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Short Communication

On the Structure of Polyacrylate-Surfactant Complexes

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Abstract. — The structure of complexes between a cross-linked polyacrylic acid and a cationic surfactant such as cetyltrimethylammonium bromide (CTAB) has been studied by SANS and SAXS. The polycomplexes were found to be composed of a set of charged lamellae of surfactant ions embedded in the oppositely charged network of cross-linked polyacrylic acid via electrostatic interactions.

1. Introduction

In recent years much attention has been paid to the chemical and physical features of complexes formed by oppositely charged polyelectrolytes and surfactants. One of the reasons for this interest is their application in a wide range of technologies, particularly in the solution of ecological problems [1]. The complexes between cross-linked polyelectrolytes (networks) and surfactants are of special interest since cross-linked charged networks feature a conformational behaviour in the process of interactions with surfactant ions [2,3]. The study of amphiphilic phases immobilized in a polyelectrolyte network is also important because of the wide distribution of these kinds of structures in living organisms. In addition, these complexes are capable of adsorbing different organic compounds from aqueous solutions, thus they are promising for technological applications.

We present here preliminary results on the structure of polycomplexes formed by weakly cross-linked sodium polyacrylate (cl-PANa) and cationic surfactants studied by small-angle X-ray and neutron scattering.

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2. Materials and Methods

The gel of weakly cross-linked polyacrylic acid was prepared by radical polymerization of freshly distilled acrylic acid (AA) with N,N'-methylenebisacrylamide (mass ratio of comonomers 100:1) in a 10% aqueous solution.

The reaction was initiated by ammonium persulfate and sodium metabisulfite (0.2% of AA mass) and was carried out for 1 day at 40 °C. The synthesized gel was neutralized with NaOH up to pH = 8. The cl-PANa was a transparent homogeneous elastic monolith. The degree of swelling, $H$, of equilibrium swollen cl-PANa was calculated as follows: $H = (m_{SW} - m_{dry})/m_{dry} = 10^3$, where $m_{SW}$ and $m_{dry}$ are the masses of swollen and dry samples, respectively. The concentration of -COO\(^-\) groups in swollen cl-PANa was ca. 10\(^{-2}\) mol/l.

Cetyltrimethylammonium bromide (CTAB) ("Serva") was used as surfactant; it was recrystallized from a mixture of ethanol and acetone (15:85 by volume). The polymer-surfactant complexes (PSC) were prepared by keeping cubic samples of swollen cl-PANa gel (3 – 10 g) in surfactant solutions with a concentration of 10\(^{-3}\) – 10\(^{-2}\) mol/l until the transformation of cl-PANa into a polycomplex was completed. As shown earlier, the PSC's formed contain equimolar amounts of charged COO\(^-\) groups of the network and surfactant cations [4].

For X-ray and neutron small-angle measurements we used URS-55, URS-60 instruments; a small-angle X-ray diffractometer "AMUR-K" [5] and a SANS diffractometer "Membrana-2" [6].

3. Results and Discussion

When the cl-PANa gel comes into contact with a surfactant solution, an opalescent layer of PSC forms on the surface of the gel sample, and transparent gel becomes opaque. Finally, if the concentration of the surfactant is sufficient, the gel transforms into a compact dense sample of PSC [4]. The sorption process goes on as a front heterogeneous reaction via the advance of a sharp boundary between the PSC layer and the bulk gel, as shown in Scheme 1. The value of swelling for the polycomplex is 100 times less than that for the initial gel.

The analysis of sorption isotherms of surfactants by the gel indicates that the cationic surfactants interact effectively with cl-PANa at surfactant concentrations of about 2-3 orders of magnitude lower than the critical micelle concentration of corresponding surfactants [4]. It has been shown that the interaction between charged network and oppositely charged surfactant ions is a cooperative reaction followed by the formation of PSC stabilized by salt bonds of ionic groups of the components and hydrophobic interactions between aliphatic chains of surfactants (Scheme 2). Wide-angle X-ray scattering data show that polycomplexes consisting of a surfactant having more than 16 carbon atoms in an aliphatic radical form a crystalline structure. In this case, X-ray patterns contain typical Bragg peaks giving a value of $d = 4.2$ Å.

Two samples have been chosen for small-angle neutron scattering experiments: cl-PANa–D\(_2\)O and cl-PANa–CTAB-2.5% D\(_2\)O, both contained the same amount of cl-PANa, namely 10 wt %. This value equals the concentration of cl-PANa of swollen samples in the equilibrium state. The use of heavy water as the solvent increases significantly the neutron scattering,

![Scheme 1](image)

Scheme 1. — The reaction between cl-PANa and cationic surfactants.
Scheme 2. — The interaction of amphiphilic surfactant ions with the charged network.

the intensity of which is proportional to the square of the contrast. 2.5% D₂O was used as a solvent for the polycomplexes of the gel with CTAB since this concentration of heavy water corresponds to the matching point of CTAB [7].

