# Interaction between Polyelectrolyte Gel−Surfactant Complexes with Oppositely Charged Polymer and Surfactant Components

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ABSTRACT: In aqueous media polyelectrolyte gel−surfactant complexes interact with ionic surfactants with the formation of the new surfactant−surfactant complexes. The reaction is accompanied by the significant swelling of the gels. The interaction between two pairs of the complexes with oppositely charged polymer and surfactant components results in the swelling of both gels due to the decomposition of polymer−surfactant complexes and the formation of surfactant−surfactant complex. The rate of the gel swelling is limited by the kinetics of the decomposition of the highly ordered nanostructures in the polyelectrolyte gel−surfactant complexes. It can be widely varied by the change in the charge density of the networks, the ionic strength of the solution, and the chemical nature of the surfactant.

## Introduction

Interpolyelectrolyte complexes formed by linear macromolecules (IPEC) are known to participate in substitution reactions with other linear polyelectrolytes or ionic surfactants.[1−3] Recently, similar reactions with the participation of polyelectrolyte gels as one of the components were studied.[4,5] It was reported that in the aqueous media anionic surfactants can replace negatively charged chains of a poly(acrylate) network in the complex with cationic linear polymers and form polymer−surfactant complexes in the phase of the anionic gel.[4] Earlier it was demonstrated that positively charged surfactant, cetylpyridinium bromide (CPB), can remove anionic surfactants from polyelectrolyte gel−surfactant complex (PSC) with the formation of the mixed stoichiometric surfactant−surfactant complex.[5] The driving force for these substitution reactions is the hydrophobic interactions between amphiphilic ions. The addition of organic solvents which eliminate the hydrophobic attraction between hydrocarbon groups of the surfactants leads to the reverse of the reactions; i.e., linear polyelectrolytes displace surfactant ions from PSC and IPEC are formed.[6] In the water−organic solvent even inorganic counterions such as chloride anions can displace the surfactant from polyelectrolyte gel.[7] This result is explained by the difference in the composition of the mixed solvent in the gel and in the solution. The water content in the gel phase is higher; hence, the solubility of amphiphilic ions in the gel phase is smaller in comparison with the solution.

One of the reasons of the intense study of IPEC and PSC gels during past decades is their wide range of practical applications such as the adsorbent polymer technology, ecology, drug delivery systems, etc.[8−10] The present paper deals with a new type of polyelectrolyte gel−surfactant system, namely with thermodynamic and kinetic studies of the interaction between the pairs of PSC with oppositely charged polymer and surfactant components. The principal peculiarity of such systems is that both charged surfactants initially form PSC with anionic and cationic networks. It was shown that such complexes are very stable due to hydrophobic interactions between amphiphilic surfactant ions.[5,11,12] Moreover, in a number of studies it was demonstrated that the ionic surfactants in PSC usually form highly ordered supramolecular structures.[13−23] The structure formation additionally stabilize the complexes. In the case under consideration both surfactants are bound in PSC; thus, the thermodynamic and kinetic properties of the systems including two PSC with different signs of charge of the components should differ from the described triple systems with one "free" surfactant component.[5]

It will be demonstrated that PSC with oppositely charged components interact with each other through salt solution with the formation of surfactant−surfactant complex. The interaction is accompanied by a significant gel swelling.

In this study diallyldimethylammonium chloride (DADMA) and sodium 2-acrylamide-2-methyl-1-propanesulfonate (AMPS) were used for the synthesis of cationic and anionic gels, respectively. The charge density of the networks was changed by the copolymerization of the charged monomers with acrylamide (AAm). Dodecyltrimethylammonium bromide (DDTAB) was chosen as a cationic surfactant. Anionic surfactants with different chemical structures of the ionic groups were sodium dodecyl sulfate (SDS) and sodium laurate (SL).

## Experimental Section

**Synthesis and Preparation of the Samples.** Monomers, DADMA (60 wt % aqueous solution), AAm, and *N*,*N*′-methylene-(bis)-acrylamide (BAA), ammonium persulfate (PS), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), SL, and SDS were purchased from Fluka Chemika-BioChemika Corp. DDTAB and AMPS were obtained from Lancaster Synthesis Inc. The gels were prepared by the free-radical copolymerization of the mixtures of monofunctional neutral and charged monomers in the presence of the cross-linking agent. The solution containing AMPS was at first neutralized by sodium hydrocarbonate up to neutral pH. The fractions of each charged monomer in the monomer mixture were 30 and 99 mol %, and the fraction of BAA was 1 mol %. The total concentrations of monomer mixtures used in copolymerization were 1.54 M (AMPS, AMPS−AAm) and 2.56 M (DADMA, DADMA−AAm). The conversion of monomers to copolymers was calculated for

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the control gels.[20,22] For the DADMA−AAm copolymer it was 95 wt %, and for the AMPS−AAm pair it was close to 100 wt %.

