Characterization of PSS/PDADMAC-*co*-AA Polyelectrolyte Complexes and Their Stoichiometry Using Analytical Ultracentrifugation

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ABSTRACT: Analytical ultracentrifugation was successfully applied to the determination of the complex composition and characterization of the particles of water insoluble polyelectrolyte complexes between sodium poly(styrenesulfonate) (PSS) and copolymers of various ratios of diallyldimetylammonium chloride (DADMAC) and acrylamide (AA). Sedimentation velocity experiments in an analytical ultracentrifuge with absorption optics allow the observation of individual species in a system of strongly polydisperse, aggregated particles of colloidal level in the presence of free polymer. It was found that the complexes are remarkably polydisperse and form nonstoichiometric particles including the major component in considerable excess. The stoichiometry factor depends strongly on the ionic strength of the solution and the concentration of the components. At low initial mixing ratios and ionic strengths of about $10^{-2}-10^{-3}$ N, sedimentation equilibrium experiments can be performed. The results of the evaluation of free PSS and complex concentration gradients using the Ω-function are similar to the findings obtained with sedimentation velocity experiments. A model where secondary aggregates are surrounded by free polymers is discussed for the sedimentation of these particles. It is demonstrated that polyelectrolyte complexes with the copolymer containing 50% DADMAC and AA form comparatively monodisperse species in aqueous salt solution having sedimentation coefficients between 4 and 40 Sv.

1. Introduction

Polyelectrolyte complexes (PECs) between strong polyelectrolytes in aqueous solutions have been under study for more than 30 years,[1,2] but as these complexes are not really water soluble and tend to aggregate strongly, it is difficult to characterize the properties of these particles. Nevertheless, such characterization appears to be very important, because PECs are likely to be a source of new materials.[3] PECs have various applications as materials for membranes with useful controlled permeabilities as well as drug and enzyme carriers. The study of the stability of these systems is shown to be particularly important due to the possible use as coacervates of proteins, bacteria, and other biological objects.[4]

In highly dilute solutions PEC formation leads to quasi-soluble particles on a colloidal level, which have been carefully investigated by static light scattering (SLS), dynamic light scattering, potentiometry, and viscometry for the system sodium poly(styrenesulfonate) (PSS)/poly(diallyldimethylammonium chloride-*co*-acrylamide) (PDADMAC-*co*-AA).[5,6] The stoichiometry of PEC particles was determined using viscometry, UV spectroscopy, and potentiometric titration, while their structural parameters were characterized by SLS applying an improved algorithm of extrapolation and a fit procedure to model the scattering curves.[7] It was shown that complex formation between PSS and PDADMAC copolymers results in highly aggregated PEC particles (with aggregation numbers of the order of 10^3). The minor component is usually completely included in the complex (which was proved by the release of the corresponding low-molecular ions). Moreover, according to viscometry data, the major component is included in excess in PEC particles.

It should be noted that UV spectroscopy and potentiometric titration indicate only the amount of ion binding between the charged sites of the polyelectrolytes. But the insoluble PECs form associates of complex structure, being amphiphilic and nonstoichiometric (Figure 1).

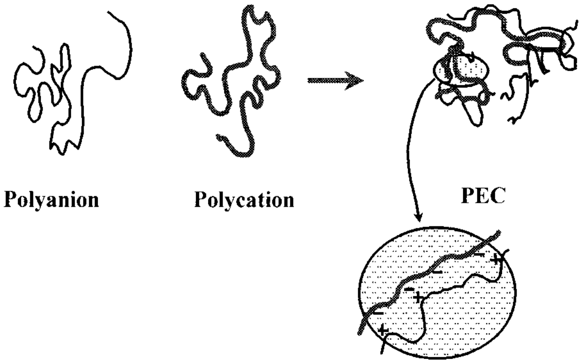

Figure 1. Schematic representation of the polyelectrolyte complex formation process.

Viscometry is not a direct method to determine the stoichiometry of PEC particles, because it applies model considerations, treating these particles as a suspension of noninteracting spheres with structural densities derived from the viscosity at the 1:1 mixing ratio. On the other hand, earlier preparative ultracentrifugation (UC) has been successfully applied to the determination of the complex composition of PECs between poly(methacrylic acid) and poly(vinylethylpyridinium) and for another pair of polyelectrolytes.[8,9] The composition of these complexes was determined via the ratio of polymer concentration in supernatant to that in the initial solution. Moreover analytical ultracentrifugation (AUC) is to our knowledge the only method that allows examination of the ratio between free polymer and polymer included in PEC for such systems directly, because of the fractionation of the species. At first we consider the case in which one polymer absorbs in the UV range, where it is possible to monitor this component using absorbance optics. This is applied to the system

