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Polyelectrolyte Complex Formation in Highly Aggregating Systems. 1. Effect of Salt: Polyelectrolyte Complex Formation in the Presence of NaCl

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ABSTRACT: Polyelectrolyte complex formation between components with strong ionic groups and high molecular weights were studied by static light scattering as a function of the mixing ratio and the ionic strength of the medium. Sodium poly(styrenesulfonate) and sodium poly(methacrylate) were used as polyanions and poly(diallyldimethylammonium chloride) and its copolymer with acrylamide were used as polycations. Very small amounts of sodium chloride lead to a drastic decrease of the level of aggregation, while higher ionic strength results in macroscopic flocculation.

Introduction

Polyelectrolyte complex (PEC) formation represents a simple but very interesting principle of structure formation with high practical relevance. The strong Coulomb interaction between oppositely charged polyelectrolytes leads to spontaneous aggregation by mixing of the component solutions.

Complex formation between polyelectrolytes with weak ionic groups and significantly different molecular weights at nonstoichiometric mixing ratios yields soluble PECs, consisting of a long host molecule and shorter sequentially attached guest polyions of opposite charge. Such systems may be considered as peculiar block copolymers containing hydrophilic single-stranded and relatively hydrophobic double-stranded segments. Comprehensive studies about soluble complexes were carried out by the groups of Tsuchida and Kabanov, stressing the preparation conditions of soluble complexes,[1−4] their structure and kinetics,[5−8] and exchange reactions between PECs and other polyelectrolytes[9−11] as a function of the polyion characteristics and the nature and concentration of salts. Although the important role of a minimal concentration of a low molecular electrolyte for the formation of soluble PECs was mentioned,[12] systematic investigations are missing.

However, in many cases of high practical relevance, e.g., as flocculants, membranes with special separation properties, or for microencapsulation, PEC formation is performed under conditions, which results in highly aggregated structures. Polyelectrolytes with strong ionic groups tend in general to macroscopic flocculation, impeding the study of such structures. However, in very diluted solutions (<0.1 mg/mL) and nonstoichiometric systems, particles on a colloidal level are formed, which can be studied by methods normally used in polymer characterization.

In previous papers[13−18] we reported about the formation, structure, and stoichiometry of such PECs in salt-free solutions. The results obtained may be summarized as follows:

Potentiometric and UV−vis spectroscopic investigations showed that from the point of view of salt binding (charge compensation between polyanions and polycations), the complexes have a 1:1 stoichiometry. Static and dynamic light scattering as well as electron and X-ray absorption microscopy reveal the PEC particles as highly polydisperse systems of nearly spherical and relatively compact structures. These particles are stabilized against further coagulation via electrostatic repulsion by an excess of the major component on the particle surfaces, which can be quantitatively determined by viscometry or analytical ultracentrifugation.

The aggregation level of the PECs is mainly controlled by the concentration of the component solutions. The structural density (reciprocal of the degree of swelling) of the particles can be influenced by the charge density of the polyelectrolytes.

First studies about the effect of salt[19,20] were mainly focused on the response of PECs formed in pure water to the addition of salt and showed a very individual behavior from dissolution to macroscopic flocculation, depending on the characteristics of the used polyelectrolytes. PEC formation at higher ionic strength led to an increasing level of aggregation.

The effect of salt on the course of PEC formation can hardly be predicted, because different processes may play an important role. To elucidate the general tendencies of the influence of salt on PEC formation, we studied this process by static light scattering as a function of the ionic strength of the medium, the molar mixing ratio X of the component solutions and the order of mixing, varying the nature of the ionic groups and the charge density of the polyelectrolytes. The molar mixing ratio X is defined as the ratio of the added charged groups to the oppositely charged ones in the starting solution, i.e., cationic to anionic ones or vice versa corresponding to the order of mixing.

