Ordered Nonstoichiometric Polymer Gel−Surfactant Complexes in Aqueous Medium with High Ionic Strength

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ABSTRACT: The effect sodium chloride on the composition and structure of network polymer−surfactant complexes (NPSC) formed by slightly cross-linked networks of poly(diallyldimethylammonium chloride) (PDADMACL) and oppositely charged surfactants of sodium dodecylbenzenesulfonate (SDBS) was studied. The comparison of the composition of NPSC with the data obtained by SAXS shows that, at some content of the surfactant ions in the gel phase, highly ordered lamellar structure in NPSC is formed. In the solution of high ionic strength and at significant excess of the surfactant molecules in the external solution, this highly ordered NPSC can be strongly nonstoichiometric. The excess of the surfactant anions in the polyelectrolyte network first increases with the increase of the ionic strength of the solution, reaching a maximum at $c = 0.3$ M NaCl, and only after that starts to decrease. The degree of spatial order in NPSC becomes more pronounced when the nonstoichiometric complexes in the solution of high ionic strength are formed. These results are explained by introducing the model in which the fitting of packing of the surfactant and polymer components in NPSC is improved by the inclusion of extra surfactant molecules together with their counterions in the highly ordered structure.

Introduction

Macromolecules of polyelectrolytes in aqueous solutions are known to form stable complexes with oppositely charged surfactants.[1−5] Analogous complexes can be formed also by the charged swollen polymer gels.[6−9] The formation of network polymer−surfactant complexes (NPSC) results in a sharp decrease of the degree of swelling (collapse) of polyelectrolyte networks. A fluorescent probe study showed that the ions of the surfactants in the gel phase aggregate at concentrations significantly below their critical micelle concentration (cmc) in solution.[10] The structure of such aggregates differs from that of micelles in solution. As a result of the formation of hydrophobic aggregates within the charged gel, NPSC are capable of absorbing different organic substances.[6] In the mixtures of water with organic solvents (e.g., with alcohol), the aggregates of the surfactants dissociate due to partial elimination of the hydrophobic interaction.[11] The theory of the collapse of the charged networks under the influence of ionic surfactants has been presented.[7]

The essential feature of NPSC is their self-organization which leads to the formation of highly ordered supramolecular structures.[12−20] Khandurina et al. reported the formation of a lamellar complex between a weakly cross-linked sodium salt of poly(acrylic acid) (PAA) and cationic surfactants, alkyltrimethylammonium bromides and alkylpyridinium chlorides (APC).[14] Later Okuzaki and Osada obtained nanostructures with cubic symmetry in the complex of poly(2-acrylamido)-2-methylpropanesulfonic acid (PAMPS) with APC.[15] The highly ordered NPSC were also observed in cationic gels of poly(diallyldimethylammonium chloride) (PDADMACL) interacting with sodium alkyl sulfates[16,19] and sodium dodecylbenzenesulfonate (SDBS).[17] Moreover, a complex of cationic gel of PDADMACL and anionic−cationic mixed surfactants also produced a regular structure.[18]

These works have demonstrated that the formation of a supramolecular lattice depends on the charge density and the chemical nature of the swollen network, on the chemical nature and the length of the hydrophobic residue of amphiphilic molecules, and on the concentration of the surfactant.[12−20] The effect of low-molecular-weight salt on the composition and properties of NPSC was also studied. It was shown that the NPSC formed by cetylpyridinium bromide and a sodium salt of partly neutralized poly(methacrylic acid) (PMAA) or copolymers of sodium methacrylate (SMA) with acrylamide (AAm) deswell in the presence of sodium bromide.[6] This effect was explained by dissociation of NPSC in the presence of salt. Potentiometric study of complex formation between slightly cross-linked networks of PAA and cationic surfactants has shown that, in the presence of low-molecular-weight salt, the equilibrium shifts to the dissociation of the complexes.[20]

Despite a large number of publications, up to now, the detailed studies of the composition and properties of NPSC were performed mainly with NPSC formed by weak polyelectrolytes[6,7,20] while less attention was paid to the consideration of the composition and properties of NPSC formed by the networks of strong polyelectrolytes.[16,17,19] Moreover, the effect of low-molecular-

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weight salt on the structure formation in NPSC has not yet been studied for the gels of strong polyelectrolytes.

In the present work the interaction between a slightly cross-linked network of strong polyelectrolyte, PDADMACL, with SDBS was studied in a wide range of concentration of surfactant and low-molecular-weight salt. The results show that, at the excess of SDBS in the solutions of high ionic strength, the nonstoichiometric NPSC enriched by surfactant molecules are formed. This unusual result is discussed in detail below.