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Table 1. Molecular Characteristics of Samples Employed in PEC Formation

polyanion[a]	$10^{-3}M_p$ (g/mol)[b]	M_w/M_n	$s_{20,w}$ (Sv)[c]
PSS-8T	8	<1.1	0.65 ± 0.02
PSS-46T	46	<1.1	1.69 ± 0.07
PSS-66T	66	<1.1	1.87 ± 0.12
PSS-183T	186	<1.1	3.65 ± 0.15
PSS-356T	356	<1.1	5.75 ± 0.2

polycation[d]	$10^{-3}M_w$ (g/mol)[e]	M_w/M_n[f]	charge distance (nm)
PDADMAC	2.5	1.6	0.55
PDADMAC-*co*-AA-73	5.8	2.1	0.64
PDADMAC-*co*-AA-47	14	5.4	0.83
PDADMAC-*co*-AA-35	23	4.9	1.01
PDADMAC-*co*-AA-21	39	5.3	1.49
PDADMAC-*co*-AA-8	42	5.9	3.43

[a] Sodium salt, charge distance is 0.25 nm. [b] Determined by gel permeation chromatography. [c] Determined at 60 000 rpm in 0.001 N NaCl solution. [d] PDADMAC-*co*-AA-X, *X* is mol % of DADMAC. [e] Determined by SLS. [f] Determined by osmometry.

PSS/PDADMAC-*co*-AA, which has already been investigated using the methods mentioned above.

2. Experimental Section

2.1. Materials. As polyanions, commercial sodium poly(styrenesulfonate) standards from Polymer Standard Service (Mainz, Germany) were used.

Poly(diallyldimethylammonium chloride) and its copolymers with acrylamide synthesized earlier by radical polymerization[10] were employed as polycations. The molecular characteristics of the materials are given in Table 1. The PDADMAC-*co*-AA samples have broad molar mass distributions because of very different copolymerization parameters of the monomers.

All polymers were thoroughly dialyzed and freeze-dried. As solvent, deionized water and NaCl solutions of various concentrations were employed. All solutions were filtered through 3 μm membrane filters, then the concentrations were checked by UV spectroscopy in the case of PSS and potentiometric titration in the case of PDADMAC-*co*-AA.

PECs were prepared by dropwise addition of the proper amounts of the polycation solution to the solution of the polyanion (PSS was always used as major component) under continuous stirring. Usually concentrations of 2×10^{-4} monomol/L for both polymers were employed. The initial molar mixing ratio *X* was set as the ratio of repeating charged monomer units of PDADMAC to PSS. Thirty minutes after mixing, the samples were subjected to AUC at various speeds at 25 °C.

2.2. Methods. For AUC experiments, the Beckman Optima XL-I ultracentrifuge (Beckman, Spinco Division, Palo Alto, CA) equipped with an integrated Rayleigh interference and UV absorption optics (190–800 nm, ±2 nm) was applied.

In sedimentation velocity experiments 400 μL of every solution was subjected to centrifugation in 12 mm double sector cells at speeds between 1100 and 60 000 rpm. Sedimentation coefficients were not corrected to standard conditions due to the wide but unknown density distribution of PEC particles.

In sedimentation equilibrium experiments 150 μL of the PEC solutions was subjected to centrifugation at 1300 and 1400 rpm for 36 h to obtain the equilibrium concentration distribution. A novel interactive version of the routine MSTAR[11] was used for the Ω analysis of the equilibrium patterns.

All sedimentograms were recorded with UV optics with water as reference, at 25 °C (at 225 nm in sedimentation velocity and at 235 nm in sedimentation equilibrium experiments). If not explicitly stated, the sedimentation coefficients refer to 25 °C in the salt solution used.

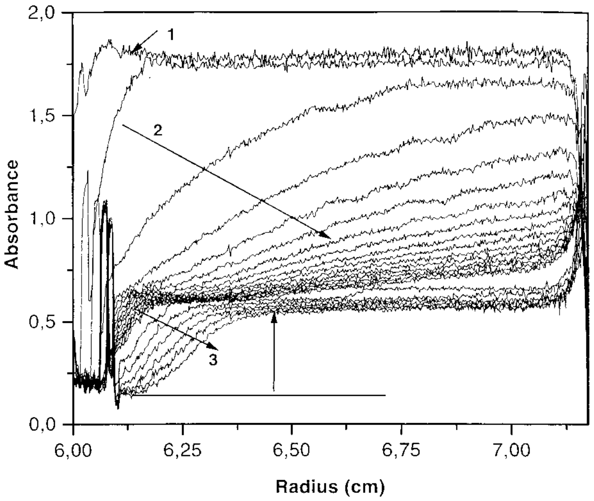

Figure 2. Sedimentation pattern for complex PSS-66T/PDADMAC with initial composition $X = 0.4$ in deionized water (1, at 1100 rpm; 2, at 20 000 rpm; 3, at 40 000 rpm; scan interval is 10 min). Absorbance values (curve 1, 1.74; upper plateau of curve 3, 0.58) permit determination of the stoichiometry of the system.

