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Interactions in the multicomponent system comprising polycationic gel, star-shaped polyanion and cationic surfactants

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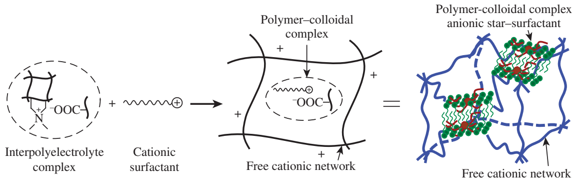
Cationic surfactants can replace a network of the same charge inside the interpolyelectrolyte complex with a star-shaped polyanion with the formation of a composite of polymer-colloidal particles distributed in a polycationic network.

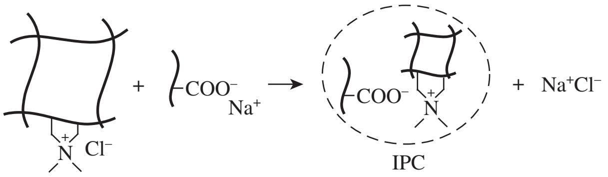


The interaction between polyelectrolytes and surfactants bearing opposite charges as well as the products of such interaction, polymer-colloidal complexes (PCC), have been extensively studied.[1–6] Due to a number of useful properties, PCCs possess promising applications in the modern industry. However, most studies are focused on the properties of two-component systems and individual complexes, while the overwhelming majority of systems with a potential practical usage are of multicomponent nature. When a third charged component is added to the system containing two oppositely charged species, various kinds of interactions could be expected. There are some reports on the analysis of interactions in triple systems of cationic or anionic surfactants and polyelectrolytes,[7–10] but this subject still needs further investigations. In addition, a new class of polyelectrolytes of star-shaped architecture was synthesized and the formation of complexes between these polymers of non-linear topology and oppositely charged polyelectrolytes and some other multicharged species were studied.[11–19] To gain a better insight into the problem of interactions in the multicomponent systems including star-shaped polyions, we examined the triple system containing lightly cross-linked cationic gel, star-shaped polyanion, and different cationic surfactants. In the test system, the polyanionic star may form the complex with either a cationic network or positively charged surfactant.

The initial objects of investigation were interpolyelectrolyte complexes (IPC), which are the products of sorption of the anionic star-shaped polyacrylic acid [$(PAA_{100})_{21}$] by the slightly cross-linked poly(diallyldimethylammonium chloride) (cPDADMAC) cationic gel.[†] The driving force of the interaction between cPDADMAC and $(PAA_{100})_{21}$ (see ref. 12) is a cooperative electrostatic binding of anionic star groups to the cationic groups of the gel (Scheme 1).

Initially highly swollen gel (H~550) transformed into a compact lightly swollen IPC (H~1) within ~36 h. To estimate the composition of IPCs, the molar amount of $(PAA_{100})_{21}$ sorbed by the gel sample was measured[‡] and the molar amount of the gel cationic groups was calculated from the sample mass and the gel swelling ability (see Procedure S1, Online Supplementary Materials). Being the ratio between molar amount of carboxylate groups of the star polyanion and that of cationic groups of the network, the composition of the resulting IPC appeared to be 1 : 1, *viz.* the IPCs contain equivalent amounts of anionic and cationic groups, and therefore all positively charged groups of the network sample are bound with negatively charged groups of the star.

Further the IPCs of cPDADMAC and $(PAA_{100})_{21}$ were immersed into surfactants solution (0.01 M)[§] and the occurring processes



Scheme 1

[†] cPDADMAC was prepared by the free-radical copolymerization of the corresponding monomer with *N*,*N*′-methylene-bis(acrylamide) (0.5 wt% from the monomer weight) as a cross-linking agent in 50% aqueous solution using potassium persulfate as an initiator (0.25 wt%).[20] The gel was washed with an excess of distilled water, the equilibrium swelling ability *H* for cPDADMAC was equal to 550 [$H = (m_{sw} - m_d)/m_d$, where m_{sw} and m_d are the weights of an equilibrium swollen and dried to a constant weight gel samples, respectively] (see Procedure S1, Online Supplementary Materials).

Star-shaped polyacrylic acid with 21 arms, each having the degree of polymerization of 100 [$(PAA_{100})_{21}$], was synthesized and kindly provided by Dr. F. A. Plamper (Aachen University, Germany) and Professor A. H. Muller (Bayreuth University, Germany). The polymer was obtained by atom transfer radical polymerization of *tert*-butyl acrylate on the β-cyclodextrin central molecule followed by hydrolysis with trifluoroacetic acid (for details of the synthesis, see ref. 21).[21] Due to being used in the form of sodium salt in all experiments, star-shaped polyacrylic acid aqueous solution (0.01 base-mol dm^{-3}) was neutralized with an equivalent of NaOH (1 M). The concentration of [$(PAA_{100})_{21}$] in the aqueous solutions was measured by potentiometric titration.

