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ORIGINAL CONTRIBUTION

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Effect of a low-molecular-weight salt on colloidal dispersions of interpolyelectrolyte complexes

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Abstract Colloidal dispersions of an interpolyelectrolyte complex were prepared by mixing dilute aqueous solutions of poly(dimethyldiallylammonium chloride) and the sodium salt of the alternating copolymer of maleic acid propene in amounts providing about a threefold excess of the charged groups of the cationic polyelectrolyte over those of the anionic polyelectrolyte. These dispersions were examined by means of analytical sedimentation, quasielastic light scattering, and laser Doppler microelectrophoresis. The experimental results obtained suggest that the particles of the interpolyelectrolyte complex are multicomplex aggregates bearing cationic charge. Such aggregates were assumed to consist of a hydrophobic core formed by coupled oppositely charged macromolecules and a hydrophilic shell formed by cationic macromolecules. Hydrodynamic and electrophoretic properties of these aggregates were found to be rather sensitive to variations in the ionic strength of the surrounding medium: with rising salt concentration, their sedimentation coefficient and hydrodynamic size increase, these increases becoming more strongly pronounced at higher salt concentrations, whereas their electrophoretic mobility gradually decreases. The salt effects revealed suggest that the aggregation level of the particles of the interpolyelectrolyte complex rises in response to an increase in the ionic strength of the surrounding medium. This phenomenon was associated with the salt-induced decrease of the stabilizing effect of the hydrophilic shells that protect such particles from progressive aggregation.

Key words Interpolyelectrolyte complex – Colloidal dispersions – Poly(dimethyldiallylammonium chloride) – Alternating copolymer of maleic acid and propene

Introduction

It is well known that electrostatic interaction between oppositely charged macromolecules leads to the formation of interpolyelectrolyte complexes (IPECs) [1]. Such macromolecular assemblies are predominantly stabilized by a cooperative system of interpolymer salt bonds although other intermacromolecular interactions, for example, hydrogen bonding, hydrophobic interactions, charge-transfer interactions, and van der Waals forces, can also play a significant role. The structure and properties of IPECs are determined by a number of factors: the characteristics of the polyelectrolyte components (e.g., nature of ionic groups, degree of polymerization, charge density, etc.) and their concentrations, the ratio between amounts of oppositely charged groups of polyelectrolytes, the conditions of the surrounding medium (e.g., ionic strength, pH, temperature, etc.) as well as the method of preparation of such macromolecular assemblies [2–4].

IPECs are of considerable interest because of their various potential applications as new polymeric reagents and materials for industry, ecology, biotechnology, and medicine. For instance, IPECs were found to be promising flocculants for colloidal dispersions [5–8]. They have also been successfully applied as efficient binders of dispersed systems such as soils and sands to protect them from water and/or wind erosion [5]. IPECs were shown to be suitable for the construction of enzymatic systems with controllable activity and stability [9, 10], for the preparation of membranes [11, 12] and microcapsules [12, 13], for the immobilization of microorganisms [14], for the surface modification of solid materials [15, 16], etc. The biocompatibility of IPECs is a unique feature that opens many possibilities for their application as coatings for medical materials used in a contact with blood and other biological liquids [17, 18].

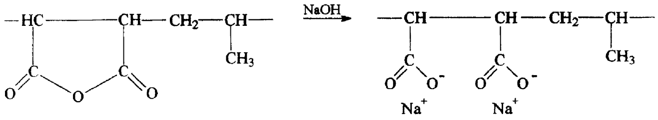
As anionic polyelectrolytes, copolymers of maleic acid and alkenes are able to interact with cationic polyelectrolytes. When charged groups of a cationic polyelectrolyte are present in excess compared to charged groups of an anionic copolymer, the formation of relatively stable colloidal dispersions that contain IPEC particles bearing net cationic charge can be observed [7, 8, 15, 16]. From a practical point of view, such macromolecular assemblies were thoroughly examined for flocculation of cellulose/clay and clay dispersions [7, 8] and for surface modification of some silicate powders [15, 16]. It has been supposed that the efficiencies of these processes are determined by properties of the macromolecular reagents applied, i.e., IPECs. In connection with this, we have carried out a study to elucidate the effect of low-molecular-weight salts on the overall characteristics of such macromolecular assemblies.