3. Results

3.1. Sedimentation Velocity Studies: PEC Stoichiometry. Figure 2 shows a typical sedimentation pattern for a PEC of PSS/PDADMAC (initial molar mixing ratio is $X = 0.4$). It can be seen from the very broad concentration profile without a distinct step (curve 2) that PECs are strongly polydisperse colloidal particles, which sediment completely at 40 000 rpm. The species which sediments slowly at 40 000 rpm is free PSS (sedimentation coefficient $s_{25,W} = 1.8$ Sv). From the sedimentogram it is possible to determine the concentration of free PSS in the system using the plateau absorption (after subtracting the base line). The absorption reading of the plateau region of PSS was taken before considerable sedimentation of free PSS has taken place to minimize errors due to radial dilution. The characteristic molar absorption coefficient for PSS was found to be 1.0×10^4 mol^{-1} L cm^{-1}.

3.1.1. Effect of the Mixing Ratio and Ionic Strength. Figure 3a demonstrates results of measurements for the complexes prepared at various mixing ratios in water and NaCl solutions. Curve 5 represents the calculated dependence of the concentration of free PSS on mixing ratio *X* assuming a molar 1:1 stoichiometry of the components in the complex

$$C_{\mathrm{PSS}}^{\mathrm{free}} = \frac{(C_0 - C_0X)V_0}{V(X)}$$

where C_0 and V_0 are the initial concentration and volume of PSS solution, respectively, and *V* is the volume of the complex solution after addition of the polycation. While 1:1 stoichiometry of ionic binding was suggested by the results of potentiometric and spectroscopic measurements,[6,10] AUC experiments (Figure 3) revealed a remarkably higher consumption of PSS for all systems investigated; i.e., the polycations bind considerably more PSS molecules than should be included by ionic binding sites. This can be understood by an excess of partly bound PSS chains on the surface of the PEC particles.

The relationship of the molar concentrations of free PSS ($C_{\mathrm{PSS}}^{\mathrm{free}}$) to the initial one ($C_0$) provides the stoichiometric factor (*f*) for the PEC particles

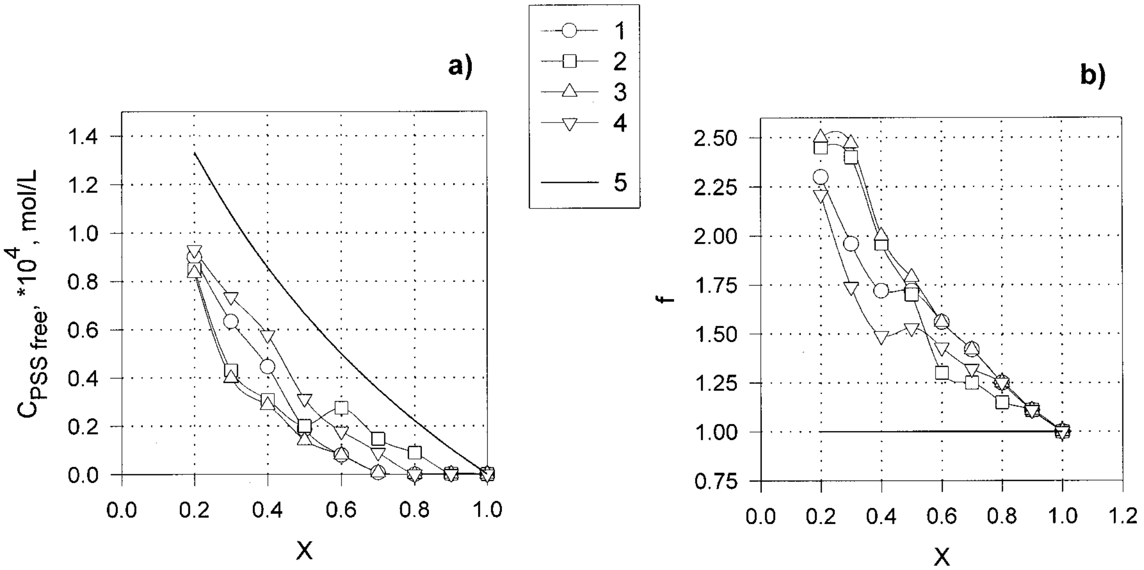

Figure 3. Concentration of the free PSS (PSS-66T) after formation of the complex (a) and stoichiometry factors (b) (from AUC data): PSS-66T/PDADMAC (1) water, (2) 0.01 N NaCl, (3) 0.1 N NaCl; PSS/PDADMAC-*co*-AA-47, water (4); (5) calculated dependence for a 1:1 stoichiometry.