Experimental Section

Materials. To study the effect of the nature of the ionic group, a laboratory-made, narrowly distributed sodium poly(styrenesulfonate) (NaPSS: $M_w = 66\,000$ g/mol, $M_w/M_n < 1.1$) and a sodium poly(methacrylate) from Polymer Standard Service (Mainz, Germany) (NaPMA: $M_p = 114\,000$ g/mol, $M_w/M_n = 1.02$) were used. As polycations we employed poly(diallyldimethylammonium chloride) (PDADMAC: $M_w = 250\,000$ g/mol, $M_w/M_n = 1.6$) and a copolymer of DADMAC and acrylamide with 47 mol % DADMAC (COP 47: $M_w = 1.4 \times 10^6$ g/mol, $M_w/M_n = 2.6$).[21] All samples were thoroughly dialyzed and freeze dried. Because of the temporal varying water content of the polyelectrolytes the concentration of solutions was carefully checked by UV−vis spectroscopy for NaPSS and by potentiometric chloride titration for the poly-

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cations. The water content of NaPMA was determined directly before the preparation of the solutions.

Deionized water or sodium chloride solutions of different ionic strengths were used as solvents.

Method of Investigation. To check the influence of several parameters on the course of PEC formation, we restricted our studies to static light scattering measurements. This method provides information about the particle mass and size as well as for larger particles ($R_G > 100$ nm) about the structure type, polydispersity, and structural density.

Instrument and Preparation Conditions. Light scattering experiments were carried out with a Sofica 42000 instrument (Wippler and Scheibling, Strasbourg, France), which was equipped with a 5 mW He−Ne laser as light source and a PC for data recording. The accuracy of the measurements was better than 1%, a necessary precondition for a detailed analysis of the scattering curves.

PEC formations were performed under comparable conditions directly in the scattering cell. In each case 10 mL of one component of a monomolar concentration of 2.43×10^{-4} mol/L (corresponds for NaPSS to a mass concentration of 5×10^{-5} g/mL) was put into the cell and 5 mL of the counterpart solution of twice of the molar concentration were added in steps of about 0.5 mL. The dosage was carried out continuously with a slow rate of 4 mL/h under gentle stirring at 22 °C. Solutions were made dustfree by filtration through 0.65, 0.45, or 0.2 μm membrane filters of cellulose nitrate (Sartorius, Germany). The scattering curves were recorded after each step of dosage, i.e., at different molar mixing ratios X.

The concentrations and refractive index increments of the PECs were calculated assuming a 1:1 stoichiometry and using the values of the components, determined by a differential refractometer (Brice-Phoenix, England).

Analysis of Light Scattering Data. For highly diluted systems of compact particles interparticular interferences can be neglected and the Rayleigh ratio $R(q)$ of the scattering intensity is given by the simple expression:

$$R(q) = KcM_w P_z(q) \tag{1}$$

where K is a contrast factor, containing the optical parameters of the system, c is the mass concentration in g/mL, M_w is the weight average of the molecular mass of the scattering particles, $P_z(q)$ is the z-average of the intraparticular scattering function, $q = (4\pi/\lambda) \sin \theta/2$, λ is the wavelength in the medium, θ is the scattering angle between the incident and the scattered beam. Describing the polydispersity of the particle system by a continuous normalized mass distribution function $p_w(M)$, one obtains:

$$M_w = \int_0^\infty M p_w(M)\, dM \tag{2}$$

and

$$P_z(q) = (1/M_w) \int_0^\infty P(q,M)\, M p_w(M)\, dM \tag{3}$$

In the framework of the Rayleigh−Debye approximation (RDA) the relation

$$P_z(q) = 1 - (1/3)\langle S^2\rangle_z\, q^2 + ... \tag{4}$$

was derived, whatever the shape and the structure of the particles, where $\langle S^2\rangle_z$ is the z-average of the square of the radius of gyration.

For particles with $R_G = \langle S^2\rangle_z^{1/2} < 50$ nm the scattering curves can be analyzed by a Zimm ($Kc/R(q)$ versus q^2) or Guinier (ln $R(q)/Kc$ versus q^2) plot, providing by extrapolation to the scattering angle zero M_w and R_G without any assumptions. However, no conclusions can be drawn from the scattering curve about the structure and polydispersity of the particle system. With increasing particle size the scattering curves become more instructive, but the stronger angular dependence causes problems in the extrapolation procedure. Recently, we derived an improved algorithm, based on a comparison of the experimental scattering curves with theoretically calculated ones for various structure types in a scaled double logarithmic plot.[22,23] In such plots changes in particle mass and size correspond to axis parallel shifts. If the scattering particles are large enough (radius > 100 nm), the structure type can be recognized by the shape of the scattering function.[23] Assuming the structure type, even the polydispersity of the particle system can be estimated, because increasing polydispersities cause a flattening of the scattering functions. Therefore, the described technique provides information about the structure type, polydispersity, particle mass and size as well as the structure density.