To 10 mL of the solution of monomers were added 5 $\mu$L of TEMED and 50 $\mu$L of 10 wt % PS. Gelation was carried out in glass tubes of a diameter of 3.8 mm at 37 °C for 24 h. The obtained gels were removed from the tubes, swollen in water for 2−3 days, cut into cylinders of height ca. 3 mm, and washed again with a large excess of distilled water for 1 month. The water was changed every 3−5 days. The washed samples were dried at 40 °C in a vacuum and kept in closed vials. Before use the samples were additionally dried in a vacuum for 6 h at 40 °C.

For the preparation of the complexes the dried networks were swollen in 0.01 M solution of sodium chloride for 48 h. Then the stock surfactant solutions containing 3-fold excess of the surfactants molecules with respect to the number of the charged groups of the gels were added, and the gels were kept in an air thermostat at 25 °C for more than 2 weeks. The initial surfactant concentration was $7.5 \times 10^{-3}$ M. In the previous studies it was shown that under these conditions the composition of PSC formed is close to stoichiometric.[20,22] The degree of swelling of the individual gels was characterized by the swelling ratio $F = m/m_0$, where $m$ is the mass of the sample in the solution and $m_0$ is the mass of the dried surfactant-free network ($m_0 = 2-3$ mg).

In the first set of experiments the kinetics of the gel swelling was measured for PSC gels immersed in the solutions of the surfactants of the same sign of charge as a network. The amount of the surfactant was equivalent to the number of the charges of the network, and the initial concentration was $2.5 \times 10^{-3}$ M. For the pairs of PSC the gel samples had an equivalent amount (within 5 mol %) of the charged groups in the networks. Typically, the amount of the charged groups in poly(AMPS) (PAMPS) or poly(DADMA) (PDADMA) samples was $2 \times 10^{-5}$ mol while in the copolymers with 30 mol % of the charged groups it was ca. $1 \times 10^{-5}$ mol. In all experiments the volume of the solution was 400 mL per 1 mmol of the charged groups of the networks. The concentration of sodium chloride was 0.01 M if not specially marked. The change in the swelling ratio was controlled by the weight, which was separately measured for PSC of positively and (or) negatively charged networks.

The composition of the complexes was determined by the gravimetric method.[20,22] It is characterized by the ratio $Q = Z_s/Z_g$, where $Z_s$ is the number of the surfactant ions and $Z_g$ is the number of the charged monomer units in the network. The obtained values of $Q$ of the complexes under the study are listed in the captions to Figures 1 and 5.

The scattering measurements were carried out at room temperature on small-angle X-ray scattering diffractometer AMUR-K (Institute of Crystallography, Russian Academy of Science) with the linear position-sensitive detector. The details are described elsewhere.[21−23]

## Results and Discussion

**Structure and Composition of PSC.** The composition of the complexes and the scattering curves obtained from PSC with the different chemical structures are listed in Figure 1. The values of $Q$ for all the complexes are close to stoichiometric. For the PDADMA−SDS complex the main and secondary peaks are located at the wave vectors, $q = 1.68$ and 2.8 nm$^{-1}$. Here $q = 4\pi \sin\theta/\lambda$, where $2\theta$ is the scattering angle and $\lambda = 0.154$ nm. The peak location has a ratio of $(1:3^{1/2})$, which corresponds to the formation of hexagonal structure of the complex which was previously described.[17−21] The main and the secondary peaks in SAXS profile of the PAMPS−DDTAB complex are located at 1.66, 2.93, 3.40, and 4.45 nm$^{-1}$. The peak location has a ratio of $(1:3^{1/2}:4^{1/2}:7^{1/2})$, and it indicates a hexagonal supramolecular structure. The SAXS curve obtained from the PDADMA−SL complex has a complicated structure and was not analyzed in this study. However, the presence of sharp peaks in the SAXS profile of the PDADMA−SL complex demonstrates its highly ordered nanostructure. The positions of the main peaks in Figure 1a−c at 1.68, 1.66, and 1.56 correspond to the characteristic size of the ordered elements of the complexes of $d = 3.7$ (PDADMA−SDS), 3.8 (PAMPS−DDTAB), and 4.0 nm (PDADMA−SL), respectively.