$$f = \frac{C_0 - C_{\mathrm{PSS}}{}^{\mathrm{free}}\dfrac{V}{V_0}}{C_0 X}$$

where the factor V/V_0 corrects the dilution by addition of the cationic solution. This parameter was used earlier in the characterization of the structure of PEC particles.[6,10] Since AUC is a relatively simple method to determine the stoichiometry factor for PEC particles, it was possible to investigate the influence of different factors on this parameter.

As it is easy to see from the Figure 3b, the stoichiometric factors depend strongly on the initial molar mixing ratio of the systems: they are considerably high at low mixing ratios and arrive to 1 at 1:1 mixing ratios. All curves in Figure 3a show that already below $X = 1$ the supernatant does not contain free PSS. Because of the findings by potentiometry, UV–vis spectroscopy, and light scattering[6] that complex formation takes place proportional to the added polycation solution nearly up to the 1:1 mixing ratio, we have to conclude that at higher X the PSS bound in excess must be detached by the polycations from the surfaces of the PEC particles, forming new ones. Otherwise, coagulation should occur because of a bridging of the PEC particles by the further added polycations, which could not be observed by light scattering.

Here it should be mentioned that the use of absorption optics gives a strong restriction on the concentration range of the PSS containing solution, because precise concentration determination with AUC is possible at the maximum of the characteristic absorbance only (accuracy of the UV optics ±2 nm). In the available concentration range the values of *f* change only slightly.

The addition of low molecular salt leads to an aggregation of the particles and phase separation. At a critical salt concentration (about 0.05 N) the gyration radii of the particles grow drastically and the biggest part of the PECs precipitates as white flakes.[12,13] The stoichiometric measurements could be carried out only up to an ionic strength of 0.2 N, because at higher ionic strength macrophase separation occurs and all PSS flocculates together with the complex. For the complex PSS-66T/PDADMAC at lower mixing ratios *f* increases with rising ionic strength (Figure 3b). The results about the influence of ionic strength on the stoichiometry of the complex PSS/PDADMAC-*co*-AA-47 at fixed initial composition $u = 0.4$ are presented in Figure 4. In this case a pronounced minimum at low salt concentration was found for the stoichiometric factors.

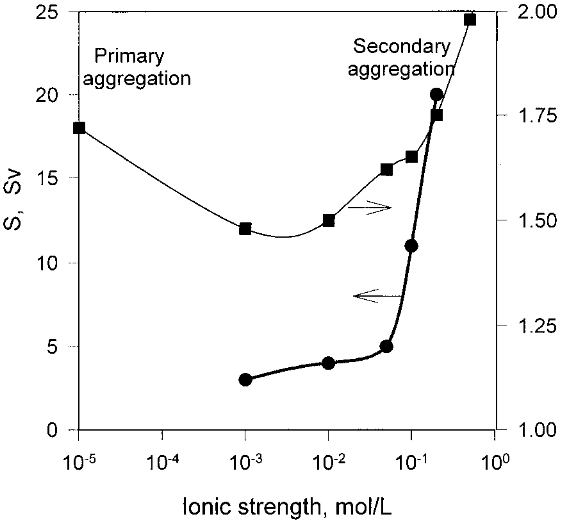

Figure 4. Dependencies of sedimentation coefficients (●) and stoichiometry factors (■) on ionic strength of the solution for PSS-66T/PDADMAC-*co*-AA-47 complexes with initial molar mixing ratio $X = 0.4$.

3.1.2. Effect of Molecular Mass and Copolymer Composition. The data about the influence of the nature of the PEC components are shown in Figure 5 (all measurements were performed at an initial component concentration of 2×10^{-4} mol/l and 0.1 N NaCl, where one can exactly distinguish PEC and free PSS patterns). One can see that the stoichiometric factors are in marginal dependence on the copolymer composition (Figure 5a) while the molar mass of PSS effects the PEC stoichiometry stronger (Figure 5b): *f* values increase at complexation with higher molecular PSS.