Experimental

Materials

Poly(dimethyldiallylammonium chloride) [P(DMDAA·Cl)] with $M_W = 400\,000$ g/mol ($M_W/M_n = 1.4$) obtained from the Fraunhofer Institut für Angewandte Polymerforschung (Teltow, Germany) was used as a cationic polyelectrolyte.

The sodium salt of the alternating copolymer of maleic acid and propene [P(Ma·Na-*co*-Pr)] or the sodium salt of the alternating copolymer of maleic acid and propene with a small number of *N*-pyrenyl maleic imide units [P(Ma·Na-*co*-Pr)*] prepared by hydrolysis of the corresponding anhydrides with 0.1 M solution NaOH at elevated temperature for a few hours were used as anionic polyelectrolytes.



The alternating copolymer of maleic anhydride and propene with $M_W = 50\,000$ g/mol (specified by the manufacturer) was obtained from Leuna (Germany). This product was modified by aminopyrene in tetrahydrofuran to synthesize the alternating copolymer of maleic anhydride and propene with a few mole percent *N*-pyrenyl maleic imide units as labels.

Sodium chloride and 2-amino-2-hydroxymethyl-1,3-propanediol were purchased from Fluka and used without further purification. Water was purified and deionized by a Milli-Q system (Millipore, Germany). A 0.01 M aqueous solution of 2-amino-2-hydroxymethyl-1,3-propanediol was used as a solvent (pH $\cong$ 9).

Sample preparation

The mixtures of oppositely charged polyelectrolytes with the constant ratio between the total concentrations of the charged groups of the polyelectrolyte components $Z = [-]/[+] = 0.3$ and various concentrations of NaCl were prepared according to two different procedures described below.

Method A

Aliquots (15 ml) of a dilute solution of the anionic polyelectrolyte ($[-] = 1.2 \times 10^{-3}$ M) with the desired concentration of NaCl were added dropwise and under continuous stirring to 15 ml of a dilute solution of the cationic polyelectrolyte ($[+] = 4 \times 10^{-3}$ M) with the same concentration of NaCl.

Method B

Aliquots (15 ml) of a salt-free dilute solution of the anionic polyelectrolyte ($[-] = 1.2 \times 10^{-3}$ M) were added dropwise and under continuous stirring to 15 ml of a dilute salt-free solution of the cationic polyelectrolyte ($[+] = 4 \times 10^{-3}$ M). After about 1 day, the desired amount of 4 M NaCl was injected.

Methods

Turbidimetry

The turbidity of the mixtures of oppositely charged polyelectrolytes was qualitatively characterized by the optical density measured at 500 nm (OD_{500}). At this wavelength, the polyelectrolytes used do not absorb light: the values of OD_{500} resulted from light scattering by the IPEC particles. The measurements were carried out by means of a Lambda 2 UV/VIS spectrometer (Perkin Elmer, UK).

Analytical sedimentation

Sedimentation experiments were carried out in the scan mode by means of a Beckman (Spinco, model E) analytical ultracentrifuge (Beckman, USA) equipped with an absorption optical detector. The values of the sedimentation coefficient S_C of the IPEC particles were calculated according to the formula

$$S_C = \frac{1}{\omega^2}\frac{\mathrm{d}\ln r}{\mathrm{d}t} , \qquad (1)$$

where r is the distance between the center of the sedimentation profile and the bottom of the sedimentation cell at different time points, t is time of rotation, and ω is the angular speed of the rotor rotation.

