the starting polycations, has been demonstrated.[28]

The aim of this paper was first to follow the formation of IPECs as colloidal dispersions, when the anionic components were two ionic/nonionic random copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) with *t*-butyl acrylamide (TBA), $P(AMPS_{37}\text{-co-}TBA_{63})$ and $P(AMPS_{54}\text{-co-}TBA_{46})$, the complementary polymers being poly(diallyldimethylammonium chloride) (PDADMAC) and an ionene type polycation, containing 95 mol % N,N-dimethyl-2-hydroxypropyleneammonium chloride repeat units (PCA_5), and second to investigate the storage colloidal stability of IPECs as a function of the polyion structure, and polyions addition order, at a

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constant titrant addition rate. The storage stability of NIPECs as colloidal dispersions with positive charges in excess, obtained from P(AMPS$_{54}$-co-TBA$_{46}$) and PCA$_5$, at a constant ratio between charges, n-/n+ of 0.6, as a function of total polyions concentration was also investigated. The complex formation and the colloidal stability of the complex dispersions were followed by turbidimetric and viscometric titrations.

RESULTS AND DISCUSSION

The influence of the concentration of complementary polyelectrolytes on the formation of the IPECs as colloidal dispersions between P(AMPS$_{54}$-co-TBA$_{46}$) and PCA$_5$ was followed by turbidimetric titration. Figure 1 shows the OD$_{500}$ curves obtained when P(AMPS$_{54}$-co-TBA$_{46}$) aqueous solutions with concentration of 10^{-3}, 5x10^{-3} and 10^{-2} mol/L were added to PCA$_5$ aqueous solution, with a concentration ten times lower, as a function of the molar ratio between charges, n$^-$/n$^+$, at a constant addition rate of 3.75 mL polyanion/mL polycation x h.

OD$_{500}$ values were used as a measure of the dispersion turbidity. A very strong maximum, followed by the decrease and level off of the OD$_{500}$ values, were observed irrespective of the polyions concentration. As can be seen, OD$_{500}$ values, both before and after the complex stoichiometry (the mixing ratio corresponding to the abrupt increase of the turbidity), were strongly influenced by the concentrations of the complementary polyions. Thus, OD$_{500}$ values increased with increasing polyion concentration, both before and after the complex stoichiometry, the lowest values being found for the lowest concentration. This behavior can be assigned to the increase of the concentration in complex particles and also to the increase of the collision number with the increase of concentration, the aggregation level being thus enhanced. It is known that turbidity values reflect the influence of some parameters that characterize the IPECs dispersions such as concentration, size, shape and polydispersity.[20-26] Therefore, the results presented in Figure 1 could be assigned also to the increase of the sizes and polydispersities of the complex nanoparticles, as it was demonstrated for other systems.[26] The complex stoichiometry was observed at a ratio n$^-$/n$^+$ of about 0.9, irrespective of the polyions concentration. The strong maximum characteristic for P(AMPS$_{54}$-co-TBA$_{46}$) as added polyion suggests a lower colloidal stability for the corresponding IPECs dispersions, such maximum being also observed for other ionic/nonionic copolymers used as added polyions.[21]
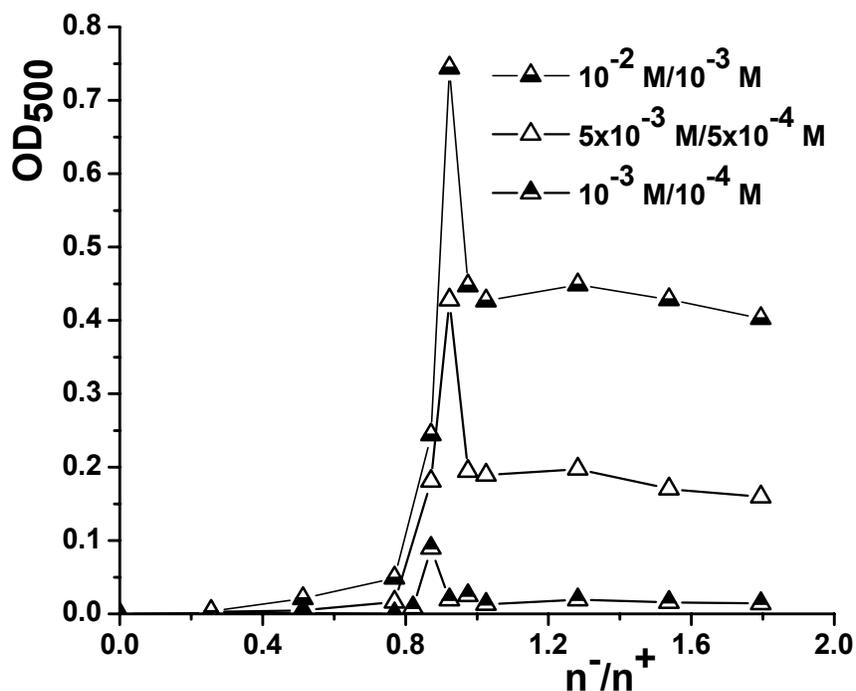