3.2. Sedimentation Velocity Studies: Sedimentation Coefficients. Earlier it was believed that insoluble complexes are so polydisperse that it is impossible to obtain their sedimentation coefficient.[2] One

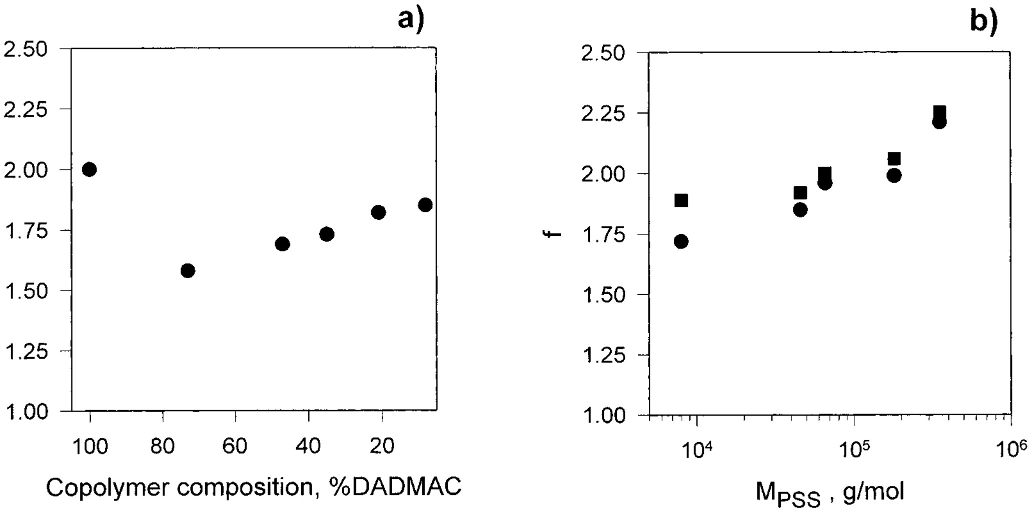

Figure 5. Stoichiometry factor for PSS-66T/PDADMAC PECs with molar mixing ratio $X = 0.4$ in 0.1 N NaCl in dependence on the polycation composition (polyanion PSS-66t) (a) and molecular mass of the polyanion (polycation, PDADMAC; (●) at $I = 0.01$ N; (■) at $I = 0.1$ N) (b).

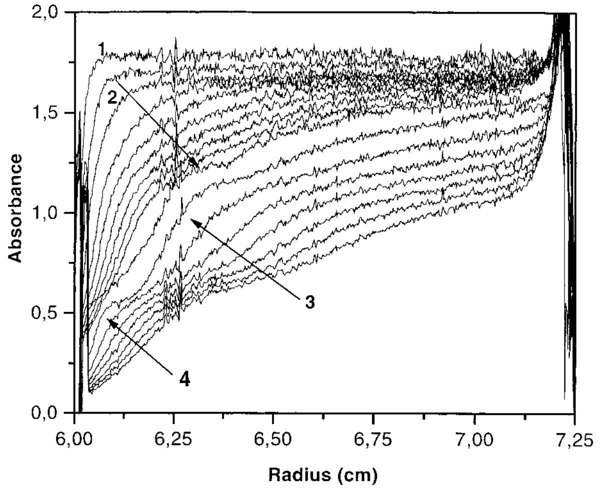

Figure 6. Sedimentation patterns for PECs of PSS-66T/PDADMAC-*co*-AA-47 in 0.01 N NaCl at (1) 1100 rpm, (2) 20 000 rpm, (3) 40 000 rpm ($s = 7.4$ Sv), and (4) sedimentation of free PSS.

could expect that it is possible "to improve" the complex solubility by hydrophilization of one polymer. Copolymerization of DADMAC with AA is a way to do this. For the complexes PSS/PDADMAC-*co*-AA some regimes exist, where under partial phase separation, their soluble part is quasi-monodisperse. To suppress the polyelectrolyte effect, the salt concentration must exceed 10^{-3} N, but it should be below 0.2 N to avoid the risk of complete precipitation in the system.

Figure 6 shows a typical sedimentogram for a PEC between PSS and PDADMAC-*co*-AA (47% DADMAC sites) with initial composition $X = 0.4$ in aqueous 0.01 N NaCl solution. One can see that in contrast to the behavior in deionized water (Figure 2), formation of the complex in salt solution leads to much more defined, relatively "monodisperse" particles with a sedimentation coefficient $s = 7.4$ Sv (calculated from patterns 1 and 2), whereas PSS sediments with $s = 2.0$ Sv (pattern 3).

Figure 7 shows the sedimentation coefficients of PSS/PDADMAC-*co*-AA-47 complexes in relation to the molecular mass of PSS and the initial molar mixing ratios. The s values increase with rising molecular weight of the polyanion (Figure 7a). The sedimentation coefficients are in critical dependence on the initial mixing ratio, near $X = 0.5$ they increase drastically (Figure 7b). This point corresponds to complete inclusion of PSS in the PEC particles. It should be mentioned that at this point a structural transition from highly swollen to very dense particles was detected by SLS. Analogous sedimentograms can also be obtained for PEC in 0.1 N NaCl solution, where precipitation occurs. But the soluble fraction has a somewhat higher sedimentation coefficient of about 10. Further increase of the ionic strength leads to high values of s and then to complete phase separation (see Figure 4).