The neutron scattering curves for these samples were fitted using the Ornstein-Zernike correlation function \( I(Q) \approx 1/(1 + Q^2 \xi^2) \) where \( I(Q) \) is the intensity of scattering and \( \xi \) is the correlation length. It was found that \( \xi = 500 \pm 25 \) Å for the sample of cl-PANa-D₂O and \( \xi = 560 \pm 27 \) Å for cl-PANa-CTAB-2.5% D₂O (Fig. 1). We conclude that the dimension of

Fig. 1. — Small-angle neutron scattering curves for cl-PANa-D₂O sample (1) and for cl-PANa-CTAB-2.5% D₂O (2). Solid lines are the simulation curves.
large-scale density fluctuations of a pure gel is approximately that of a polycomplex. Some increase in the dimensions of the polycomplex seems due to parameters such as humidity and the temperature of air, which were not controlled in our experiments.

Concerning the SAXS data of the cl-PANa-CTAB sample, our X-ray structural studies of PSC suggest the existence of a certain periodicity. Figure 2 shows typical X-ray diffractograms of PSC in both dry and water-swollen states. The scattering curves of dry and swollen samples have two well-pronounced diffraction maxima associated with interplanar spacings $d_1$ and $d_2$ ($d = 2\pi/Q$, where $Q$ is the scattering vector for a maximum). The ratio of $d_1/d_2$ is equal to two. This suggests a lamellar structure with a period of 33 Å and 42 Å for dry and swollen samples, respectively. From the halfwidth of the first maximum one can estimate a dimension of these ordered structures, since the halfwidth of the first maximum $\Delta Q/Q = 1/N$, where $N$ is the lattice period number. In our case $N = 14$, thus the dimension of these ordered structures is $N_d = 590$ Å. This value is in good agreement with that obtained for a correlation radius of the polymer network ($\xi = 560$ Å). In this connection one can assume that the lamella growth during the polycomplex formation process takes place mainly in the regions of the increased density of polyelectrolyte network. So the density inhomogeneities of the initial gel is likely to set the dimension of the lamellar aggregates of the PSC.

For dry PSC the period of lamellar structure is noticeably larger than the calculated length $L$ of the fragment CH-COO$^-$ +N(CH$_3$)$_3$C$_n$H$_{2n+1}$, but smaller than its double value ($L \approx 25$ Å for CTAB). These speculations suggest that the PSC structure shows neither the bilayer packing characteristic of side hydrocarbon chains of comblike poly(alkylacrylate) [8] nor the monolayer packing. We believe that the period of the lamellar structure is determined by the overlapping of hydrocarbon surfactant radicals, as well as by the size of ionic surfactant group.

Our preliminary investigations showed that the lamellar structure is characteristic for all systems cl-PANa- various surfactant cations studied; and the lamellar thickness ($d$) increases with increasing hydrocarbon chain length of alkyltrimethylammonium homologues. Moreover, X-ray diffraction patterns of uniaxially-oriented PSC samples indicated an orientation of surfactant ions perpendicular to polyion fragments of the network [9]. Thus, X-ray data considered
above allow the PSC structure to be represented as a system of charged surfactant lamellae embedded in an oppositely charged network as shown in Scheme 3.

It should be pointed out that the water content of PSC samples has an effect on the lamellar structure. Swelling in water is followed by an increase of lamellar period, \( d \), due to hydration process of ionic groups. It is noteworthy that upon drying of PSC samples neither gradual shift nor broadening of the first SAXS maximum are observed. The SAXS data shows that the intermediate state is characterized by at least two types of lamellar structure, the periods of which correspond to the swollen and dry states. Upon removal of water molecules from the swollen PSC sample, the intensity of the maximum associated with long periods decreases while the intensity of the maximum associated with smaller periods increases. We believe that the discrete character of structural changes of PSC on drying is intriguing and invites to further studies.

The structural data obtained are important for an adequate description of the mechanism of transport of surfactant ions in an oppositely charged gel network. We have shown recently that the adsorption of oppositely charged surfactant ions by charged networks proceeds as a frontal heterogeneous reaction [9]. This process features the existence of a sharp well-defined boundary between the outer layer of a dense weakly swollen polycomplex \( (H \approx 1) \) and the inner strongly swollen layer of intact gel \( (H \approx 10^6) \). Our results attest that the advance of a sharp boundary of polycomplex inside the gel is accompanied by a growth of the lamellae from the periphery to the center of the sample. This process is likely to proceed via the transport of individual surfactant ions and their addition to a growing facet at the boundary between the outer layer of the polycomplex and the inner part of the intact gel [4].

Finally, we would like to emphasize a certain similarity between the structure of PSC and stoichiometric polycomplexes composed of linear polyelectrolytes, in particular, those with surfactant ions. Profiles of these diffractograms correspond to the profile of the diffractogram obtained from the swollen cl-PANa-CTAB sample. It implies that the structural parameters of linear and chemically cross-linked polyelectrolyte analogs are virtually the same, i.e. at low cross-linking densities (one cross-link per 100 monomer units) the network structure of polyelectrolyte is not noticeably distorted with surfactant ions.
References


[7] This value was not determined experimentally but was estimated after calculation of the scattering length density, $\rho_n$, for CTAB which is $\rho_n \simeq -0.20 \times 10^{-10} \text{cm}^{-2}$.

[8] Plate N.A. and Shibaev V.P., Comb-Like Polymers and Liquid Crystals (Moscow, Khimiya, 1980).