Experimental Section

Preparation of the Samples. Diallyldimethylammonium chloride (DADMACL) (60% aqueous solution), *N*,*N*′-methylene(bis)acrylamide (BIS), ammonium persulfate (PS), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), and SDBS were purchased from Fluka Chemical Co. The gel was prepared by free radical copolymerization of monomers in aqueous solution. The amount of 0.023 g of BIS was added to 10 mL of the solution of DADMACL, and the mixture was heated to 55 °C until the cross-linker was completely dissolved. After the mixture was cooled to 37 °C, 5 mL of TEMED and 50 mL of 10% PS were added to the solution of monomers. Polymerization was carried out at 37 °C for 48 h in glass tubes, diameter of 4.5 mm at 37 °C. After this the obtained gel was removed from the tube and washed in a large excess of distilled water for 2 months. Water was changed every 3−5 days. The gel was cut into the disks with diameters of 10 mm and heights of about 2 mm. After stepwise drying at 37 and 90 °C up to constant weight (the weight of the dried samples was ca. 3 mg), the disks were swollen at 37 °C in flasks containing water or salt solutions for 2 days. After the swelling of the gel the given amount of 0.1 M solution of SDBS was added and the prepared samples were equilibrated for at least one month at 37 °C. The composition of the solution was characterized by the initial ratio, Q_0, between the number of the surfactant molecules and the number of the cations of the network. The total volume of the solution was 400 L/mol of the charged groups of the network. Thus the surfactant concentration of 2.5×10^{-3} M corresponds to an equimolar content of PDADMACL cations and SDBS anions in the system.

The degree of swelling of the samples $F = w/w_o - 1$ was estimated from the weights of dry PDADMACL network (w_o) and of swollen sample (w). The composition of the complexes was characterized by its water content, β ($\beta = (w - w_{NPSC})/w_{NPSC}$), where w_{NPSC} is the weight of dry NPSC, and by the ratio, Q, between the number of surfactant ions, M_S, and the number of cations of the network in the gel phase, M_N. The values of Q were determined by three ways. First of all, they were calculated from the values of SDBS concentration before and after equilibration with PDADMACL determined spectrophotometrically. The values of Q can be calculated using the following formula:

$$Q = (M_S - DV/\epsilon)/M_N \tag{1}$$

where ϵ is the extinction coefficient of SDBS at $\lambda = 224$ nm (we obtained the value of $\epsilon = 13\,350$ M^{-1} cm^3), V is the volume of the solution, and D is its optical density. Optical density was measured by a Hewlett-Packard 8452 spectrophotometer.

The second method of determination of Q was based on the comparison of the weights of the dried samples before and after the interaction with the surfactant.

The third method of estimation of the composition of NPSC is based on the determination of sodium concentration in the samples. For the type 1 of elementary units the content of sodium is 0, while for type 2 it is about 6.6%. Thus, for $Q_0 > 1$, assuming that the ions of sodium in the NPSC are connected only with SDBS anions, the values of Q can be calculated from the following formula:

$$Q - 1 = \alpha M_1/(M_4 - \alpha M_2) \tag{2}$$

where α is the weight fraction of sodium in dry NPSC, $M_4 = M_{Na} = 23$.

Table 1. Water Content, β, and Composition of NPSC Estimated by Weight Method (Q_w) and from UV Absorbance (Q_{UV}) at Different Concentrations of Sodium Chloride (c) and Initial SDBS Content (Q_0)[a]

no.	c	Q_0	Q_w	Q_{UV}	β	$c_{eq} \times 10^4$ (M)
1	0	0.44	0.53	0.41	0.96	0.5 <
2	0	0.71	0.69	0.68	0.92	0.7 <
3	0	0.88	0.83	0.86	0.77	0.8 <
4	0	1.33	1.04	0.91	0.62	8.0 >
5	0	2.65	1.26	1.23	0.55	31.0 >
6	0	4.42	1.24	1.29	0.54	70.4 >
7	0.01	1.33		0.89		8.6 >
8	0.01	2.65	1.35	1.35	0.44	27.9 >
9	0.01	4.42	1.56	1.30	0.41	70.3 >
10	0.03	1.33	1.04	0.90	0.47	8.4 >
11	0.03	2.65	1.50	1.21	0.56	31.4 >
12	0.03	4.42	1.33	1.45	0.41	66.5 >
13	0.10	1.33	1.06	0.98	0.52	6.3 >
14	0.10	2.65	1.58	1.44	0.34	25.7 >
15	0.10	4.42	1.56	1.62	0.31	62.1 >
16	0.30	0.44	0.53	0.40	0.86	1.2 <
17	0.30	0.71	0.69	0.64	0.65	1.7 <
18	0.30	0.88	0.80	0.81	0.55	1.9 <
19	0.30	1.33	1.14	1.03	0.32	5.1 >
20	0.30	2.65	2.18	1.98	0.36	12.2 >
21	0.30	4.42	2.75	2.32	0.38	44.8 >
22	1.00	saturated	0.79		0.67	4.6 >

[a] The column c_{eq} presents the equilibrium surfactant concentration in the external solution obtained by UV spectrophotometry.

Table 2. Comparison of the Composition of NPSC Estimated by Weight Method (Q_w), from UV Photometry (Q_{UV}) and by Emission Flame Photometry (Q_{efp}) at Different Concentrations of Sodium Chloride (c) and Initial SDBS Content (Q_0)

c	Q_0	Q_w	Q_{uv}	Q_{efp}
0	1.33	1.04	0.91	1.03
0	2.65	1.26	1.23	1.05
0	4.42	1.24	1.29	1.09
0.3	1.33	1.14	1.03	1.18
0.3	2.65	2.18	1.98	1.61
0.3	4.42	2.75	2.32	2.16

The content of sodium ions was determined by emission flame photometry using wavelength 589 nm at the maximum of transmission. The measurements were performed using atomic absorption spectrometer “Carl Zeiss Jena” AAS1 by the method of external standard. Comparison samples were prepared by dilution of standard “Merck” solution.