3.3. Sedimentation Equilibrium Measurements. In very dilute low-molecular salt solutions insoluble PECs form fractions, which are relatively monodisperse and have sedimentation coefficients comparable to those of free PSS. This fact is in very good agreement with the data obtained from SLS measurements for PSS/PDADMAC-*co*-AA complexes formed in NaCl solutions of various concentrations.[14] It was observed that, for example, the aggregation number of PECs prepared in 0.01 N salt medium is lower by a factor 50 than that in the "salt-free" regime. For such particles it is possible to obtain sedimentation equilibrium patterns (if a system contains species that are too large, the speed necessary for a sedimentation equilibrium experiment would be lower than 1000 rpm, the minimum speed of the ultracentrifuge) and to apply the Ω analysis.

3.3.1. Principle of Ω Analysis. This method permits a separation of the contributions of the components in any interacting system in sedimentation equilibrium and a calculation of the concentration profile of each species in the mixture:

$$A_1 + ... + A_i + ... \underset{K_1}{\overset{K_2}{\rightleftharpoons}} P_1 + ... + P_i + ...$$

One can separate all known components, using the Ω function, defined as

$$\Omega(r) = \frac{A(r)}{A(r_F)} \exp(\phi_i M_i (r_F{}^2 - r^2))$$

where

$$\phi_i = \frac{(1 - \bar{v}_i \rho_0)\omega^2}{2RT}$$

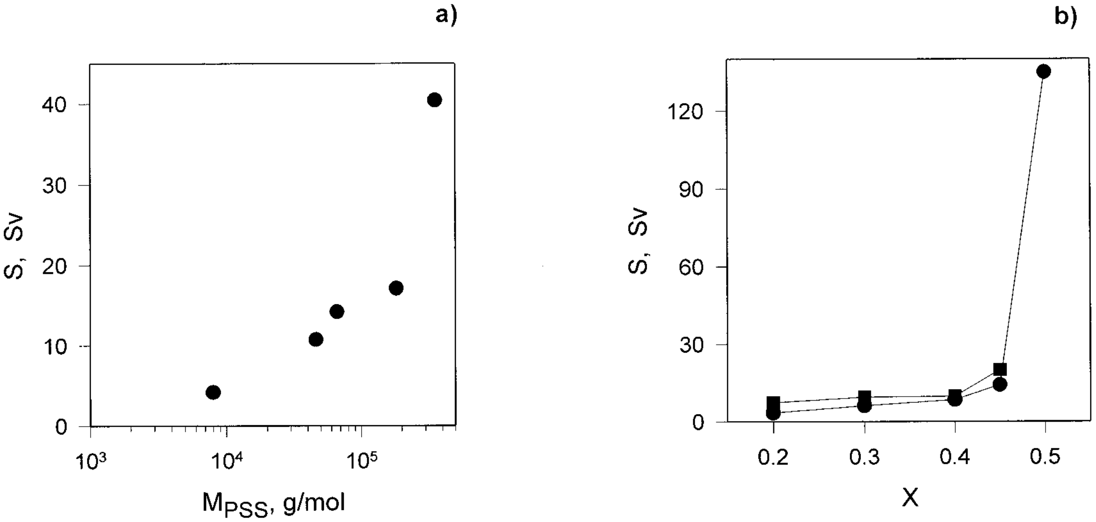

Figure 7. Dependence of sedimentation coefficients of PECs PSS/PDADMAC-*co*-AA-47 on molecular mass of PSS at 0.01 N NaCl (a) and on initial molar mixing ratio (PSS-66t, (●) at $I = 0.01$ N; (■) at $I = 0.1$ N) (b) (component concentration is 2×10^{-4} monomol/L).

and $A(r)$ is the absorbance at radial distance r, r_F is the selected fixed radial distance, $\bar{v}_i$ is the partial specific volume of the ith species, M_i is its molecular weight, T is the temperature, and ω is the angular velocity of centrifugation. First one calculates the Ω function for the smallest sedimenting species that provides by extrapolation to $C = 0$ the gradient of its activity (or concentration in assumption of thermodynamic ideality) at the complete dilution limit. The concentration can be expressed in absorbance units:

$$\lim_{A(r)\to 0} \Omega_i(r) = \frac{A_i(r_F)}{A(r_F)} \Rightarrow A_i(r) = A_i(r_F) \exp(\phi_i M_i(r^2 - r_F{}^2))$$

This procedure must be repeated for the following components. From the concentration gradients of the individual components, it is possible to calculate the reaction constants K_1 and K_2. This method does not include any fits or assumptions about the system and is applicable to any interacting system, which yields an exponential equilibrium pattern. The details of the Ω analysis and the MSTAR routine are described in refs 11 and 15.