Quasielastic light scattering

Quasielastic light scattering was used to determine the z-average translation diffusion coefficient D_C of the IPEC particles. The corresponding values of the hydrodynamic radius R_H of such particles were calculated from the values of D_C obtain according to the Stokes-Einstein equation

$$R_H = \frac{kT}{6\pi\eta_s D_C} , \qquad (2)$$

where k is Boltzmann's constant, T is the temperature, and η_s is the dynamic viscosity of the solvent. The measurements were carried out at a fixed angle of 90° by means of a Zeta Master S device (Malvern, UK) equipped with a 4 mW diode laser (670 nm) as a light source.

Laser Doppler microelectrophoresis

Laser Doppler microelectrophoresis was used to determine the electrophoretic mobility U_E of the IPEC particles. The measurements were carried out at a fixed angle of 90° by means of a Zeta Master S device (Malvern). A 5 mW He-Ne laser (633 nm) was used as a light source.

Polyelectrolyte titration

Polyelectrolyte titration carried out by means of a PCD 02 particle charge detector (Mütek, Germany) was applied to determine concentrations of the charged groups of the polyelectrolytes used in their stock solutions. The principle of this method is based on the compensation of the streaming potential induced due to adsorption of charged macromolecules onto a surface of a test vessel made of polytetrafluoroethylene by titration with a standard solution of a strong oppositely charged polyelectrolyte. The concentration of the charged groups of the polyelectrolyte in the solution examined is calculated from the amount of standard solution needed to reach the zero value of the streaming potential.

All measurements were made at room temperature (about 293 K).

Results and discussion

Turbid dispersions prepared upon mixing transparent solutions of oppositely charged polyelectrolytes were examined over the range of NaCl concentrations up to approximately 0.3 M. At such salt concentrations, these dispersions are rather stable on the colloidal level, at least for a few days, whereas considerable macroscopic precipitation of the IPEC formed is observed at higher concentrations of NaCl.

Figure 1 presents the curves illustrating time changes in the optical density (OD_{500}) measured half an hour after the preparation of the mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr). At 0.05 and 0.09 M NaCl (curves 1 and 2), the values of OD_{500} are virtually independent of time. At 0.15 and 0.20 M NaCl (curves 3 and 4), a slow increase in the values of OD_{500} is found, this effect tending to level off with time. About a day after mixing