The composition of NPSC is listed in Tables 1 and 2. The comparison of the values of Q obtained by different methods shows that the method of gravimetry gives somewhat higher values of Q than those calculated by formula (1) (Table 1), while the method of flame photometry gives smaller values (Table 2). This discrepancy is sufficiently small and does not influence the results and conclusions of this study. Among all of the methods, only UV spectroscopic measurements give the values of equilibrium concentration of SDBS in the solution; the values of Q obtained by this method will be used below.

X-ray Scattering. The scattering measurements were carried out on small-angle X-ray scattering diffractometer AMUR-K (made in the Institute of Crystallography, Russian Academy of Sciences[21]) with the linear position-sensitive detector (produced in the Institute of Nuclear Physics, Siberian Division of the Russian Academy of Sciences[22]). The detector has a window of 10 × 100 mm; the range of measured angles is up to 8°. The monochromatization is achieved with a crystalline monochromator; the wavelength was 0.1542 nm. The sample holder is made from stainless steel and has the windows made of poly(ethylenetherephthalate) (thickness 0.01 mm); the thickness of the samples is about 1 mm. The samples

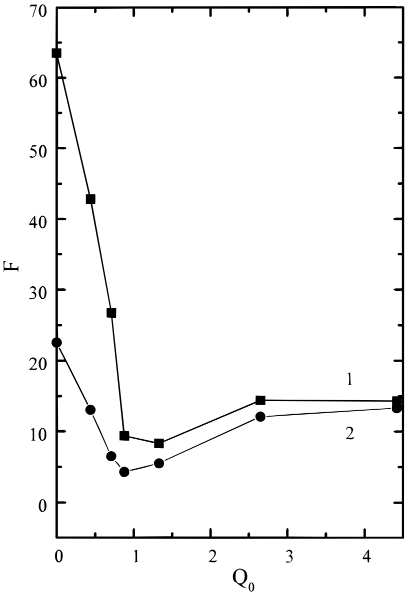


Figure 1. Plot of the equilibrium degree of swelling, F, of PDADMACL gel versus Q_0 in the absence (1) and in the presence (2) of 0.3 M sodium chloride solution.

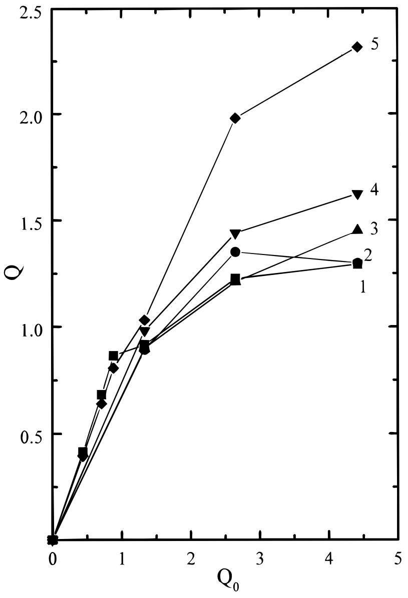
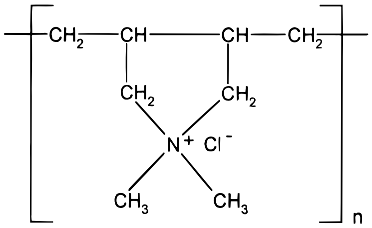


Figure 2. Plot of Q versus Q_0 in the absence of added sodium chloride (1) and for 0.01 (2), 0.03 (3), 0.1 (4), and 0.3 M (5) sodium chloride solution.

of complexes do not have the same thickness along the window of the holder (10 mm); therefore, we cannot calculate the desmeared curves. The X-ray studies were performed at 37 °C, that is, at the temperature at which the NPSC were prepared.

Results

Collapse and Composition of Complexes. The repeating unit of PDADMACL as determined by ^{1}H and ^{13}C NMR spectroscopy[23,24] can be presented as follows:



In accordance with the results of the previous studies the equilibrium of the formation of NPSC can be represented by the following reaction:

$$[\backslash\text{-N}^+\ \text{Cl}^-] + [\text{Na}]^+ + [\text{RSO}_3]^- = [\backslash\text{-N}^+\ \text{RSO}_3^-] + [\text{Na}]^+ + [\text{Cl}]^- \quad (3)$$

The interaction of the gel with SDBS leads to a strong decrease of the degree of swelling of the gel, F. Figure 1 shows dependencies of F equilibrated with SDBS on Q_0 in water and in 0.3 M sodium chloride solution. Both in water and in salt solution the increase of Q_0 results in significant growth of the extent of the gel collapse.

It could be expected that in the presence of low-molecular-weight salt the degree of swelling of NPSC will be higher than in water due to competition replacement of the surfactant ions by chloride anions of salt in the complex with the cationic network. However, the effect is the opposite. The extent of the collapse is higher and the water content of the gels, β, listed in Table 1, is significantly lower in 0.3 M salt solution than in water. Even in 1.0 M sodium chloride solution the value of β is lower than in water, although it is higher than in 0.3 M salt solution. These results seem to be in some contradiction with the data obtained for NPSC formed by the networks of weak polyelectrolytes where the addition of 0.3[6] and 0.4 M[20] sodium chloride resulted in the dissociation of NPSC.

The study of the kinetics of the gel contraction shows that the main changes in the gel volume occur within 1 day of the observation. The collapse is completed within about 7−10 days.