In the following we restrict our considerations to the model of polydisperse systems of homogeneous spheres, which has been proved quite well in describing the scattering curves of the PEC solutions investigated. Electron microscopic studies[17] on the PECs between NaPSS and PDADMAC confirmed the spherical shape of the complex particles as well as the high polydispersity found by static light scattering. However, one should be aware that deviations from the spherical shape and decaying density profiles result in similar effects as the polydispersity,[24] but they play a marginal role in the studied complex systems. Complex formation leads to a collapse of the coil structure of the polyelectrolyte chains. The PEC particles consist of highly densely packed cores, which are surrounded by polyions of the excess component but yield the dominating contribution to light scattering.

As distribution function we used a special logarithmic distribution of radii with the size parameter a_m and the polydispersity σ

$$p_w(a) = \frac{a^{-5/2} \exp[-(\ln a - \ln a_m)^2/2\sigma^2]}{\sqrt{2\pi}\sigma {a_m}^{-3/2} \exp[9\sigma^2/8]} \tag{5}$$

which manages that M_w becomes independent of σ

$$M_w = (4\pi/3)\rho N_A {a_m}^3 \tag{6}$$

where N_A is Avogadro's number and ρ is the average polymer density in the particle.

The radius of gyration is given by

$$\langle S^2\rangle_z = \frac{3}{5}\, {a_m}^2 e^{5\sigma^2} \tag{7}$$

The parameter σ corresponds for low polydispersities to the relative standard deviation. The choice of the type of distribution function is of minor importance.[23]

The intraparticular scattering function of spheres with the radius a is given as[25]

$$P(q) = \left(3\, \frac{\sin aq - aq \cos aq}{a^3 q^3}\right)^2 \tag{8}$$

From the assignment of an experimental curve to an appropriate theoretical one the polydispersity can be estimated and the position of the experimental on the fitting curve yields M_w and a_m as well as ρ according to eq 6.

Results

Reliability of Interpretation of Scattering Curves. The accuracy of the fitting procedure is demonstrated in Figure 1 by the scattering curves of two complexes (NaPSS/PDADMAC and NaPSS/COP 47 in pure water at a mixing ratio $X = 0.5$). The experimental curves could be fitted quite well by theoretical scattering curves of polydisperse systems of spheres. The main advantage consists in the fact that all measured points were used to recognize the appropriate theoretical curve and to determine the structural parameters, which are given in Table 1. While the values of the z-average of the radius of gyration differ by a factor 2, the radii a_m, corrected with regard to the

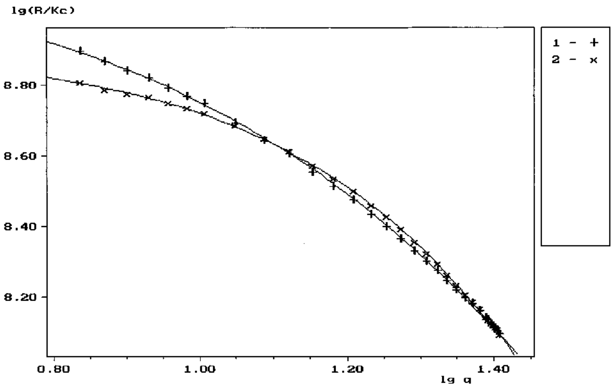

Figure 1. Scattering curves of the PECs NaPSS/PDADMAC (1) and NaPSS/COP 47 (2) in pure water at a mixing ratio $X = 0.5$. Scaled double logarithmic plot: crosses, experimental points; full lines, theoretical curves, corresponding to the parameters given in Table 1.