Fig. 1 – OD$_{500}$ values of the IPECs as colloidal dispersions based on P(AMPS$_{54}$-co-TBA$_{46}$) and PCA$_5$, as a function of polyion concentration.

The formation of IPECs colloidal dispersion between P(AMPS$_{37}$-co-TBA$_{63}$) and P(AMPS$_{54}$-co-TBA$_{46}$), on the one hand, and PDADMAC and PCA$_5$, on the other hand, as a function of polyions structure and mixing order was viscometrically followed. The variation of the specific viscosity (η_{sp}) values as a function of the molar ratio between charges and the mixing order of the oppositely charged polyions was plotted in Fig. 2. The concentration of the titrant was 5x10^{-3} M and that of the staring solution 5x10^{-4} M, in these experiments.
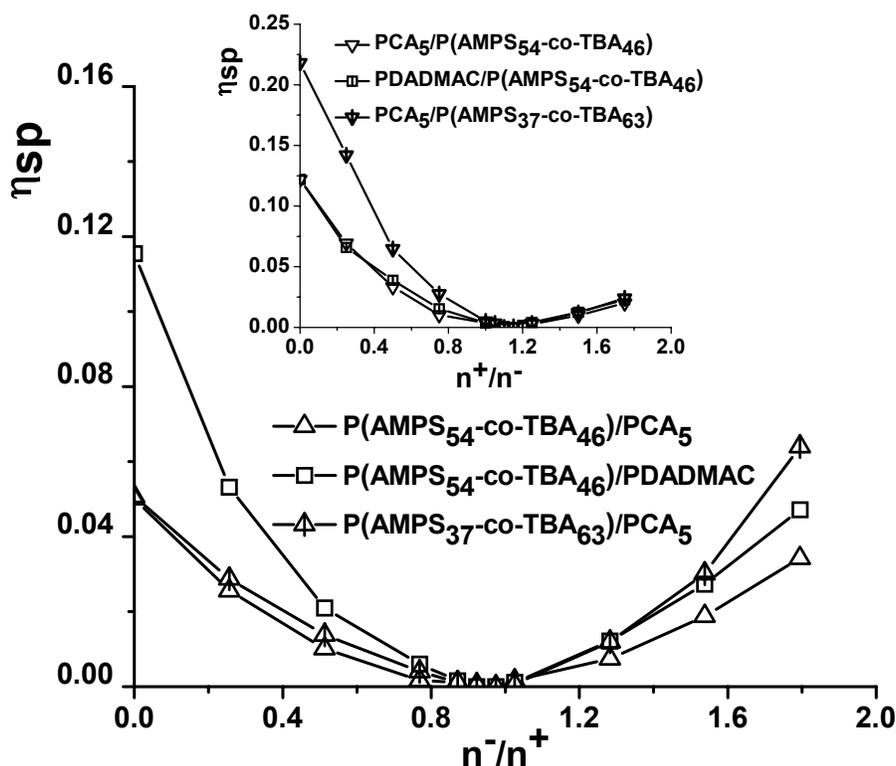

Fig. 2 – Specific viscosity values of IPECs as colloidal dispersions based on P(AMPS$_{37}$-co-TBA$_{63}$) and P(AMPS$_{54}$-co-TBA$_{46}$) as polyanions, and PDADMAC and PCA$_5$, as polycations; the concentration of the titrant was 5x10^{-3} mol/L and that of the starting solution 5x10^{-4} mol/L; the inset: the same polyion pairs with a reversed addition order.