From the data listed in Figure 1, it follows that, after the collapse at $Q_0 > 1$, further increase of the surfactant concentration leads to the growth of the weight of the network. This growth is especially large (more than 2-fold) in the presence of salt. It should be attributed to the additional absorption of the large surfactant ions by NPSC, because the water content of the gels decreases or practically does not change in this region of surfactant concentration (Table 1).

The essential feature of the complexes obtained at $Q_0 < 1$ is their macroscopic structural heterogeneity. After equilibration the transparent gels become turbid on their boundaries especially in their corner parts. These parts of the disk samples represent the dense layer of NPSC while the inner part consists of a transparent highly swollen gel. At the same time the gels obtained at $Q_0 > 1$ become completely turbid. The nonhomogeneous distribution of the surfactant ions in the volume of the polyelectrolyte network was explained theoretically.[25]

The important feature of NPSC studied is the formation of nonstoichiometric complexes containing large excesses of surfactant ions in comparison with the amount of cations of the network in the region $Q_0 > 1$. Figure 2 shows the isotherms of absorption of the surfactant by the network as a function of Q_0 in water and in solutions of sodium chloride of different concentrations. Both in water and in solutions of salt up to the value of $Q_0 = 0.9$, practically all of the surfactant ions are absorbed by the gel phase. At high Q_0 in water, the number of SDBS anions in the gel phase is about 30% higher than the number of PDADMACL cations.

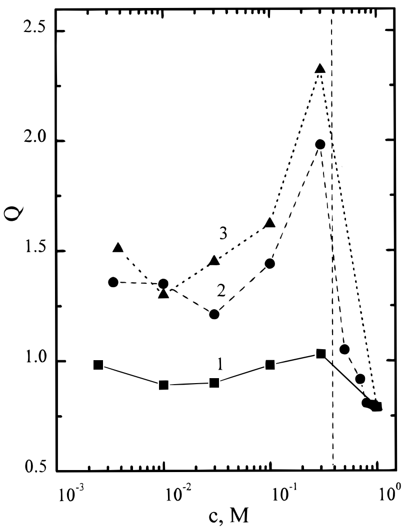


Figure 3. Plot of Q versus concentration of sodium chloride solution, c, at $Q_0 = 1.33$ (1), 2.65 (2), and 4.42 (3).

The increase of salt concentration up to 0.3 M results in a significant additional increase of the amount of the surfactant absorbed by the network ($Q = 2.32$ at $Q_0 = 4.42$). The last fact cannot be explained on the basis of equilibrium (3); it also contradicts the previously reported experimental results obtained for NPSC with weak polyelectrolyte, PAA,[20] and the prediction of the theory.[7]

At $Q_0 < 1$ the comparison of the stability of NPSC cannot be based on the values of Q listed in Table 1 because they are practically independent of the concentration of salt within the experimental errors. The comparison of the values of c_{eq} (Table 1) shows that they decrease with the decrease of salt concentration. Thus, the addition of salt decreases complex stability in the region of concentrations corresponding to $Q_0 < 1$. Such behavior of NPSC is in good accordance with the equilibrium represented by the scheme (3). Thus, the behavior of NPSC below $Q_0 \sim 1$ and at higher values of $Q_0 > 1$ is completely different: at low concentrations of the surfactant the addition of salt decreases the stability of complexes while at $Q_0 > 1$ the increase of the ionic strength leads to stabilization of the complexes.

The state of the surfactant ions in the solution plays an important role in the formation of NPSC.[6,7] At low concentrations of the surfactant and the low-molecular-weight salt, the ions of the surfactant are not aggregated in the solution and the activity of the surfactant is roughly proportional to its concentration. The aggregation and micelle formation of the amphiphilic ions lead to much less pronounced dependence of the surfactant activity with the increase of the average surfactant concentration. The presence of the surfactant aggregates in the external solution was estimated by solubilization of water-insoluble dye, Sudan-1, by the SDBS solutions equilibrated with PDADMACL gels.

The results of these experiments are shown in Table 1, where the markers > and < show the concentrations in the solution above and below cmc respectively. It can be seen that all of the solutions equilibrated with nonstoichiometric NPSC with $Q > 1$ contain aggregates of the surfactant ions while the concentration of the solutions equilibrated with nonsaturated complexes obtained at $Q < 1$ is below cmc.

Figure 3 shows the dependence of Q at constant values of Q_0 on the concentration of sodium chloride, c. In the range of $c \sim 0.1-0.3$ M the value of Q significantly increases and reaches the maximal value of 2.32 at $Q_0 = 4.42$. Further increase of salt concentration up to 1.0 M results in a pronounced decrease of Q which is accompanied by the formation of precipitate of the surfactant. The existence of the maximum on the dependence of Q on c at large values of Q_0 seems to be in contradiction with the equilibrium (3) and the results of the previously reported experimental data obtained for NPSC formed by weak polyelectrolyte, PAA.[20]

The formation of precipitate is an important feature of surfactant solutions in the presence of a large amount of low-molecular-weight salt. The concentration at which the precipitate is observed significantly decreases with the increase of salt concentration. For instance at 37 °C, the temperature used in this study, SDBS forms transparent solutions with water even at concentrations of 30 wt %, while in 1.0 M solution of sodium chloride the solution becomes opaque already at SDBS concentrations of about <1.5% ($\sim 4.6 \times 10^{-4}$ M). The formation of precipitate limits the range of surfactant concentration available for the preparation of NPSC with a high excess of the surfactant.