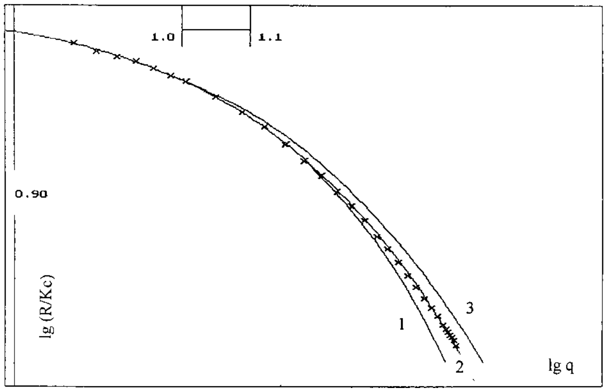

Figure 2. Scattering curve of the PEC NaPSS/COP 47 in water at $X = 0.5$ (crosses) and theoretical curves for $\sigma = 0.35$ (1), $\sigma = 0.4$ (2), and $\sigma = 0.45$ (3).

Table 1. Structural Parameters of the Complexes NaPSS/PDAMAC and NaPSS/COP 47 in Pure Water at a Molar Mixing Ratio $X = 0.5$

PEC	σ	$10^{-8}M_w$ (g/mol)	a_m (nm)	R_G (nm)	ρ (g/mL)
NaPSS/PDADMAC	0.65	12.6	100	224	0.49
NaPSS/COP 47	0.40	7.78	99	115	0.32

polydispersity, are nearly the same. Ignoring the polydispersity would lead for the first complex to a structural density that is wrong by nearly an order of magnitude. The reliability of the estimation of the polydispersity is illustrated in Figure 2.

PECs between NaPSS and PDADMAC. The dependence of the particle mass M_w and size R_G of complexes between NaPSS and PDADMAC and vice versa on the mixing ratio X is represented in Figure 3 at different ionic strengths. The course of PEC formation is very similar for the systems NaPSS/PDADMAC and PDADMAC/NaPSS (the first indicates the starting solution). In pure water a very high level of aggregation with more than 1000 chains per complex particle was reached. The particle mass decreased slightly with increasing mixing ratio as has already been observed in ref 16. At the 1:1 mixing ratio macroscopic flocculation occurred. The last point in the X-dependence of all systems corresponds to the last measurable scattering curve before the flocculation. In the initial range the radius of gyration decreased much stronger than the mass, but this corresponds mainly to a change in the polydispersity and not in the structural density ρ, which increases slightly, as shown in Figure 4. The values of ρ are very high, revealing the compact structure of the PECs.

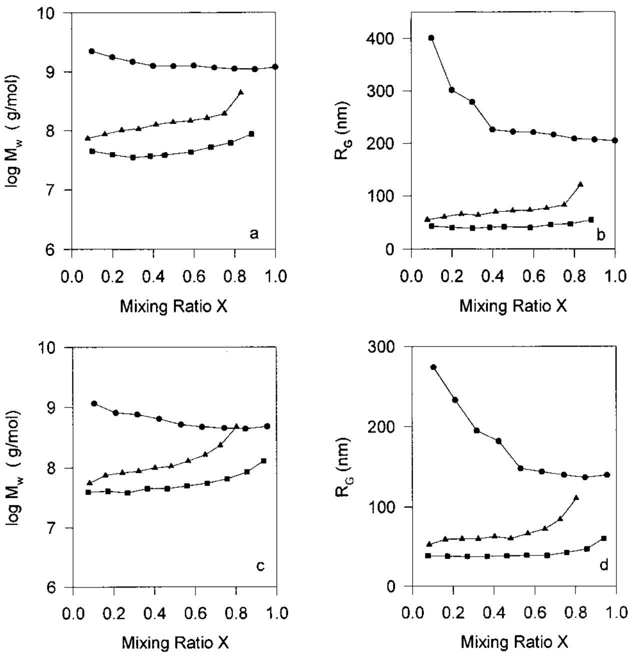

Figure 3. Particle mass M_w and size R_G of the complexes NaPSS/PDADMAC (a, b) and PDADMAC/NaPSS (c, d) as function of mixing ratio X at different ionic strengths: pure water (●), $I = 1 \times 10^{-2}$ mol/L (■), $I = 1 \times 10^{-1}$ mol/L (▲).