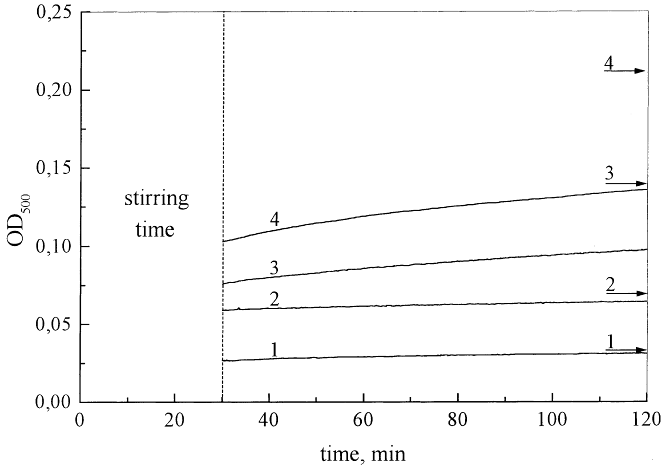


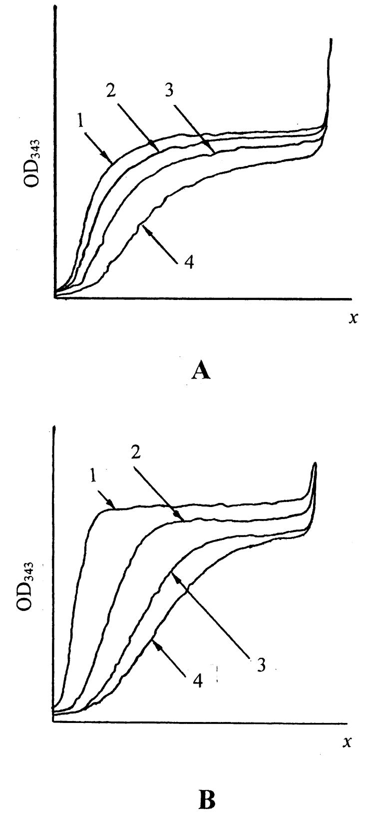
Fig. 1 The time dependencies of the optical density OD_{500} obtained for mixtures of poly(dimethyldiallylammonium chloride) [P(DMDAA·Cl)] and the sodium salt of the alternating copolymer of maleic acid and propene [P(Ma·Na-*co*-Pr)] with NaCl concentrations of 0.05 (1), 0.09 (2), 0.15 (3), 0.20 M (4). The *arrows* show values of OD_{500} measured a day after the preparation of these mixtures

the solutions of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr), time changes in OD_{500} become so insignificant that turbidity of the prepared mixtures can be considered to be nearly constant over a relatively long period of time. In connection with this, the results reported later in this paper concern experiments carried out a day after the preparation of colloidal dispersions of IPEC.

The effect of NaCl on the values of OD_{500} obtained for mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) is shown in Fig. 2. A gradual increase in OD_{500} is detected upon a rise in the salt concentration. This tendency appears to be negligible at lower concentrations of NaCl but it becomes pronounced with rising concentration of NaCl. To clarify the observed salt-induced changes in turbidity of the colloidal dispersions of IPEC, such dispersions were examined by means of analytical sedimentation, quasielastic light scattering, and laser Doppler microelectrophoresis.

Typical sedimentation profiles obtained for mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr)* are given in Fig. 3. These profiles were recorded at 343 nm which corresponds to one of the peaks in the absorption spectrum of the labeled anionic polyelectrolyte. As is seen, each sedimentation profile contains only one distinct step, and this is of a clear sigmoidal shape. This step moves to the bottom of the sedimentation cell very rapidly and can be detected only at relatively low angular speeds of the rotor rotation at which macromolecules of the polyelectrolyte components used show no sedimentation. Thus, the observed step can undoubtedly be associated with IPEC particles formed in mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr)*.

Figure 4 shows that the sedimentation coefficient S_C of these particles strongly increases with rising concentration of NaCl. It is interesting that the dependence of S_C on salt concentration seems to have an inflection point at about 0.15 M NaCl. At lower salt concentrations, a relatively weak salt-induced increase in the values of S_C is observed, but it becomes drastic at higher salt concentrations.



A

B

Fig. 3 The sedimentation patterns obtained for mixtures of P(DMDAA·Cl) and the sodium salt of the alternating copolymer of maleic acid and propene with a small number of *N*-pyrenyl maleic imide units [P(Ma·Na-*co*-Pr)*] with NaCl concentrations of **A** 0.05 and **B** 0.18 M. **A** ω = 12 000 rpm, 300 (1), 560 (2), 900 (3), and 1620 s (4); **B** ω = 6400 rpm, 180 (1), 250 (2), 640 (3), and 990 s (4); OD_{343} is the optical density measured at 343 nm and *x* is the distance from the meniscus of the sedimentation cell

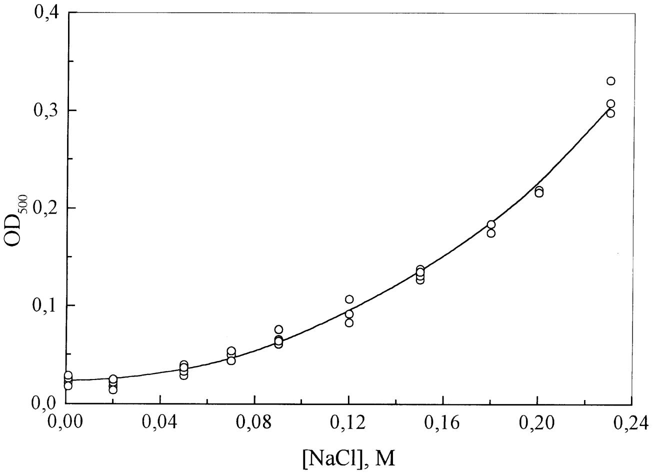


Fig. 2 The dependence of the optical density OD_{500} obtained for mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) on the concentration of NaCl