Thus, the results described above enabled us to make two important conclusions: (i) complexes of PDADMACL gel with oppositely charged surfactant (SDBS) can be nonstoichiometric, especially in the presence of a large amount of salt; and (ii) the excess of surfactant molecules in the gel−surfactant complexes at first increases with the increase of ionic strength of solution, reaching a maximum at about 0.3 M solution of sodium chloride, and only after that starts to decrease.

Structure of the Complexes. Up to date there are only a few recent papers where the structure of complexes was studied by direct physical measurements.[12−20] In all of these studies highly ordered structures of gel−surfactant complexes of different symmetry were observed. Up to now all of the studies were performed with NPSC obtained in the absence of low-molecular-weight salt.

Figure 4 (curves 1 and 2, and 4 and 5) shows SAXS curves obtained from NPSC at $c = 0$ (curves 1, 2) and 0.3 M sodium chloride (4, 5) and $Q_0 = 0.44-0.71$, that is, in the range of concentrations where the gels remain swollen. Despite a large difference in the degree of swelling of the gels, the scattering curves obtained from the samples equilibrated in water and in the presence of salt are similar; they all have one broad maximum at 2θ of about 2.7°.

The gel prepared in water is inhomogeneous and consists of white turbid peripheral layers enriched with SDBS anions and an opaque highly swollen central inner part. The curve obtained from the white turbid part of the gel (curve 1(a)) has a more pronounced maximum than that obtained from the opaque part (curve 1(b)). These results demonstrate that the degree of order in NPSC depends on the local distribution of the surfactant ions within the charged network. In the regions with enhanced local concentration of the amphiphilic ions the degree of structural ordering is higher.

An increase of Q_0 up to 0.88 results in the appearance of a sharp peak from the sample prepared in water (Figure 4, curve 3). The existence of a sharp peak shows the formation of highly ordered structure in NPSC. At the same time, the degree of order in NPSC obtained in 0.3 M salt is low, as it follows from the profile of the

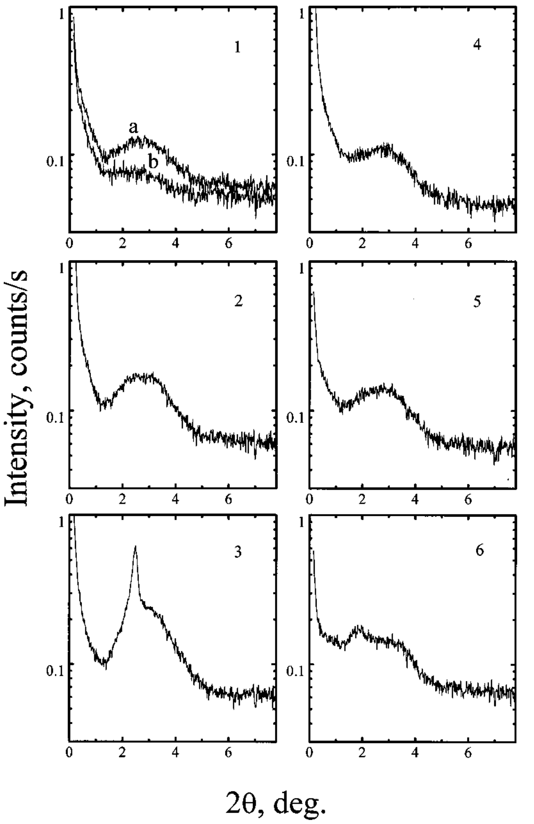


Figure 4. X-ray intensity profiles for PDADMACL−SDBS complexes in water (1−3) and in 0.3 M sodium chloride solution (4−6) at $Q_0 = 0.44$ (1, 4), 0.71 (2, 5), and 0.88 (3, 6). (a) and (b) correspond to the curves obtained from the outer and central parts of the sample, respectively. Here and in later figures the temperature of complexes for X-ray experiments is 37 °C.

scattering curve with two broad weakly pronounced maxima (Figure 4, (6)).

A further increase of Q_0 up to 1.33−4.42 results in significant changes in the profile of the scattering curves. The curves obtained from the samples prepared both in water and in 0.3 M salt have one main sharp peak and well-resolved secondary peaks (Figure 5). The relative positions of the main and secondary peaks (1:2) manifest the formation of lamellar structure of the NPSC. Therefore, at $Q_0 > 1$ the formation of highly ordered structure in NPSC is observed.

The positions of all peaks are listed in Table 3. In the interval of $Q = 0.9{-}2.32$ the position of the main peak lies between $2\theta = 2.70{-}2.77°$ for NPSC obtained in water and $2\theta = 2.62{-}2.70$ for the complexes obtained in 0.3 M salt. These values correspond to characteristic lamella size $d = 2.9{-}3.4$ nm. It should be noted that the characteristic size of the ordered elements of the complex (2.9−3.3 nm) is lower than the double length of the fully straight surfactant molecules.

The comparison of the scattering curves obtained from NPSC prepared in water and in the presence of 0.3 M sodium chloride ($Q_0 = 2.65{-}4.42$) demonstrates a marked increase of the relative intensity and sharpening of the secondary peak and of the main peak for NPSC obtained in salt solutions. These results demonstrate the higher degree of order in the nonstoichiometric complexes obtained in the presence of salt at high values of Q_0.