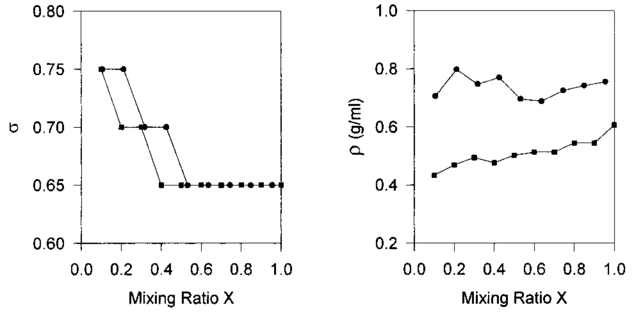

Figure 4. Polydispersity σ and structural density ρ of the complexes NaPSS/PDADMAC (●) and PDADMAC/NaPSS (■) in water as function of X.

Complex formation in NaCl solution of an ionic strength of 1×10^{-2} mol/L yielded a significantly lower level of aggregation (factor 30). The particle mass increased with rising mixing ratio and macroscopic flocculation occurred somewhat earlier. The change of R_G corresponds fully to the behavior of M_w. Because of the small size of the PEC particles, the scattering curves could not be analyzed in more detail.

In 0.1 *m* NaCl the level of aggregation was again higher and increased with rising mixing ratiol flocculation occurred at $X = 0.8$.

PECs between NaPSS and COP 47. To judge the influence of charge density of a polyelectrolyte on the course of PEC formation, we studied the systems NaPSS/COP 47 and COP 47/NaPSS. The results are shown in Figure 5. In pure water the course of complex formation corresponds largely to the complex formation with PDADMAC. Particle mass and size decreased marginally with rising X; flocculation occurred close to the 1:1 mixing ratio. PEC formation depended little on the order of mixing.

The picture changes drastically in the presence of salt. The structural parameters of the PEC particles are

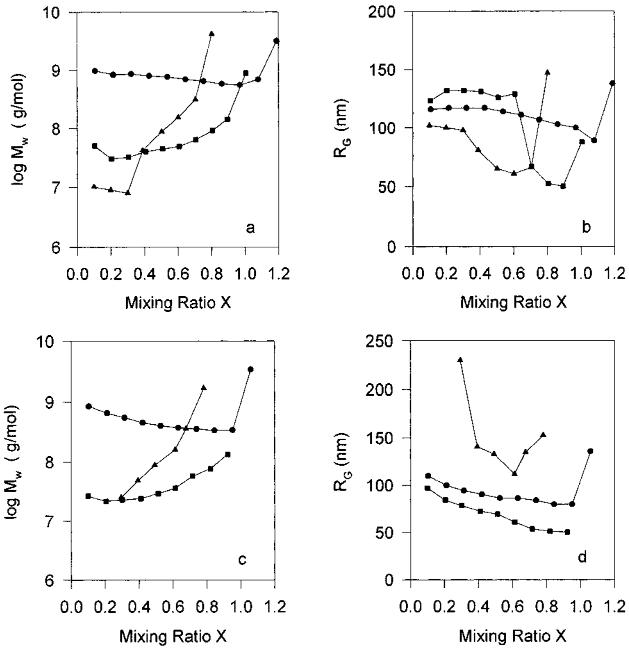

Figure 5. Particle mass M_w and size R_G of the complexes NaPSS/COP 47 (a, b) and COP 47/NaPSS (c, d) as function of mixing ratio X at different ionic strengths: pure water (●), $I = 1 \times 10^{-2}$ mol/L (■), $I = 1 \times 10^{-1}$ mol/L (▲).