The continuous decrease of the η_{sp} values before the stoichiometric point is correlated with the decrease of concentration of the component in excess from the starting solution, and also with the increase of NaCl concentration. As can be seen, before the stoichiometric point higher values of the η_{sp} were obtained when PDADMAC was the starting solution comparative with PCA$_5$. Comparing the systems P(AMPS$_{37}$-co-TBA$_{63}$)/PCA$_5$ and P(AMPS$_{54}$-co-TBA$_{46}$)/PCA$_5$, one can observe that η_{sp} values were almost identical before the stoichiometric point, irrespective of the polyanion structure, because PCA$_5$ was the polyion in excess in both cases. After the stoichiometric point, η_{sp} values reflect the polyanion in excess, the higher η_{sp} values being obtained when the titrant was

P(AMPS$_{37}$-co-TBA$_{63}$), comparative with P(AMPS$_{54}$-co-TBA$_{46}$). When P(AMPS$_{54}$-co-TBA$_{46}$) was used as titrant, the starting solution being either PDADMAC or PCA$_5$, the differences between η_{sp} values could be ascribed to the specific interactions between this polyanion and the complementary polycation, the lower values being obtained for the system P(AMPS$_{54}$-co-TBA$_{46}$)/PCA$_5$. This suggests that in this case a higher amount of polyanion has been incorporated in the complex particles. When the polyanion was the starting solution (the inset, Fig. 2), the higher values of η_{sp} before the stoichiometry were found for P(AMPS$_{37}$-co-TBA$_{63}$), comparative with P(AMPS$_{54}$-co-TBA$_{46}$), in agreement with η_{sp} values obtained in the previous case. After the stoichiometric point, η_{sp}

values were close each other, irrespective of the polycation structure. The complex stoichiometry was influenced by the mixing order of polyions, the molar ratio between charges corresponding to the stoichiometry being pushed to higher values when the polycation was the titrant, comparative with curves obtained when the titrant was the polyanion, for the same pair of polyelectrolytes.

Figures 3a and 3b illustrate the colloidal stability of two types of IPECs dispersions based on P(AMPS$_{54}$-co-TBA$_{46}$) and PDADMAC (Fig. 3a)
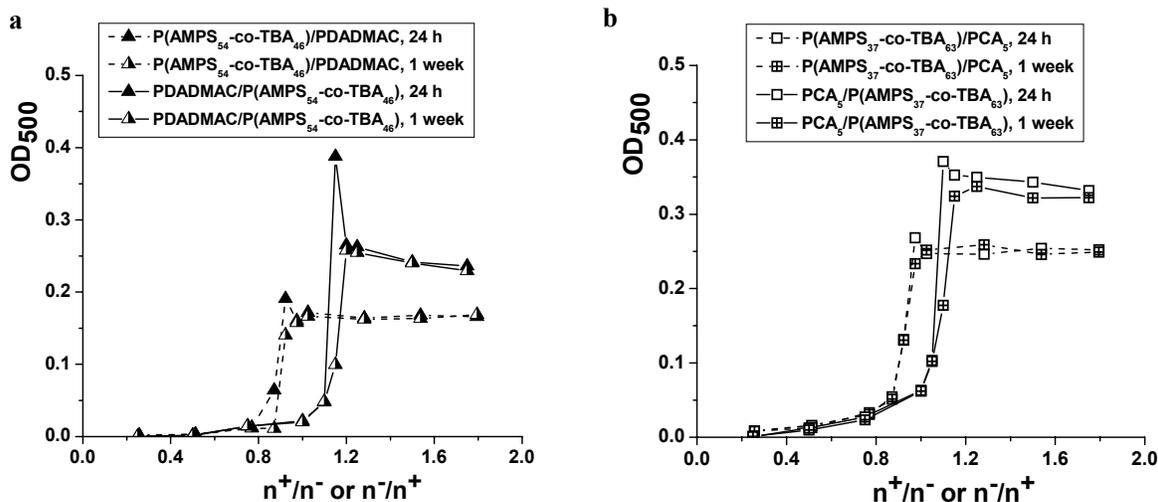
and P(AMPS$_{37}$-co-TBA$_{63}$) and PCA$_5$ (Fig. 3b) as complementary polyions, comparing the OD$_{500}$ values measured after 24 h from the preparation with values obtained after one week of storage. In all these experiments both possibilities of mixing were taken into account, that is, polyanion as titrant/polycation as starting solution and polycation as titrant/polyanion as starting solution, the concentration of the starting solution being 5×10^{-4} M and that of the titrant 5×10^{-3} M.

Fig. 3 – Colloidal stability of IPECs colloidal dispersions based on: (a) P(AMPS$_{54}$-co-TBA$_{46}$) and PDADMAC; (b) P(AMPS$_{37}$-co-TBA$_{63}$) and PCA$_5$; the concentration of the starting solution was 5×10^{-4} mol/L and that of the titrant 5×10^{-3} mol/L.