In concentrated solutions of salt, SDBS form precipitate. Despite very low equilibrium concentration of the dissolved surfactant in the presence of precipitant PDADMACL gel immersed in a saturated solution of SDBS in 1.0 M sodium chloride significantly shrinks and becomes turbid forming NPSC with the surfactant. The surfactant content in the complex $Q = 0.79$ is relatively low. However, the analysis of the SAXS curve for this gel shows that, even at this very high ionic strength of the solution, the self-organization in the gel

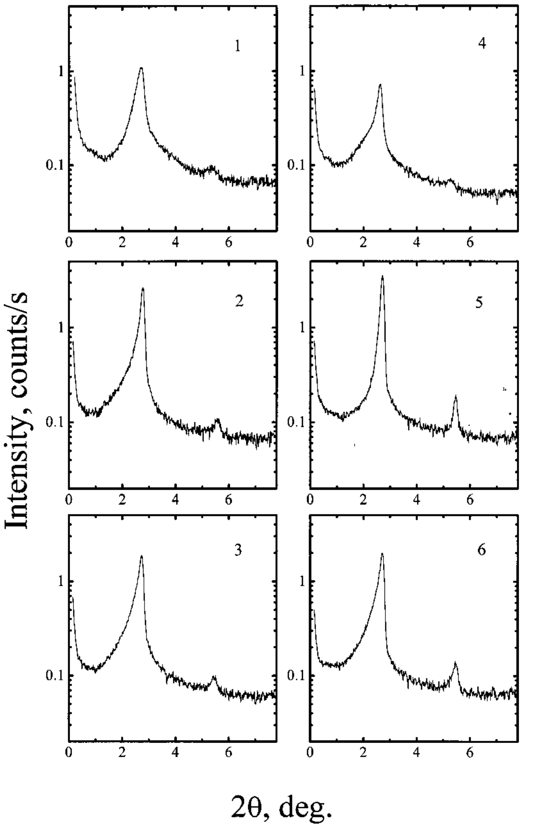


Figure 5. X-ray intensity profiles for PDADMACL−SDBS complexes in water (1−3) and in 0.3 M sodium chloride solution (4−6) at $Q_0 = 1.33$ (1, 4), 2.65 (2, 5), and 4.42 (3, 6).

Table 3. Position of Maxima in SAXS Curves (Max 1 and Max 2) and Characteristic Size d of SDBS Solutions and Precipitates and NPSC of Different Composition (Q_{uv}) Prepared at Different Initial Concentrations of SDBS Solution (Q_0) and Different Concentrations of Sodium Chloride (c)

SDBS/NPSC	c	Q_0	Q_{uv}	max 1, 2θ (deg)	max 2 2θ (deg)	d_1 (nm)	d_2 (nm)
SDBS, 30%, 37 °C	0			~2.7[a]			3.3
SDBS, 30%, 20° precip.	0			2.70	5.50	3.3	1.6
				~2.75		3.3	
SDBS, 37°C, precip.	0.3			2.66	5.29	3.3	1.7
SDBS, 37°C, precip.	1.0			2.82	5.69	3.1	1.6
NPSC	0	0.44	0.41	~2.8		3.2	
NPSC	0	0.71	0.68	~2.8		3.2	
NPSC	0	0.88	0.86	2.47	~3.1	3.6	2.9
NPSC	0	1.33	0.91	2.70	5.35	3.3	1.7
NPSC	0	2.65	1.23	2.77	5.58	3.2	1.6
NPSC	0	4.42	1.29	2.72	5.45	3.2	1.6
NPSC	0.3	0.44	0.40	~2.7		3.2	
NPSC	0.3	0.71	0.64	~2.8		3.2	
NPSC	0.3	0.88	0.81	~1.8	~3.1	4.9	2.9
NPSC	0.3	1.33	1.03	2.62	5.27	3.4	1.7
NPSC	0.3	2.65	1.98	2.70	5.46	3.3	1.6
NPSC	0.3	4.42	2.32	2.70	5.46	3.3	1.6
NPSC	1.0	saturated	0.79	2.49	4.97	3.5	1.8

[a] Position of the wide maxima is designated "~".

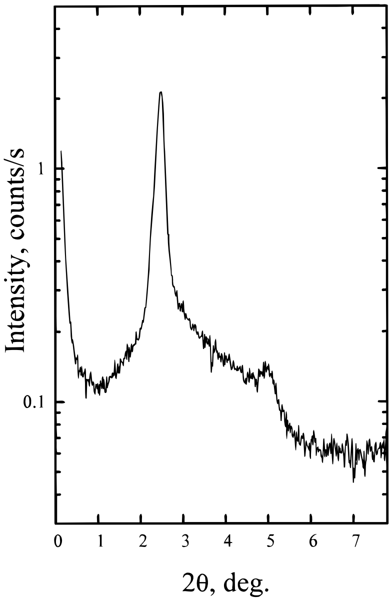


Figure 6. X-ray intensity profile for PDADMACL−SDBS complexes in a saturated solution of SDBS in 1.0 M sodium chloride solution stored for 1 week after the mixing of the components.

phase occurs resulting in the formation of lamellar packing of the surfactant ions in NPSC (Figure 6).