3.3.2. PEC Stoichiometry as a Function of Initial Molar Mixing Ratio. Using the Ω analysis we have determined the total concentration distribution of free PSS (in absorbance units) in the system PSS-66T/PDADMAC in 0.01 N NaCl, suppressing the high nonideality of polyelectrolyte solutions by the salt. The values of $M = 66\,000$ g/mol and $\bar{v} = 0.525$ mL/g (from Anton-Paar precision density meter measurements) were used. PDADMAC was considered as non-absorbing species. The ratio between the concentration of free PSS and its initial concentration provides the stoichiometry factors in the system.

A typical equilibrium pattern for the components and the stoichiometry factors from the Ω analysis are presented in Figure 8. The f values are high and rise with decreasing initial complex composition and with increasing concentration, fairly similar to the sedimentation velocity data. The f values are very slightly scattered about a mean value, indicating the irreversible character of polyanion/polycation interaction.

4. Discussion

The sedimentation patterns of PECs between NaPSS and PDADMAC and its copolymers with AA suggest the formation of highly polydisperse systems of colloidal particles. This is in good agreement with the results obtained by light scattering and electron microscopy.[6] The reaction between two strong polyelectrolytes is irreversible and leads to the formation of highly aggregated structures, in very diluted systems to particles on a colloidal level. The structural parameters of the PEC particles depend strongly on the mixing regime and order, but PEC formation can be carried out in a reproducible way under defined conditions. The obtained PEC particle dispersions are stable for long times (months). The level of aggregation and the polydispersity of the PEC particles are particularly high in salt-free media. This phenomenon can be explained in the following way. During PEC formation the polyelectrolyte chains change via ionic binding from hydrophilic species to strongly hydrophobic ones, causing spontaneous aggregation. Ionic binding can take place between two chains under conformational changes corresponding to a zip mechanism or by incorporation of more and more additional polyions. Particles of different sizes and structures are generated. In salt-free solutions the polyelectrolytes have a more extended conformation, favoring the charge compensation by the incorporation process. Complete charge compensation would lead to hydrophobic aggregates which are not stabilized against further coagulation. However, an excess binding of the major component, especially on the surface of the PEC particles, results in an electrostatic stabilization. Nevertheless, a partial coagulation cannot be excluded. These complicated processes are the reason for the high level of aggregation and polydispersity.

The presence of salt leads to a more coiled structure of the polyelectrolyte chains and a favoring of charge compensation by conformational changes, lowering the level of aggregation. But at high ionic strength the stabilizing shell of the excess component is screened and coagulation takes place.

The existence of a shell of the major component is confirmed by the findings about the PEC stoichiometry. In all cases high values of the stoichiometry factors were found, which decrease with increasing initial mixing ratios (Figure 3b).

This tendency was observed by viscometry measurements too. But the f values from viscometry are remarkably smaller than the values obtained by AUC.