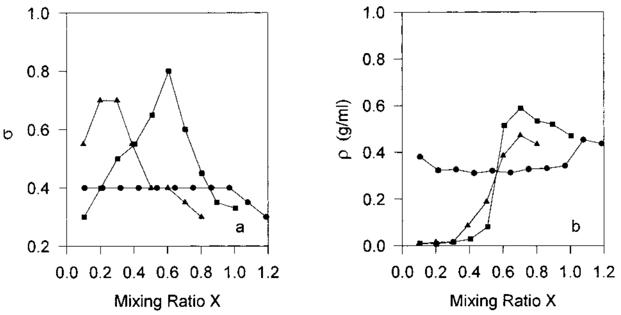

Figure 6. Polydispersity σ and structural density ρ of the complex NaPSS/COP 47 as function of X at different ionic strengths: pure water (●), $I = 1 \times 10^{-2}$ mol/L (■), $I = 1 \times 10^{-1}$ mol/L (▲).

strongly dependent on the mixing ratio. For the combination NaPSS/COP 47 the level of aggregation in 0.01 *m* NaCl solution was again remarkably lower than that in pure water, but rose strongly with increasing X, reaching the same value at high mixing ratios. The radius of gyration was relatively high up to a mixing ratio of 0.5, where it decreased rapidly, indicating a change to a more compact structure.

Similar effects took place in 0.1 *m* NaCl solutions. At low X complexes on a nearly molecular level were formed. The mass of 1×10^7 g/mol corresponds to about five chains of COP 47 in a complex particle. Above $X = 0.3$ the particle mass rose drastically and at $X = 0.8$ flocculation occurred.

A detailed analysis of the scattering curves reveals the complicated character of the structural changes (Figure 6). While all parameters of the PEC in pure water changed only slightly, the polydispersity in the salt solutions shows a maximum in the X dependence. This must be taken into account in the calculation of the density ρ. Results obtained are given in Figure 6b. Even an ionic strength of 0.01 *m* led to the formation of highly swollen particles ($\rho < 0.05$ g/mL) up to a mixing ratio of 0.5. Then the density increased sharply to values comparable to the structures in pure water.

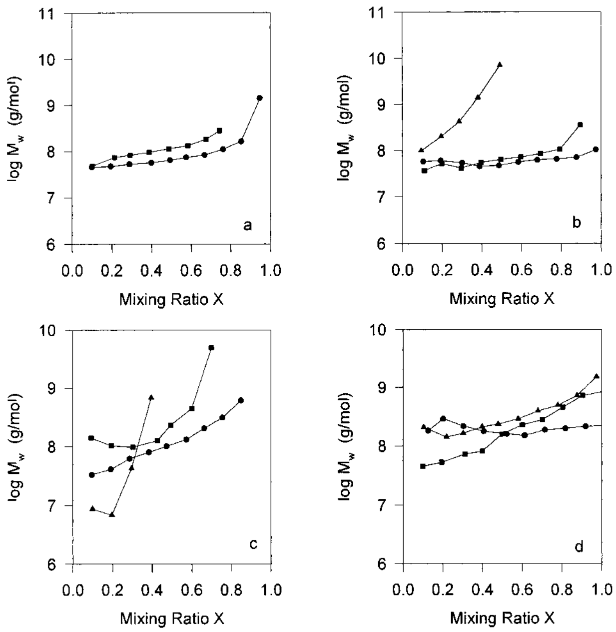

Figure 7. Particle mass M_w of the complexes NaPMA/PDADMAC (a), PDADMAC/NaPMA (b), NaPMA/COP 47 (c), and COP 47/NaPMA (d) as function of mixing ratio X at different ionic strengths: pure water (●), $I = 1 \times 10^{-2}$ mol/L (■), $I = 1 \times 10^{-1}$ mol/L (▲).

For the system COP 47/NaPSS the behavior in pure water and 0.01 *m* NaCl corresponds to a great extent to that of the previous combination. In 0.1 *m* NaCl a clearly pronounced PEC formation started at $X = 0.3$. M_w increased strongly with X, R_G went through a minimum, and the particles became more compact. Flocculation occurred again at $X = 0.8$.

PECs between NaPMA and PDADMAC or COP 47. To study the effect of the nature of the ionic group, we used the weaker polyelectrolyte NaPMA instead of NaPSS. To avoid overloading with too much detail, only the results on the change of the particle mass are given in Figure 7.