The position of the maximum for the gel obtained in a 1.0 M solution of salt corresponds to d spacing of the lattice of 3.5 nm, that is, to a somewhat higher period of packing in NPSC in comparison with the complex obtained in 0.3 M NaCl solution (sample 21 in Table 1). The comparison of the water content of these two gels with the size of the lamellas shows that the change in β from 0.67 to 0.38 corresponds to a much stronger change in the volume of the gel than in the size of the lamellas. This result can be explained by the coexistence of highly ordered regions in the gel phase with disordered parts (or "lakes"; this fact was previously described by us in ref 17).

Figure 7 shows the X-ray scattering profile obtained from 30 wt % SDBS solution in water (curve 1), that is, at a higher concentration of the surfactant ions than in the NPSC. One can see that, for the aqueous solution, the curve exhibits only a very broad maximum. This result shows that the medium of the cationic PDADMACL gel definitely favors the process of self-organization of the anionic surfactant. An analogous conclusion was previously made by us in the study of the complexes formed by the PDADMACL network and another anionic surfactant, sodium dodecyl sulfate.[17]

The sharp peaks appear in the solutions of SDBS either upon the decrease of the X-ray experiment temperature (as it is presented in Figure 7, curve 2) or upon the increase of the concentration of salt (Figure 7, curve 3); that is, the precipitation of SDBS is responsible for the origin of the sharp peaks. These peaks are similar to those observed for NPSC. Consequently, the regular nanostructure in gels is due to the "precipitation" of the surfactant in the network medium with the formation of lamellas.

To end up the study of the structure of NPSC, we would like to emphasize some key conclusions: for low values of Q_0 salt is not favorable for the emergence of highly ordered structure while for high values of Q_0 the situation is the opposite; the high degree of spatial order increases when the nonstoichiometric complexes (enriched with surfactants) are formed; in the presence of salt at high concentration of surfactant the kinetics of formation of highly ordered structure accelerates.

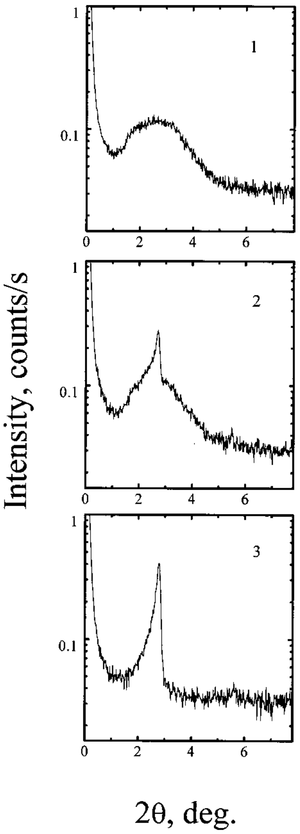


Figure 7. X-ray intensity profiles for a 30% solution of SDBS in water at $T = 37$ °C (1) and for SDBS precipitates obtained from the solution in water at $T = 20$ °C (2) and from saturated SDBS solution in 1.0 M sodium chloride solution (3) at $T = 37$ °C.

Discussion

Theoretical analysis of the equilibrium in the system including the slightly cross-linked polyelectrolyte network formed by flexible chains, oppositely charged surfactant, and low-molecular-weight salt was performed by Khokhlov et al.[7] Schematic representation of the formation of NPSC is given by equilibrium (3).[6,7,20] In the concentration range of surfactant below its cmc in the solution, the amphiphilic ions concentrate in the gel phase due to reaction of ion exchange. When the concentration of the surfactant ions in the gel phase c exceeds its critical aggregation concentration, cac, the aggregates of the surfactant are formed in the gel phase due to hydrophobic interaction of hydrocarbon groups of the amphiphilic ions. Strongly charged aggregates are attracted to oppositely charged monomer links of the network chains and induce their folding and the collapse of polyelectrolyte gel.

Experimental results obtained by the method of fluorescence probe[10,11] together with theoretical analysis show that the values of cac in the gel phase are much less than cmc in the surrounding solution. The additional driving force for the formation of the aggregates in the phase of a charged gel in comparison with solution is the gain in translational entropy of the counterions of the network and of the surfactant: the formation of NPSC in the gel phase leads to release of

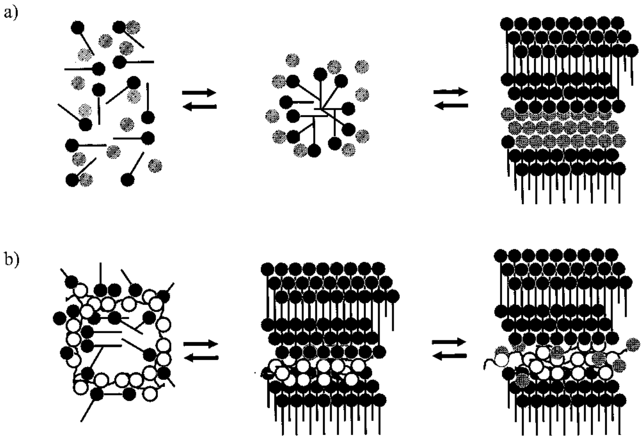


Figure 8. Schematic representation of the surfactant aggregation in the external solution (a) and within the gel (b) at different surfactant concentrations.

the counterions of a network in the solution, while in the solution the formation of surfactant micelles or aggregates results in significant restrictions in translational motion of the counterions. According to the theory, the gain in entropy should increase with the increase of the volume of the solution and the collapse should be most pronounced in dilute solutions of surfactants in the absence of salt. Another conclusion which follows from this scheme is that the stability of NPSC should decrease sharply with the increase of Q at $Q_0 > 1$.