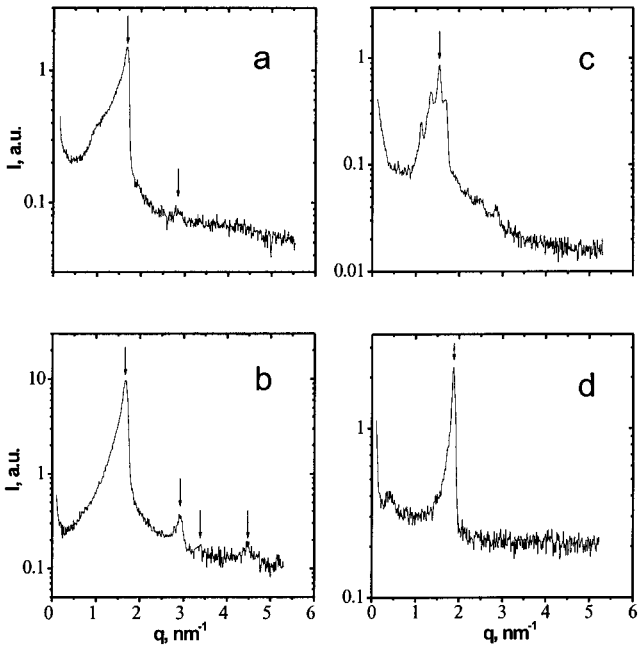


**Figure 1.** SAXS profiles of PSC used in the study. Complexes: PDADMA−SDS ($Q = 0.90 \pm 0.05$) (a); PAMPS−DDTAB ($Q = 0.95 \pm 0.05$) (b); PDADMA−SL ($Q = 0.95 \pm 0.05$) (c); the mixed SDS−DDTAB surfactant complex (d).

After mixing, the oppositely charged surfactants SDS and DDTAB taken in the stoichiometric ratio form a precipitate. Observations in the polarizing microscope show that this precipitate consists of small particles which are optically anisotropic and have a size of ca. 30 $\mu$m. The SAXS profile obtained from these aggregates is shown in Figure 1d. It has one main sharp peak at $q = 1.88$ nm$^{-1}$ corresponding to the $d$ spacing of 3.3 nm. This value is lower than the double length of the fully stretched surfactant molecule. For instance, the double length of SDS molecule is 4.1 nm.[24] The low $d$-spacing of the surfactant ions in the mixed complex can be explained by a strong electrostatic attraction between oppositely charged amphiphilic ions.

**Swelling of PSC Due to Interaction with the Surfactants.** Previously, it was reported that the interaction between PDADMA−SDS PSC and cationic surfactant CPB results in the dissociation of PSC and in the formation of a new stoichiometric SDS−CPB complex in the gel phase.[5] Figure 2a shows the time dependence of F for the PDADMA−SDS stoichiometric complex immersed in the solution of DDTAB containing the equivalent amount of the cationic surfactant. In the presence of DDTAB the significant swelling of the complex is observed. The swelling process is completed within ca. 100 h. The swelling ratio of the gel after the reaction becomes the same as for the surfactant-free PDADMA network in the solution of sodium chloride (Figure 2a, dashed line). In parallel with the swelling of the gel, the formation of the precipitate of the mixed surfactant complex is observed in the solution. If the