It is important to note that the values of S_C remarkably exceed the corresponding values of sedimentation coefficients of the polyelectrolyte components used. Indeed, S_C is found to increase from about 150 Sv (at 0.05 M NaCl) to about 1500 Sv (at 0.20 M NaCl) (Fig. 4), while the values of sedimentation coefficients measured at the same salt concentrations for the corresponding polyelectrolytes are evaluated to be within a few svedbergs. This pronounced difference suggests that the macromolecular assemblies detected can be considered as multicomplex aggregates. It is worth mentioning that the formation of similar aggregated structures was also observed for other pairs of oppositely charged polyelectrolytes, in particular, for poly(sodium styrenesulfonate) and P(DMDAA·Cl) [19, 20].

The results of the quasielastic light-scattering experiments carried out to determine the hydrodynamic radius R_H of IPEC particles formed in mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) are presented in Fig. 5. The values of R_H are nearly constant and are approximately 100 nm at lower concentrations of NaCl, whereas a considerable salt-induced increase is observed at higher concentrations of NaCl, this increase becoming steeper with rising salt concentration. It is important to note that the pronounced increase in R_H (Fig. 5) is detected at virtually the same concentrations of NaCl that correspond to the strong increase in S_C (Fig. 4).

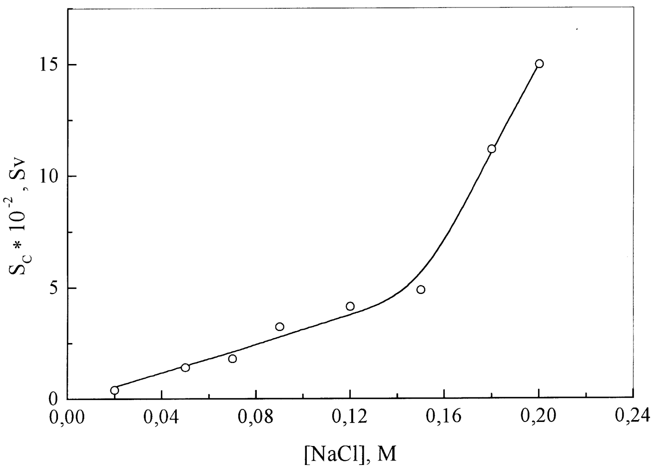


Fig. 4 The dependence of the sedimentation coefficient S_C of the interpolyelectrolyte complex (IPEC) particles formed in mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr)* on the concentration of NaCl

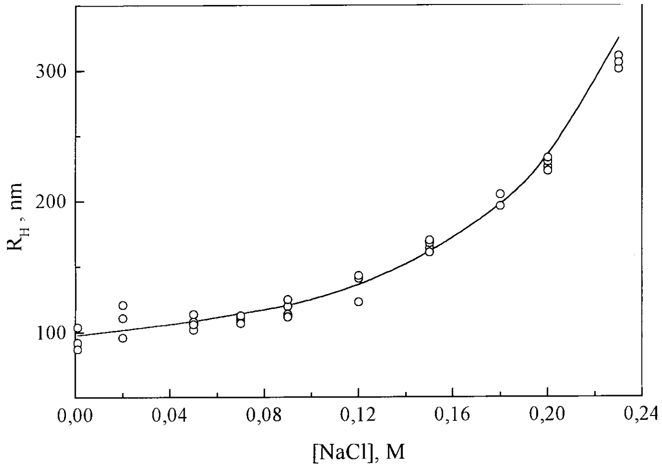


Fig. 5 The dependence of the hydrodynamic radius R_H of the IPEC particles formed in mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) on the concentration of NaCl