In comparison to NaPSS, complex formation of all four combinations started in pure water on a significant lower level of aggregation, but the particle mass increased with rising mixing ratio. An ionic strength of 0.01 mol/L led to a slight increase of the degree of aggregation. At $I = 0.1$ mol/L in the system NaPMA/PDADMAC macroscopic flocculation occurred after the first step and during the whole course of complex formation. With the combinations PDADMAC/NaPMA and NaPMA/COP 47 only at lower mixing ratios, stable colloidal particles were formed, followed by flocculation. However, in the system COP 47/NaPMA the presence of salt had a marginal effect on the level of aggregation at all mixing ratios.

Concentration and Salt Dependencies of the System NaPSS/PDADMAC. For the system NaPSS/PDADMAC we studied the influence of the ionic strength in more steps. Figure 8 depicts the structural parameters of the PECs at a mixing ratio $X = 0.5$. Both in the ionic strength dependence of M_w and R_G a clearly pronounced minimum occurred at $I = 5 \times 10^{-3}$ mol/L. The changes in M_w and R_G are adequate for compact spheres. The polydispersity parameter was found for all systems to be about $\sigma = 0.5$, and the structural density was near $\rho = 0.6$ g/mL. The minimum value $M_w = 2.6 \times 10^7$ g/mol is lowered by the factor 50 in comparison to the particle mass in pure water; i.e., very

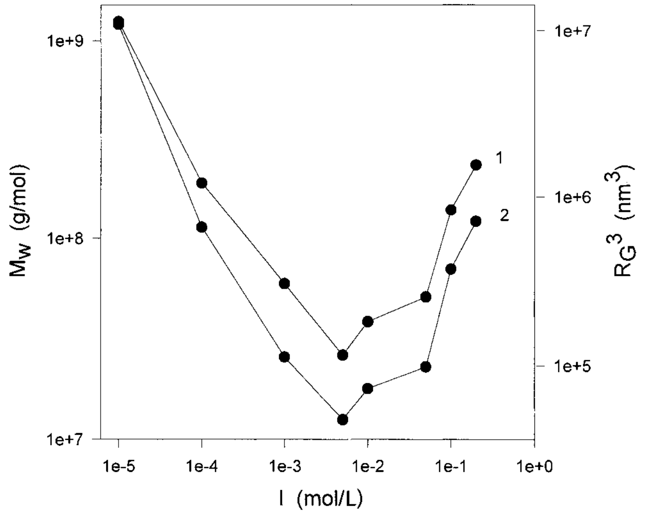

Figure 8. Particle mass M_w (1) and size R_G (2) of the complex NaPSS/PDADMAC at $X = 0.5$ as function of the ionic strength.

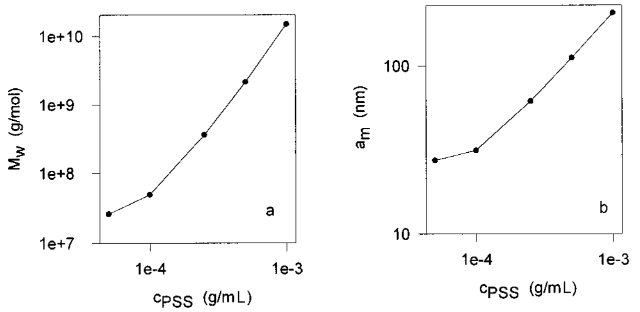

Figure 9. Particle mass M_w (a) and size R_G (b) of the complex NaPSS/PDADMAC at $X = 0.5$ and $I = 5 \times 10^{-3}$ mol/L as function of the NaPSS concentration in the starting solution.

small amounts of salt have large effects on the aggregation behavior in PEC formation.

Another possibility to vary the level of aggregation is a change of the concentration of the component solutions. PECs were prepared in 5×10^{-3} m NaCl solutions at a mixing ratio $X = 0.5$ and diluted appropriately for the light scattering measurements. Figure 9 shows the dependence of M_w and a_m on the concentration of the starting NaPSS solution. Neglecting the lowest concentration, a nearly linear increase in the double logarithmic plot was found for both M_w and a_m, corresponding to the power laws $M_w \sim c^{2.47}$ and $a_m \sim c^{0.826}$. This gives the expected relation $M_w \sim a_m{}^3$ for homogeneous spheres. However, the concentration dependencies are much stronger than the expressions obtained for the system PDADMAC/NaPSS in pure water.[16]