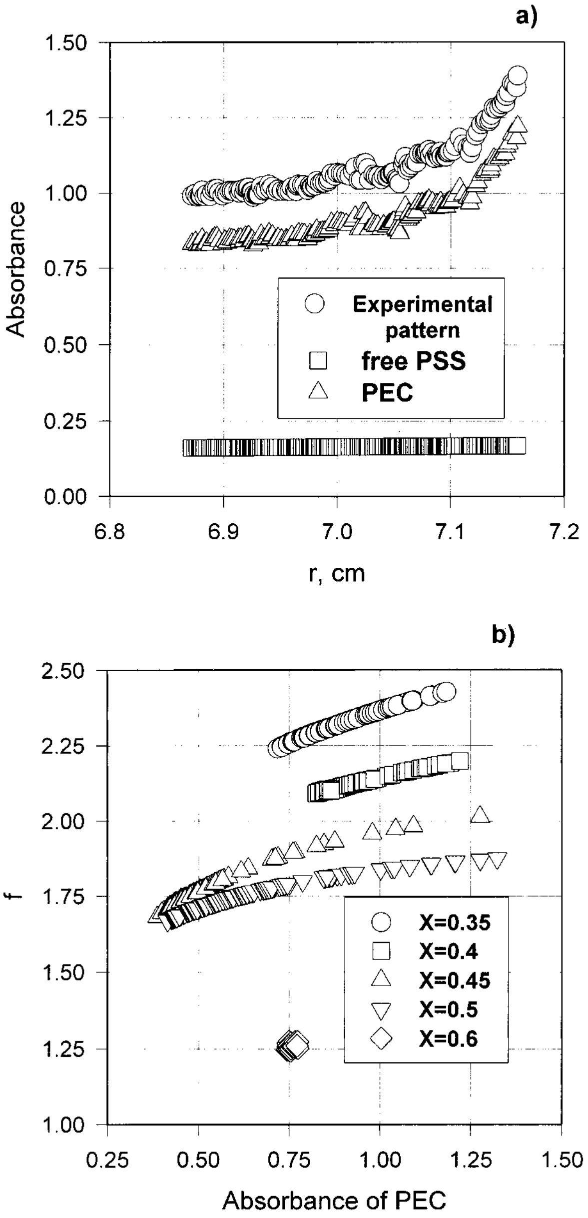

Figure 8. Equilibrium patterns for PEC PSS-66T/PDADMAC with $X = 0.4$ in 0.01 N NaCl and components from Ω analysis (a). Stoichiometry factors via complex absorption for different initial compositions (b).

For the PECs between PSS-356T and the polycations given in Table 1, they vary only between 1.5 and 1 for initial mixing ratios of 0.2 to 1. The differences may be explained by the special features of the methods. While viscometry displays only the chains, which are incorporated into the complex under transition to a compact structure, sedimentation experiments monitor also very loosely attached chains as bound by the PEC.

Now the influence of different parameters on the stoichiometry factor will be discussed. Figures 3b and 8b show that f decreases strongly with increasing mixing ratio. Obviously, PSS interacts specifically with the PECs and there is an equilibrium between free and bound PSS in solution. With increasing mixing ratio, i.e., depletion of the amount of free PSS, the stoichiometry factor must decrease. The f values determined by sedimentation equilibrium measurements are somewhat higher than the values obtained by velocity measurements. This may be caused by the fact that in the first case also temporarily attached chains can be forced to sediment together with the PEC particles. The scattering of the data at low mixing ratios supports this explanation.

The ionic strength affects the stoichiometry factor of the complex PSS-66T/PDADMAC marginally, and no strong correlation could be observed. This is in agreement with the results of SLS, which reveals strong changes of the level of aggregation with the ionic strength but no changes in the internal structure of the PEC particles. However, the stoichiometry factor of the PECs PSS-66T/PDADMAC-*co*-AA-47 ($X = 0.4$) shows a pronounced minimum (Figure 4), probably caused by the strong structural changes from highly aggregated and compact particles at extremely low ionic strength to small and swollen ones in the range $I = 10^{-3}$–10^{-1} N NaCl and the secondary aggregation up to onset of flocculation at high ionic strength.[14] Sedimentation coefficients could be determined only in salt-containing systems. At the given mixing ratios and ionic strengths about 10^{-3} N NaCl, a significant lower level of aggregation and a high degree of swelling were found by light scattering. The increase of the sedimentation coefficient, given in Figure 4, corresponds to secondary aggregation, leading again to compact and large particles.

The effect of the polycation composition on the PEC stoichiometry is demonstrated in Figure 5a. With the exception of the pure PDADMAC, we found a slight but steady increase of f with rising content of AA, which can be explained by the increasing degree of aggregation and swelling and the greater surfaces of the PEC particles.[6]

The influence of the molecular mass of the PSS samples used in complex formation is somewhat stronger. The stoichiometry factor rises with increasing molecular mass (Figure 5b), which can easily be understood by the rising chain length of the attached excess component. The value $f = 2.25$ for PSS-356T at an initial mixing ratio $X = 0.4$ means that no free PSS exists in the complex solution.

For the PECs PSS/PDADMAC-*co*-AA-47 in 0.01 N NaCl also the sedimentation coefficient was studied in relation to the molecular mass of PSS and for PSS-66T at two ionic strengths as a function of the initial mixing ratio X (Figure 7). The increasing s values suggest a growth in particle size in correlation to the molecular mass of PSS (Figure 7a). The steep increase of s at $X \cong 0.45$ (Figure 7b) is in full agreement with the findings of light scattering which reveal a transition from swollen to compact particles in this range.

Conclusions. The method of analytical ultracentrifugation was applied to the study of insoluble PEC particles of two strong polyelectrolytes. It was shown that such complexes are nonstoichiometric and polydisperse. Ionic strength and initial mixing ratio affect considerably the stoichiometry of the PEC particles. Regimes of relative monodispersity were found in water/salt media, and sedimentation coefficients for PSS/PDADMAC-*co*-AA complexes could be obtained. Deviations from the 1:1 stoichiometry increase with increasing amounts of acrylamide in the polycation and for a given polycation also with growing chain length of PSS.

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