Analysis of the equilibrium (3) shows that the increase of the concentration of low-molecular-weight salt should result in dissociation of the NPSC complexes. In the previous works this conclusion was confirmed in the studies of the complexes formed by cationic surfactants, alkyl pyridinium, or alkyl trimethylammonium salts, with anionic networks formed by neutralized cross-linked PMAA[6,7] and PAA[20] or by copolymers of SMA with AAm.[6,7] In accordance with reaction 3 the increase of the ionic strength of the solution leads to dissociation of polymer–surfactant complexes and to the gel swelling.

The results of this work show that the consideration of a system including polyelectrolyte network, ionic surfactant, and low-molecular-weight salt should be modified in comparison with the previous studies.[6,7,20] In Figure 8 we have schematically shown the possible changes in the surfactant ordering with the increase of the surfactant concentration in the outside solution (a) and within the gel (b). In the outside solution below the cmc we should have single surfactant molecules and counterions (no micelles), then above cmc the spherical micelles floating in the solution (without the long-range order) should be observed; at still higher concentrations the ordered structures with long-range order are formed (for example, the lamellar structure is shown in Figure 8a). The counterions are incorporated in this ordered structure ensuring the electroneutrality of the system.

The corresponding changes which occur within the gel upon the increase of the concentration of surfactant molecules are illustrated in Figure 8b. One can see that, at very low surfactant concentration, no micelles are formed, then the surfactant molecules are organized in the micelles, the charge of these micelles being neutralized by the opposite charges on the gel chains. This type of ordering is dominant at low enough surfactant concentrations within the gel (below the concentration corresponding to $Q = 1$).

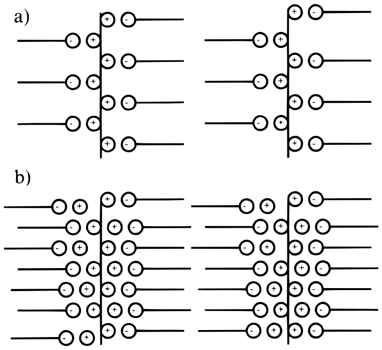


Figure 9. Schematic representation of the regular structure of stoichiometric (a) and nonstoichiometric (b) PDADMACL-SDBS complex.

However, the 1:1 charge complex ($Q = 1$) may be not the optimal one from the viewpoint of steric fitting. This is illustrated in Figure 9. If the distance between the charges along the chain is high enough, the density within the surfactant microdomains, in the case of 1:1 complex, may be too low (Figure 9a); this fact prevents the formation of highly ordered structures. In this case, upon further increase of the concentration of surfactants in the external solution, it might be thermodynamically advantageous to incorporate extra surfactant molecules together with their counterions inside the gel–surfactant complex (Figure 9b). In this way the fitting of packing of polymer and surfactant components in NPSC can be significantly improved. Thus, we conclude that, at high concentration of the surfactants in the external solution, the steric requirements may favor the formation of nonstoichiometric gel–surfactant complexes with the incorporation of surfactant counterions in the structure (Figure 8b). These nonstoichiometric complexes should have a higher degree of order, as we have observed experimentally (see Figure 5).

It is not surprising that the nonstoichiometric complexes were observed for the system studied in the present article (complex of PDADMACL and SDBS), while for the complexes of PAA and PMAA with cationic surfactants the 1:1 composition was reported.[20] Indeed, due to the high value of the distance between alternating ionic groups on the PDADMACL chain (about 0.7 nm), the situation for the 1:1 PDADMACL–SDBS complex is very much like Figure 9a, so all of the arguments of the previous paragraph remain valid. On the other hand, for PAA and PMAA the distance between the alternating charges along the chain (ca. 0.5 nm) is very close to that obtained for the surfactant component from the packing considerations (~0.4 nm), so in the 1:1 complex there is no misfit of packing, and therefore it is the most favorable composition.

The approach to the gel–surfactant complex formation presented above also gives the explanation for the fact that the formation of nonstoichiometric complexes is most pronounced in the solutions of high ionic strength. Indeed, in this case the unfavorable contribution from the translational entropy of the surfactant counterions incorporated in the structure of NPSC shown in Figure 9b is less important than for the salt-free case.

On the other hand, at a very high concentration of salt the formation of the ion pairs between the network cations and the surfactant anions will be completely suppressed. In this case precipitation of the surfactant can occur independently in the outer solution. Thus, the formation of highly ordered structures in the gel phase will become thermodynamically unfavorable. The last effect takes place upon the increase of the concentration of the sodium chloride solution from 0.3 up to 1.0 M. Then the value of Q falls down (Figure 3), and the precipitate of the surfactant is formed in the solution.

In conclusion it should be noted that other important factors, namely, chemical structure of the ions of NPSC may play an essential role in the formation of complexes. For example, complexes formed between linear sodium dextrane sulfate and sodium poly(styrenesulfonate) and alkyltrimethylammonium salts of cationic surfactants are considerably stronger than analogous complexes formed by polycarbonic acids.[1,2] Such interactions must be especially strong in highly ordered structures in NPSC due to the high density of packing of the ions and hydrophobic tails and due to low water content and dielectric constant in the complexes.

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