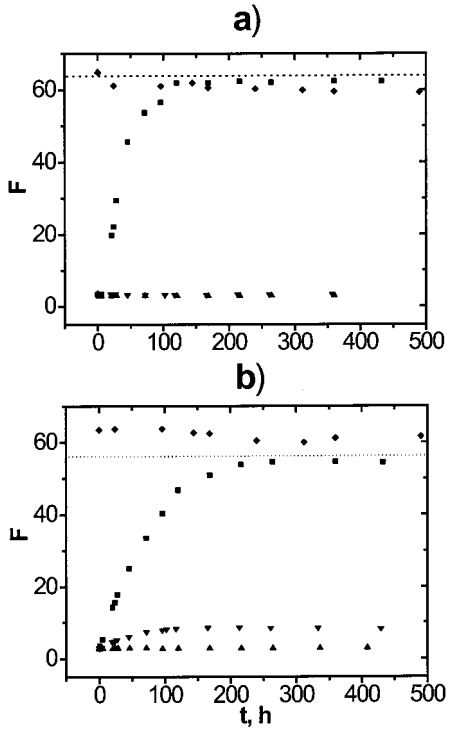


**Figure 2.** Kinetics of swelling of PDADMA−SDS (a) and PAMPS−DDTAB (b) PSC in the solutions of DDTAB ((a), squares); SDS ((b), squares); 0.01 and 0.3 M sodium chloride (up and down triangles in (a) and (b)). Deswelling of PDADMA (a) and PAMPS (b) gels in the presence of SDS−DDTAB complex (diamonds in (a) and (b)). Dashed and dotted lines in (a) and (b) show the swelling ratio of the surfactant-free PDADMA and PAMPS gels in 0.01 M solution of sodium chloride, respectively.

components of the reaction are mixed in a different order, i.e., at first the stoichiometric complex between the surfactants is formed and after the PDADMA gel is added to the solution, in such a case the gel remains transparent and its swelling ratio remains practically the same as in the corresponding salt solution (Figure 2a). SAXS measurements show no ordered structures in the gel in this case. On the scattering curve a monotonic decay of the X-ray intensity is observed.

Thus, the reaction between PSC and the surfactant can be described by the following equation:

$$[[\backslash]{-}K^+RX^-] + R'Z^+ + B^- \Rightarrow [[\backslash]{-}K^+B^-] + [RX^-R'Z^+] \quad (1)$$

where $K^+$ are the cations of the network, $B^-$ are the counterions of the cationic surfactant, and $RX^-$ and $R'Z^+$ are the surfactant ions. Equation 1 demonstrates the fact that in the presence of the surfactant with the same sign of charge as the polyelectrolyte network a partial or a complete dissociation of PSC occurs, and the new complex between oppositely charged surfactants is formed.

More detailed analysis shows that after the reaction a certain amount of the surfactant remains in the gel phase. The mass of the dried PSC becomes higher than $m_0$. From the comparison of the masses of the dried gel before and after reaction 1, it can be calculated that 2 months after the addition of DDTAB the gel phase still contains about 0.5 mol of binary SDS−DDTAB complex per one monomer unit of the network. Figure 3a shows SAXS profile obtained from the PDADMA−SDS gel 2

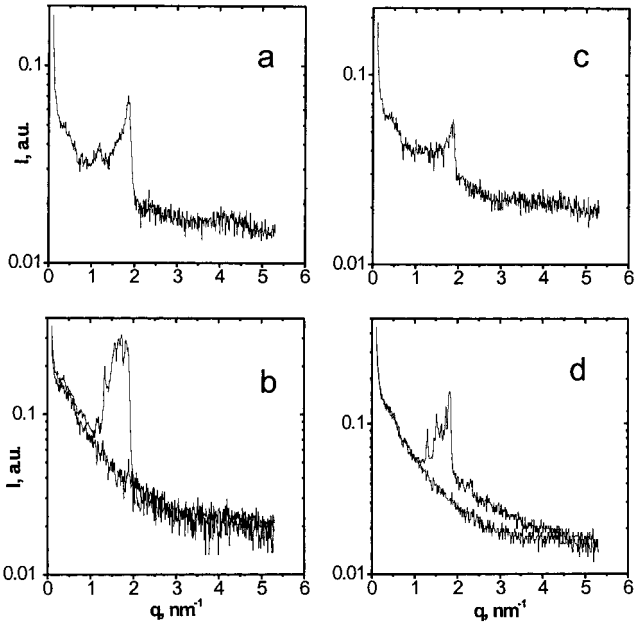


**Figure 3.** SAXS profiles of PDADMA−SDS (a, c) and PAMPS−DDTAB (b, d) PSC 2 months after their interaction with DDTAB (a), SDS (b), and between each other (c) and (d).

months after the addition of DDTAB. The scattering curve is strongly different from that obtained from the initial PDADMA−SDS PSC. It exhibits a sharp main peak at $q = 1.86$ nm$^{-1}$ corresponding to the $d$ spacing of 3.4 nm. The peak position is practically the same as for the SDS−DDTAB complex. Thus, during the reaction between the PDADMA−SDS complex and DDTAB PSC completely decomposes while a new SDS−DDTAB complex is formed both in the solution and in the gel phase. The presence of the mixed complex in the gel phase can be explained by kinetic reasons. It does not practically affect the swelling ratio of the PDADMA network. The obtained result shows that the chains of PDADMA are not included in the highly ordered crystal-like domains of the SDS−DDTAB complex in the phase of the gel.