Combining the Svedberg and Stokes-Einstein equations, one can easily obtain the relation between the molar mass M_C of the IPEC particles formed, S_C, and R_H:

$$M_C = 6\pi\eta_S S_C R_H \frac{N_A}{(1 - \nu\rho_S)} \tag{3}$$

where N_A is Avogadro's number, ν is the partial specific volume of the particles, and ρ_S is density of the solvent. Because M_C is proportional both to S_C and R_H, the simultaneous salt-induced increases in the values of S_C and R_H found at higher concentrations of NaCl (Figs. 4, 5) indicate a corresponding rise in M_C. However, numerical calculations of the values of M_C according to Eq. (3) have not been made because ν is an unknown parameter whose determination for the system studied is rather difficult.

Thus, on the whole, the experimental results obtained suggest that a rise in the salt concentration in mixing solutions of oppositely charged polyelectrolytes favors the formation of the more aggregated macromolecular assemblies. This phenomenon is supposed to be responsible for the observed salt-induced increase in turbidity of colloidal dispersions of IPEC (Figs. 2) as well as for the observed salt-induced changes in hydrodynamic characteristics of IPEC particles (Figs. 4, 5). It is worth mentioning that similar inferences (but only for the case when the ionic strength of the surrounding medium is not extremely low) were drawn with respect to aggregated structures that appear as a result of electrostatic interaction between poly(styrene sulfonate) and P(DMDAA·Cl) [19, 20].

Table 1 contains the values of OD_{500} obtained for the mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) prepared according to two different procedures, i.e., method A and method B, as well as the values of R_H measured for the IPEC particles formed in these mixtures. As is seen, both the values of R_H and the values of OD_{500} are nearly independent of the procedure

Table 1 Values of the optical density OD_{500} obtained for the mixtures of poly(dimethyldiallylammonium chloride) [P(DMDAA·Cl)] and the sodium salt of the alternating copolymer of maleic acid and propene [P(Ma·Na-*co*-Pr)] prepared according to method A and method B and the values of the hydrodynamic radius R_H measured for the interpolyelectrolyte complex (IPEC) particles formed in these mixtures

	Method A		Method B	
[NaCl], M	OD_{500}	R_H, nm	OD_{500}	R_H, nm
0.05	0.04 ± 0.01	110 ± 5	0.05	110
0.12	0.09 ± 0.01	140 ± 10	0.12	140
0.15	0.14 ± 0.01	170 ± 5	0.13	160
0.20	0.22 ± 0.02	230 ± 5	0.25	220

used. Thus, addition of NaCl to the previously prepared salt-free mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) leads to the formation of larger macromolecular assemblies from smaller ones. At the same time, a decrease in the concentration of NaCl does not result in the opposite process, i.e., the generation of smaller macromolecular assemblies from larger ones. Indeed, the value of R_H measured for the IPEC particles formed in mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) at 0.18 M NaCl only slightly decreases (less than 5%) upon a twofold dilution of this dispersion with the pure solvent, while OD_{500} demonstrates an expected twofold reduction (Table 2). These results point out that the formation of multicomplex aggregates is an irreversible process. Thus, the system considered seems to be rather far from thermodynamic equilibrium.

The results of the laser Doppler microelectrophoresis experiments carried out to determine the electrophoretic mobility U_E of the IPEC particles formed in mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) are shown in Fig. 6. The values of U_E are found to be positive over the range of NaCl concentrations examined. This fact convincingly indicates that the macromolecular assemblies detected bear cationic charge. A gradual decrease in U_E is observed upon a rise in the salt concentration. This behavior can be associated with small ions that screen the cationic charge of the multicomplex aggregates: the screening effect of small ions increases with rising ionic strength of the surrounding medium. When U_E reaches a value of about 1.5×10^{-8} m/(s × V) (the corresponding value of the ζ potential calculated for Smoluchowskii's limit is about +20 mV), pronounced macroscopic precipitation of the IPEC particles formed is detected.