A strong maximum was observed when P(AMPS$_{54}$-co-TBA$_{46}$) was used as added polyanion (Fig. 3a), and these results confirm the results already presented in Figure 1 for polyion pair P(AMPS$_{54}$-co-TBA$_{46}$)/PCA$_5$ at the same concentrations. The presence of a maximum at the complex stoichiometry was also observed when P(AMPS$_{37}$-co-TBA$_{63}$) was used as polyanion, but the maximum was much lower than in the first case (Fig. 3b). On the other hand, the OD$_{500}$ values were much higher when the polyanion with a lower charge density was used as added polyion, because a higher amount of polyanion was necessary for the compensation of positive charges up to the complex stoichiometry. The higher values of OD$_{500}$ when either PDADMAC or PCA$_5$ were used as added polyions show that the polycations under study are less efficient in the stabilization of IPECs particles against collision, bigger aggregates being formed in this case. Except the disappearance of the maximum corresponding to the stoichiometry,

very small differences or no differences were observed, both before and after the stoichiometry, after one week of storage, for all systems under study, irrespective of the addition order. This shows a high colloidal stability during the storage time at the polyions concentration selected for this investigation, even if both polyanions contain a nonionic comonomer (TBA).

The system P(AMPS$_{54}$-co-TBA$_{46}$)/PCA$_5$ was selected for the study of the colloidal stability of NIPECs dispersions with positive charges in excess, prepared at a constant ratio between charges, n$^-$/n$^+$ of 0.6, and increasing concentrations of the polyions. The OD$_{500}$ values found after 24 h and one week from the NIPECs preparation were plotted in Fig. 4 versus the total polyion concentration (the sum of the concentrations of both polymeric components), c$_p$. Two consecutive measurements were performed after one week of storage: one without shaking and another one after shaking, both values being included in Fig. 4.
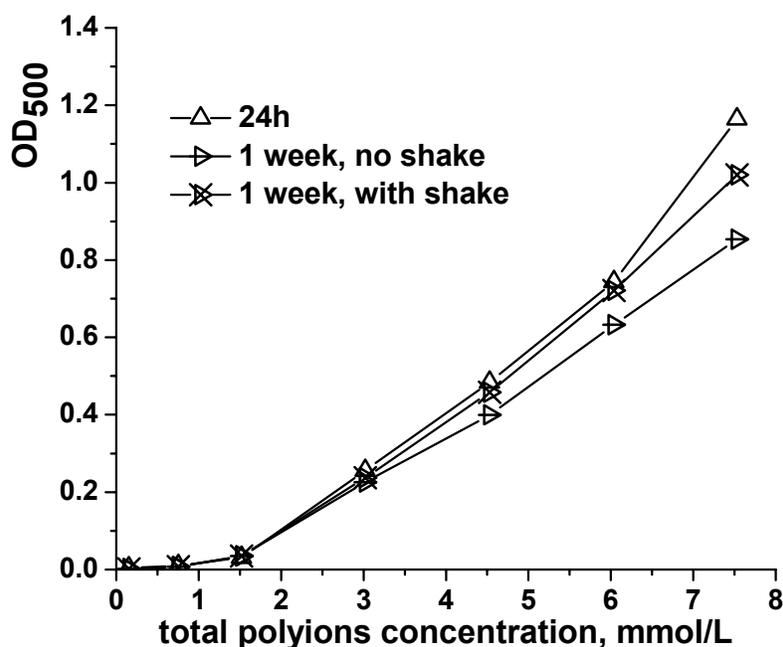
Fig. 4 – OD_{500} values of NIPECs with positive charges in excess prepared from
P(AMPS$_{54}$-co-TBA$_{46}$)/ PCA$_5$, at a constant ratio between charges of 0.6, after 24 h
and one week from preparation, plotted versus the total polyion concentration.