In the solutions of sodium chloride with the concentrations of 0.01 and 0.3 M (Figure 2a) the swelling ratio does not practically change. Calculations show that under the conditions of the experiment in a 0.3 M solution of sodium chloride there is more than a 100-fold excess of chloride ions over the number of SDS ions in the system. Despite this, the dissociation of PSC is not pronounced, and the complex is not destroyed.

The kinetics of the swelling of the PAMPS−DDTAB PSC is shown in Figure 2b. In the presence of SDS the analogous process of the swelling of PSC and the formation of SDS−DDTAB precipitate in the solution occurs. The kinetic curves for both systems are similar. As well as PDADMA gel surfactant-free PAMPS gel does not change its properties in the solution containing a stoichiometric mixture of the oppositely charged surfactants. Both processes can be described by scheme 1 with the only difference being that the signs of the charges for the PAMPS−DDTAB−SDS system should be reversed.

The swelling behavior of the PAMPS−DDTAB PSC is not completely the same as for the PDADMA−SDS complex. Even 2 months after the beginning of the swelling in the presence of SDS the PAMPS−DDTAB gel contains transparent and turbid parts. The SAXS

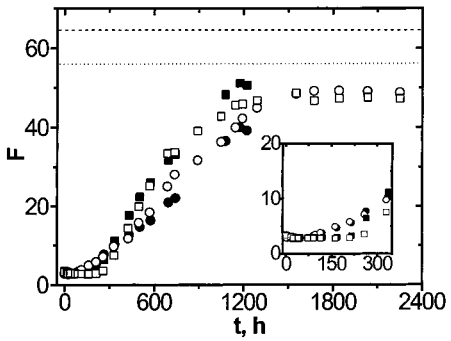


**Figure 4.** Kinetics of swelling of PDADMA−SDS (squares) and PAMPS−DDTAB (circles) complexes in one and the same solution of sodium chloride. Open and closed marks correspond to two independent experiments. Initial parts of the curves are shown within the diagram. Dashed and dotted lines show the swelling ratio of the surfactant-free PDADMA and PAMPS gels in 0.01 M solution of sodium chloride, respectively.

profile obtained from the transparent part exhibits no maximum, while the SAXS profile obtained from the opaque part exhibits a number of overlapping peaks (Figure 3b). All these peaks are shifted to lower $q$ values (i.e., to a higher $d$-spacing) in comparison with the peak corresponding to the SDS−DDTAB complex. The obtained result shows that during the reaction of the PAMPS−DDTAB gel with SDS the latter one penetrates in the gel and forms a new ternary complex which includes the charged monomer units of the gel in its structure. Probably this complex coexists with the initial PSC domains which were not completely destroyed during the interaction.

The marked swelling of the PAMPS−DDTAB gel is observed in the solution of sodium chloride with the concentration of 0.3 M (Figure 2b). This fact demonstrates a partial dissociation of the PAMPS−DDTAB complex. However, the threshold value of $F$ in the latter case is much lower than the corresponding value for the surfactant-free PAMPS gel in the salt solution (Figure 2b, dotted line).

**Interaction between PSC.** Figure 4 shows the swelling behavior of the PDADMA−SDS and PAMPS−DDTAB complexes immersed in one and the same solution of 0.01 M sodium chloride. Special attention was paid to avoid any direct contact between the gels. They were put on the bottom of the reaction vial so that the distance between the samples was about 1.5 cm. For a better control two independent experiments were carried out with the two pairs of PSC. It can be seen that the interaction between PSC in solution results in a slow but significant swelling of the gels. The experimental points obtained in two independent experiments are close. In parallel with the swelling of the gels the precipitate of the mixed surfactant−surfactant complex is formed in the solution. Thus, the reaction between PSC with the oppositely charged ionic components can be represented by the following simplified equation:

$$[[\backslash]{-}K^+RX^-] + [[\backslash]{-}A^-R'Z^+] + B^- + C^+ \Rightarrow [[\backslash]{-}K^+B^-] + [[\backslash]{-}A^-C^+] + [RX^-R'Z^+] \quad (2)$$

where $A^-$ are the charged monomer units of the anionic network and $B^-$ and $C^+$ are the ions of salt. The analysis of the swelling curves in Figure 4 shows that the swelling of PSC is observed after rather a long induction period. During this period the value of $F$ for the PAMPS−DDTAB complex does not change while for the PDADMA−SDS complex a slight decrease of the gel swelling occurs. The origin of the induction period can be due to different reasons. One of them is that the reaction of the decomposition of PSC accelerates after bringing the gel into the direct contact with the product of the reaction, i.e., the precipitate of the SDS−DDTAB complex. In this case the induction period should be reduced if the mixed surfactant−surfactant complex will be initially added in the reaction system. However, the experiments have shown that this is not the case.

The presence of the induction period on the swelling curves can originate from the particularities of the structure of PSC. The dissociation of PSC and the swelling of the outer layer of the collapsed gel are controlled by the state of the inner part of the polymer network. It should be noted that along with the chemical cross-links the gel contains domains with a crystal-like structure of the complex.[21] These domains play a role of additional cross-links.[4] Thus, the partial destruction of the PSC domains in rather a thick layer of the gel will occur before the pronounced macroscopic swelling of the sample is observed. The fast decomposition of the initial crystal-like domains in PSC accompanied by the gel swelling can be induced by the addition of the surfactant with the same sign of charge as the network to the complex (Figure 2). This fact can be explained by a rapid inclusion of the second surfactant in the original binary domains of PSC and the substitution of the ionic bonds between the polyelectrolyte network and the oppositely charged surfactant by the surfactant−surfactant bonds.

The kinetics of the swelling of the PDADMA−SDS complex is characterized by a longer induction period in comparison with the PAMPS−DDTAB complex (Figure 4). During this period the gel shrinks slightly. This particularity of the PDADMA−SDS complex can originate from its chemical structure. The distance between the charges along the PDADMA chain is too long, and the stoichiometric complexes are not optimal from the viewpoint of the steric fitting of the hydrophobic tails of the surfactants. Thus, it is thermodynamically advantageous to incorporate extra surfactant molecules (in our case the ions of DDTAB) inside the gel−surfactant complex.[22,23] In this way the packing of the hydrophobic surfactant tails in PSC can be significantly improved and the gel will be kept in a highly ordered state for rather a long period of time. Thus, the transition (2) from the pair of PSC to the surfactant−surfactant complex (eq 2) can pass through the intermediate ternary PDADMA−SDS−DDTAB complex.

The threshold values of $F$ after the swelling of PSC are lower in comparison with those of the surfactant-free gels swollen in a 0.01 M solution of sodium chloride (Figure 4). The analysis of the scattering curves obtained from the PDADMA−SDS PSC after 2 months of observation shows that a certain amount of the highly ordered mixed SDS−DDTAB complex is present in the gel (Figure 3c). The gravimetric study shows that the dried PSC gel contains ca. 25 wt % or about 0.1 mol of the surfactant molecules per 1 mol of the monomer unit of the gel. This amount is 5-fold lower in comparison with the PDADMA gel after the reaction of PSC with DDTAB. On the other hand, the change in the swelling ratio of the PDADMA after its immersing in the presence of the mixed surfactant complex is very small (Figure 2). No peaks are observed on the scattering curves in the latter case. Thus, it can be assumed that

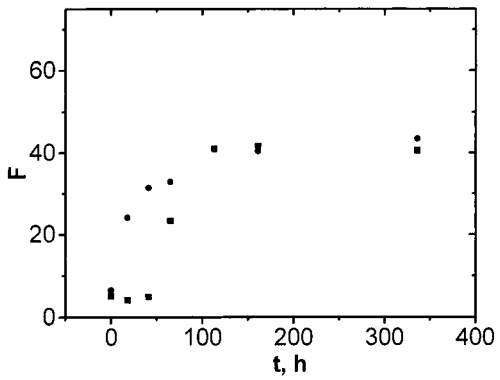


**Figure 5.** Kinetics of swelling of DADMA−AAm−SDS ($Q = 0.80 \pm 0.05$, squares) and AMPS−AAm−DDTAB ($Q = 0.85 \pm 0.05$, circles) PSC in one and the same solution of sodium chloride. Copolymers contain 30 mol % of the ionic groups.