For the interpretation of the experimental results obtained, a consideration similar to those described in Refs. [19, 20] can be used. The formation of the multicomplex aggregates bearing cationic charge is assumed to be the result of the processes schematically depicted in Fig. 7. At first, fast coupling between oppositely charged macromolecules is supposed to lead to the appearance of primary macromolecular assemblies. In aqueous media, such assemblies can undergo progressive aggregation via hydrophobic interactions. This process is expected to result in the formation of multicomplex aggregates. At the same time, the free cationic macromolecules, which are not involved in interpolyelectrolyte complexation, can be absorbed onto surfaces of the growing macromolecular assemblies that become similarly charged. This process counteracts further aggregation of such assemblies and finally completely prevents it. As a result of these two processes, multicomplex aggregates of a "core-shell"

Table 2 The values of OD_{500} obtained for mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) before and after dilution and the values of R_H measured for the IPEC particles detected in these mixtures

Parameter	[NaCl], M	Before dilution	After isoionic two fold dilution	After two fold dilution
OD_{500}	0.09	0.07	0.04	–
	0.18	0.19	–	0.10
R_H, nm	0.09	120 ± 5	120 ± 5	–
	0.18	200 ± 5	–	200 ± 10

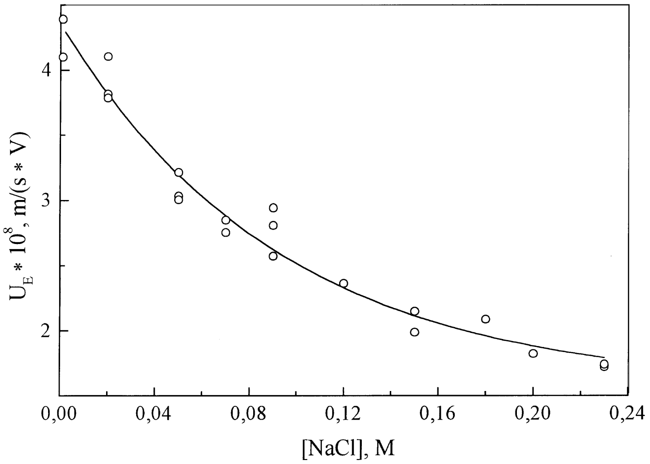


Fig. 6 The dependence of the electrophoretic mobility U_E of the IPEC particles formed in mixtures of P(DMDAA·Cl) and P(Ma·Na-*co*-Pr) on the concentration of NaCl

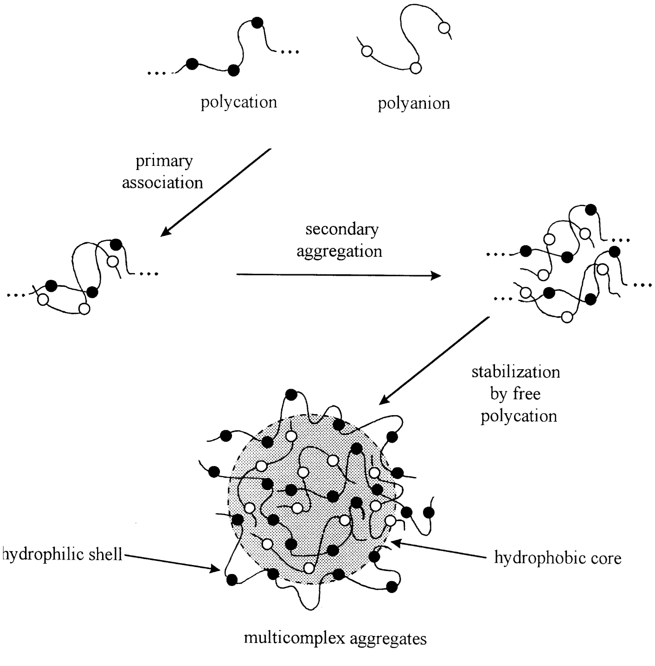


Fig. 7 The scheme of the formation of the multicomplex aggregates

structure with a hydrophobic core formed by the coupled oppositely charged macromolecules and the hydrophilic shell formed by loops and tails of the cationic macromolecules absorbed onto the hydrophobic core are assumed to appear (Fig. 7).