Discussion

In all systems investigated PEC formation is very sensitive to the presence of salt. While in deionized water very high levels of aggregation were reached, small amounts of salt decrease these levels drastically. This may be understood by the change of the polyelectrolyte conformation from a more or less stiff to a coiled structure due to the screening of the Coulomb repulsion along the charged chains. The level of aggregation of the PEC particles results from the competition of two effects in charge compensation between the oppositely charged components. The ionic binding may take place between the charged groups of two chains via conformational adaptation like a zip mechanism or by incorporation of additional polyions. For stiff chains with different charge densities (distance between two charges: NaPSS and NaPMA, $b = 0.25$ nm; PDADMAC, $b = 0.55$ nm; COP 47, $b = 0.83$ nm) charge compensation along two chains is strongly hindered. Higher chain flexibility and a more coiled structure make the conformational adaptation of chains easier, leading to a lower level of aggregation.

However, the primary particles must be stabilized against further coagulation, which is ensured by an excess binding of the major component.[17] This amount of polyelectrolyte forms an electrostatically stabilizing shell around the PEC particles. With increasing ionic strength the repulsion between the shells is screened and secondary aggregation can take place between the primary particles. The level of aggregation should increase again. This explains the occurrence of a minimum in the ionic strength dependence.

In pure water there is a slight tendency of decreasing particle mass and size with increasing mixing ratio. Two effects may be responsible for this. The amount of the major component bound in excess decreases with rising mixing ratio up to a 1:1 stoichiometry at $X = 1$. Additionally, the concentration of the free major component decreases with rising X, favoring charge compensation by conformational changes. In contrast to the findings in pure water, we observed at higher salt contents an increase of the particle mass with rising X. Since the stabilizing shells of the polyelectrolyte bound in excess are reduced with increasing X, secondary aggregation should be favored. The onset of macroscopic flocculation is expected at lower mixing ratios.

In the PEC systems with COP 47 as polycation these effects are stronger pronounced. The reason may be the quite different structure of these PECs at low mixing ratios. In contrast to the high and nearly X-independent values of the structural density of all PECs in pure water and also of the PECs with PDADMAC in salt solutions, these PECs are highly swollen up to a mixing ratio $X = 0.5$ (see Figure 6). This is obviously caused by the different charge densities of the polyelectrolyte components and the incorporation of the hydrophilic acrylamide. At higher mixing ratios the particles collapsed and secondary aggregation occurred.

The nature of the ionic group has also a great influence on the PEC formation. Using NaPMA as polyanion, we found in pure water a significantly lower level of aggregation. This can be understood by the weaker ionic binding between the cations and the carboxylic groups in comparison to sulfonate groups. Probably, complex formation may be partly reversible and sterically unfavorable bonds can be removed, enabling a better mutual arrangement of the oppositely charged chains. The main effect of salt consists in the secondary aggregation. An exception is the system COP 47/NaPMA, where the presence of salt affected the complex formation much less. The stabilizing shell of COP 47 with the hydrophilic acrylamide may suppress the secondary aggregation.

Finally, the concentration dependence of the aggregation level of the system NaPSS/PDADMAC will be discussed. The balance between the charge compensation processes via conformational changes and the incorporation of additional polyions depends strongly on the concentration of the component solutions. Higher concentrations favor the second process. In comparison to the complex formation in pure water the first one dominates in 5×10^{-3} mol/L NaCl solution and the balance becomes more sensitive to the polyelectrolyte concentration, causing a stronger concentration dependence of the particle mass and size of the PECs.

Conclusions

Static light scattering studies revealed a great influence of the presence of NaCl during PEC formation. At low ionic strength the main effect consists in a drastic reduction of the level of aggregation, offering an additional possibility, beside the variation of the polyelectrolyte concentration, to control mass and size of the PEC particles. In most systems the internal structure of the PECs is marginally affected by salt.

Higher ionic strengths cause secondary aggregation and macroscopic flocculation at mixing ratios below 1:1, probably due to the screening of the electrostatically stabilizing shell of the major component around the PEC particles.

A prediction of the effects of the presence of salt during complex formation is very difficult, because of the complicated processes of structure formation in an interplay with the specific characteristics of the polyelectrolyte components.

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