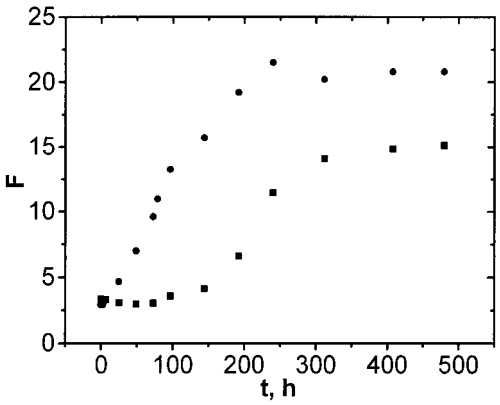


**Figure 6.** Kinetics of swelling of PDADMA−SDS (squares) and PAMPS−DDTAB (circles) complexes in one and the same solution of 0.3 M sodium chloride.

the mixed SDS−DDTAB complex in PSC gel remains due to kinetic reasons.

The swelling behavior and the structure of the PAMPS−DDTAB PSC are somewhat different from the behavior of PDADMA−SDS PSC. After 2 months of the observations the gel contains a large clear peripheral part and a small dense central part while for the PDADMA−SDS complex no difference between these gel parts is observed.

The SAXS profile obtained from the clear part of the gel does not show any maxima (see Figure 3d). The profile obtained from the central part of the gel has a complex structure shown in Figure 3d. The location of some of the overlapping peaks is the same as their location in the SAXS profile obtained from the PAMPS−DDTAB PSC immersed in the solution of SDS. However, the distinct difference in the shape of the scattering curves demonstrates the different structure or the composition of both PSC. The total amount of both surfactants in the dried sample is not higher than 0.2 per one monomer unit of the network. It is much less than the amount of the surfactants remaining in PSC after its reaction with SDS. In the latter case the reaction solution contains a large initial concentration of SDS which can penetrate into the gel and react there with the formation of the kinetically stable highly ordered complexes.

**Effect of the Charge Density of the Networks on the Interaction between PSC.** It is known that the stability of PSC falls with the decrease of the charge density of polyelectrolyte networks.[11,12] The effect of the charge density of the networks on the kinetics of the interaction between PSC was evaluated from the comparison of the rates of swelling of the pairs of gels with 30 and 99 mol % of the charged groups in the copolymers. Figure 5 illustrates the time dependencies of $F$ for PSC with 30 mol % of the charged polymer groups in a 0.01 M NaCl solution. Both gels swell after immersing in one and the same solution of salt. The swelling curve of the complex of the AMPS−AAm copolymer with DDTAB has no induction period. For the complex of the DADMA−AAm copolymer with SDS on the early stage of the reaction a slight shrinking of the gel occurs, which is followed by its strong swelling.

The decrease of the gel swelling for PSC of the DADMA copolymer can be explained in the same way as for the PDADMA−SDS complex. On the initial stage of the reaction the cations of DDTAB diffuse in the gel and additionally fit the ordered structure in the PSC. However, such fitting is not observed in the case of the complex containing AMPS monomer units. The explanation of this difference can come from the peculiarities of the copolymerization of DADMA with AAm. It is well-known that the composition of DADMA−AAm copolymers is strongly heterogeneous due to the different reactivity of monomers in the reaction.[20] The chains of such copolymers contain the long sequences of the DADMA monomer units. As well as PDADMA chains, this sequences will form the intermediate PSC containing the ions of DDTAB.

The comparison of Figures 4 and 5 shows that the decrease of the charge density of the networks from 99 to 30 mol % results in a marked increase in the rates of the swelling of both anionic and cationic copolymer gels. Thus, the variation in the charge density of polyelectrolyte networks which forms the PSC is an efficient way to control the kinetics and the degree of swelling of mixed PSC gels with oppositely charged components.