The aggregation process in such a system is expected be rather sensitive to variations in the ionic strength of the surrounding medium. Indeed, a rise in salt concentration suppresses the stabilizing effect of the cationic macromolecules absorbing onto surfaces of the growing aggregates because of the more effective screening of the cationic charges of such macromolecules by small ions. As a consequence, the formation of macromolecular assemblies with higher levels of aggregation is facilitated.

Thus, the experimental data reported in this work provide clear evidence that the characteristics of the macromolecular assemblies formed by oppositely charged polyelectrolytes can be controlled by variations in the ionic strength of the surrounding medium. The experimental results obtained can be useful for development of new methods for direct synthesis of macromolecular assemblies with desired characteristics.

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References

1. Smid J, Fish D (1988) In: Mark HF, Bikales NM, Overberger CG, Menges G (eds) Encyclopedia of polymer science and engineering, vol II. Wiley, New York, pp 720–739
2. Tsuchida E, Abe K (1982) Adv Polym Sci 45:1–123
3. Kabanov VA, Zezin AB (1984) Pure Appl Chem 56:343–354
4. Philipp B, Dautzenberg H, Linow KJ, Koetz J, Dawydoff W (1989) Progr Polym Sci 14:91–172
5. Kabanov VA, Zezin AB, Kasaikin VA, Yaroslavov AA, Topchiev DA (1991) Usp Khim (in Russian) 60:595–601
6. Suzuki A, Kashiki I (1987) Ind Eng Chem Res 26:1464–1468
7. Petzold G, Lunkwitz K (1995) Colloids Surf A 98:225–233
8. Petzold G, Nebel A, Buchhammer HM, Lunkwitz K (1998) Colloid Polym Sci 276:125–130
9. Zezin AB, Izumrudov VA, Kabanov VA (1989) Makromol Chem Macromol Symp 26:249–264
10. Kohjiya S, Maeda K, Yamashita S (1991) J Appl Polym Sci 43:2219–2222
11. Kalyuzhnaya RI, Rudman AR, Vengerova NA, Razvodovskii EF, El'tsefon BS, Zezin AB (1975) Vysokomol Soed Ser A (in Russian) 17:2786–2792
12. Dautzenberg H, Arnold G, Tiersch B, Lukanoff B, Eckert U (1996) Progr Colloid Polym Sci 101:149–156
13. Lee KY, Park WH, Ha WS (1997) J Appl Polym Sci 63:425–432
14. Kokufuta E, Matsumoto W, Nakamura I (1982) J Appl Polym Sci 27:2503–2512
15. Buchhammer HM, Kramer G, Lunkwitz K (1994) Colloids Surf A 95:299–304
16. Kramer G, Buchhammer HM, Lunkwitz K (1997) J Appl Polym Sci 65:41–50
17. Valueva SP, Efimov VS, Rozkin MYa, Gulyaeva ZhG, Zezin AB, Kopylova EM, El'tsefon BS, Lopukhin YuM (1981) Khim-Farm Zh (in Russian) 2:85–91
18. Zezin AB, El'tsefon BS, Rudman AR, Vengerova NA, Kalyuzhnaya RI, Valueva SP, Kopylova EM, Chepurov AK, Efimov VS, Kabanov VA (1987) Khim-Farm Zh (in Russian) 7:788–801
19. Karibyants N, Dautzenberg H, Coelfen H (1997) Macromolecules 30:7803–7809
20. Dautzenberg H (1997) Macromolecules 30:7810–7815