One can observe three regions concerning the storage stability of these dispersions: first region, $c_p < 3$ mmol/L, is characterized by a very high storage stability, OD_{500} values being approximately the same after 24 h and one week of storage; in the second region, $3 < c_p < 6$ mmol/L, OD_{500} values were lower after one week of storage, when the measurements were performed without shaking the samples comparative with the values found after 24 h; OD_{500} values found for the same samples after shaking became almost similar with those measured after 24 h; for $c_p > 6$ mmol/L, the NIPECs storage stability was poor. The presence of the nonionic comonomer led to the decrease of the storage colloidal stability of the complex aggregates, at high concentrations, comparative with the NIPECs dispersions with positive charges in excess prepared with NaPAMPS as polyanion.[26]

EXPERIMENTAL

Materials

Poly(diallyldimethylammonium chloride) (PDADMAC) purchased from Aldrich was used as received. The polycation PCA$_5$ was synthesized and purified according to the methods previously described.[29] Copolymers of AMPS were synthesized and purified according to ref. 30. Polyions characteristics were summarized in Tab. 1.
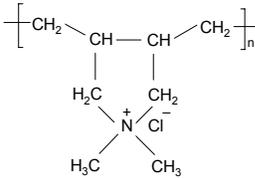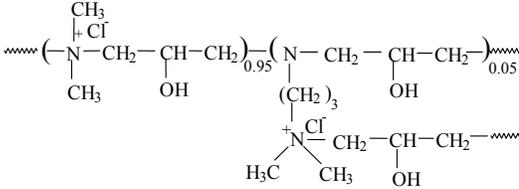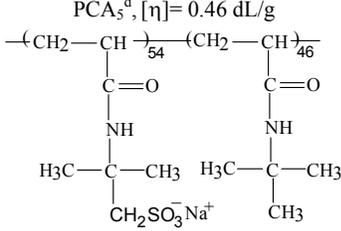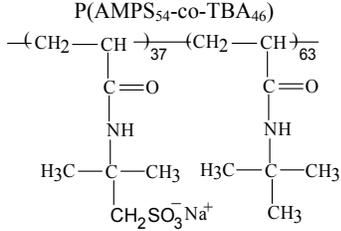
Methods

IPEC Preparation

Aqueous solutions of the complementary polyelectrolytes with different concentrations were prepared by adequate dilution of the stock solutions (10^{-1} mol/L for the added polyion, and 10^{-2} mol/L for the starting polyion), taking into account the molar mass of the repeat unit in g/charge, see Tab. 1) with distilled water. Variable volumes of the aqueous solution of polyanion, or polycation were continuously added to the aqueous solution of the starting polyion, with a constant titrant addition rate of 3.75 mL/mL starting polyion x h, under magnetic stirring, at room temperature (about 25 ^{o}C), until a certain ratio between opposite charges was achieved. The concentration of the added polyelectrolyte was always 10 times higher than that of the starting polyion. The IPECs dispersions were still stirred for 60 min., and were characterized after 24 h if other duration was not specified.

Complex characterization

The complex dispersion was characterized first by the optical density of NIPECs as colloidal dispersions at $\lambda = 500$ nm (OD_{500}), as a function of the polyions concentration and polyion addition order. OD_{500} measurements were carried out with a SPECORD M42 spectrophotometer (standard 1cm quartz cell). Viscosities were measured with an Ubbelohde viscometer with internal dilution, at 25 ^{o}C.

Table 1

Characteristics of oppositely charged polyions

Sample	M_w (g/mol)[a]	M_u (g/charge)[b]	b (nm)[c]
PDADMAC	240000	162.7	0.5
PCA$_5$[d], [η]= 0.46 dL/g	-	140.35	0.57
P(AMPS$_{54}$-co-TBA$_{46}$)	175000	337	0.463
P(AMPS$_{37}$-co-TBA$_{63}$)[d], [η]= 0.47 dL/g	-	440.66	0.667

[a] Molar mass determined by SEC;
[b] Mass per charge;
[c] Charge distance;
[d] Intrinsic viscosity determined in 1M NaCl, at 25 °C.

CONCLUSIONS

Polyions concentration strongly influenced the OD_{500} values, both before and after the complex stoichiometry; the higher the polyion concentration was, the higher OD_{500} values.

The viscometric study showed that the $η_{sp}$ values depended on the structure of the complementary polyions and the stoichiometric point was influenced by the polyion mixing order, the ratio n^-/n^+ corresponding to the stoichiometry being pushed to higher values when the polycation was the titrant.

A good colloidal stability of the complex dispersions was found after one week of storage when the concentration of the starting solution was 5×10^{-4} mol/L and that of the titrant 5×10^{-3} mol/L. NIPECs colloidal dispersions, with a ratio n^-/n^+ of 0.6, obtained from P(AMPS$_{54}$-co-TBA$_{46}$) and PCA$_5$, had a very good storage stability up to a maximum concentration in the macromolecular components of about 3 mmol/L.

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