**Effect of Salt Concentration on the Interaction between PSC.** The increase of the ionic strength of the solution is known to reduce the stability of stoichiometric PSC.[11,12] However, at intermediate concentration of 1,1-salt the stability of nonstoichiometric PSC of PDADMA can increase.[22,23] The effect of the salt on the kinetics of the swelling of PSC can be evaluated from the comparison of the corresponding kinetic curves for PDADMA−SDS and PAMPS−DDTAB gels listed in Figures 4 and 6. It can be seen that the increase in the concentration of sodium chloride from 0.01 to 0.3 M strongly accelerates the process of the gels swelling. On the other hand, the increase of the ionic strength of the solution decreases the threshold values of $F$ of the swollen gels. This fact is well-known and is explained by a decrease of the osmotic pressure of the counterions in the swollen polyelectrolyte networks in the presence of salts. The swelling of the PDADMA−SDS complex begins after the induction period when a slight deswelling of the gel is observed. The origin of the induction period and of the shrinking of the PDADMA−SDS complex during the initial period of the reaction between PSC has already been previously discussed.

**Effect of the Chemical Structure of the Surfactant on the Interaction between PSC.** The chemical structure of the ions can play an essential role in the formation of polyelectrolyte complexes. For example, the complexes formed between linear sodium dextrane sulfate and sodium poly(styrenesulfonate) and alkyltrimethylammonium salts of cationic surfactants are

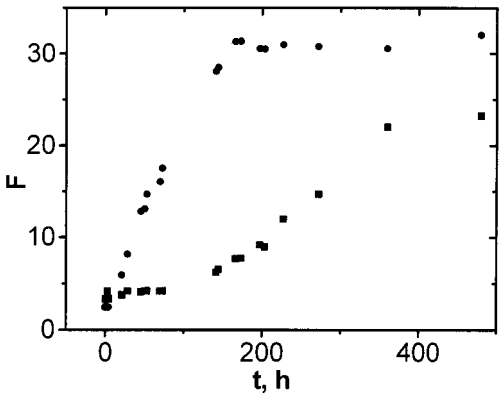


**Figure 7.** Kinetics of swelling of PDADMA−SL (squares) and PAMPS−DDTAB (circles) complexes in one and the same solution of sodium chloride.

considerably stronger than the analogous complexes formed by polycarbonic acids.[25,26] Electrostatic interactions must be especially strong in highly ordered structures in PSC due to a high density of packing of the ions and hydrophobic tails and due to the low water content and the low dielectric constant in the complexes. Hence, it could be assumed that the chemical structure of the ionic group of the surfactant should affect strongly the stability and the kinetics of the decomposition of PSC.

The influence of the chemical structure of the ions of the surfactant on the kinetics of the swelling of PSC with oppositely charged components was studied for PDADMA−SDS and PDADMA−SL complexes interacting with the PAMPS−DDTAB complex (see Figures 4 and 7). The swelling of the PAMPS−DDTAB gel which reacts with the PDADMA−SL complex is a much faster process in comparison with the swelling of the same gel in the presence of the PDADMA−SDS complex The PDADMA−SDS complex has a much longer induction period, and its swelling rate is significantly lower than for the complex of PDADMA with SL. The obtained result demonstrates that the kinetics of the swelling of the PSC having oppositely charged ionic components is strongly affected by the stability of both complexes involved in the reaction. When the more stable PDADMA−SDS complex is displaced by PDADMA−SL gel in the reaction with PAMPS−DDTAB gel the faster release of the surfactant from the weaker PSC promotes a more rapid decomposition of the PAMPS−DDTAB PSC.

The low stability of the PDADMA−SL complex in comparison with PDADMA−SDS PSC is explained not only by its slightly shorter hydrophobic tail but also by a difference in the chemical structure of the ionic group of the surfactant. It is known that IPEC[25,26] formed by polyelectrolytes with sulfo groups are more stable than the analogous complexes containing carboxylic groups. Thus, the change in the chemical structure of the ionic group of the surfactant gives one more possibility to control the thermodynamic and kinetic properties of the systems based on PSC with oppositely charged components.

## Conclusion

The interaction between the PSC and the ionic surfactants having the same sign of the charge as the network leads to a strong swelling of the gels. The driving force of the reaction is the formation of a new complex between the oppositely charged surfactants.

The interaction between two PSC containing oppositely charged surfactants leads to a strong swelling of both gels. The main mechanism of the interaction between the PSC includes the release of the surfactant ions from the complexes and the formation of new more stable complexes between oppositely charged surfactants. The rate of these processes is controlled by the rate of the decomposition of the highly ordered structures in PSC.

The kinetics and the amplitude of the swelling can be controlled by the change of the charge density of the networks, the chemical nature of surfactants, and the ionic strength of the solution.

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