[‡] IPCs were obtained by immersing the gel samples (1–1.5 g) into an aqueous salt-free $(PAA_{100})_{21}$ solution (0.01 base-mol dm^{-3}) under twofold excess of carboxylate groups relative to the amount of amino groups of the network.

[§] Cetylpyridinium chloride (CPC, TCI), dodecylpyridinium chloride (DPC, Tokyo Kasei Kogyo Co. Ltd.), cetyltrimethylammonium bromide (CTAB, Aldrich), dodecyltrimethylammonium bromide (DTMAB, Sigma-Aldrich), and benzyldimethylhexadecylamonium chloride (BDMHA, Sigma) were used as received. The concentrations of surfactants were measured spectrophotometrically by the absorption band intensity at 258 nm.

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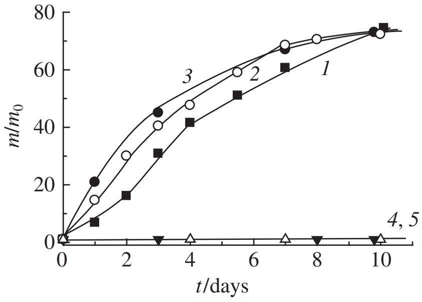


Figure 1 The relative mass of the IPC samples *vs.* time after immersing into the different surfactant solutions: (*1*) CTAB, (*2*) CPC, (*3*) BDMHA, (*4*) DPC, and (*5*) DTMAB, gel sample mass was 1 g, $T = 20\,°\mathrm{C}$.

were studied. Different behavior of the system depending on the surfactant used was revealed for IPC samples in contact with surfactant solutions. Below we consider the processes that take place in the course of interaction of [cPDADMAC–$(PAA_{100})_{21}$] complexes with CTAB, CPC, and BDMHA. In Figure 1, the changes of IPCs mass are shown, *viz.* the relative mass value, m/m_0, where m is the sample mass at a given time and m_0 is the mass of the initial IPC (for experimental details, see Procedure S2). In the systems with CTAB (curve *1*), CPC (curve *2*), and BDMHA (curve *3*), a significant increase of the sample masses is observed. After approximately ten days, the swelling of the samples reached its maximum value and remained constant. At the same time, the decrease of the surfactant concentration in the solutions was revealed. The kinetic curves of sorption of CPC (curve *1*) and BDMHA (curve *2*) from their aqueous solutions by IPCs [cPDADMAC–$(PAA_{100})_{21}$] are shown in Figure 2, where the ν/ν_0 is the ratio of molar amounts of surfactant sorbed by the IPC sample to that of either the carboxylate groups of the star-shaped polyanion or the network amino groups since initial IPCs contain equal amounts of negatively and positively charged groups (for calculation details, see Procedure S3).

Along with the remarkable increase of the IPCs mass and volume, the sorption of surfactants by [cPDADMAC–$(PAA_{100})_{21}$] complexes occurred. Note that the maximum molar amount of the surfactant sorbed by IPCs was equal to that of star-shaped polyacrilic acid carboxylate groups, and the additional uptake of the surfactants from a solution did not proceed after this degree of sorption was achieved. Rather significant changes in the appearance of the samples were also detected. The compact rubbery slightly yellowish initial IPCs transformed into fragile, highly swollen, milky-white products of surfactant sorption. Note that the star-shaped polyacrilic acid did not release from the reaction products into the surrounding solution.

The X-ray patterns of the samples showed that dried products of sorption possessed a crystal structure, lamellar in the case of CTAB and more complicated for BDMHA (see Figure S1, Online Supplementary Materials). The conclusions about the structure of swollen samples may be based on the data for dried samples, since previously[22] for the interaction of polyelectrolyte gel with oppositely charged surfactants it was shown that the crystal structure of PCCs formed just during the interaction between the components. The similar crystal structures were detected for both swollen and dried samples of PCCs with only slightly changes in the parameters.

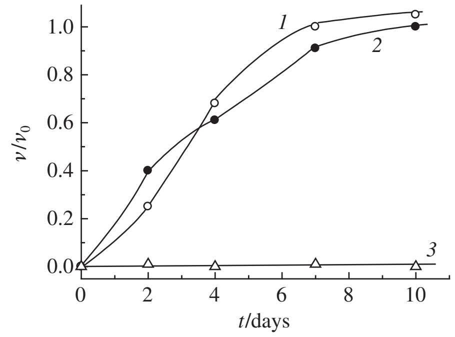
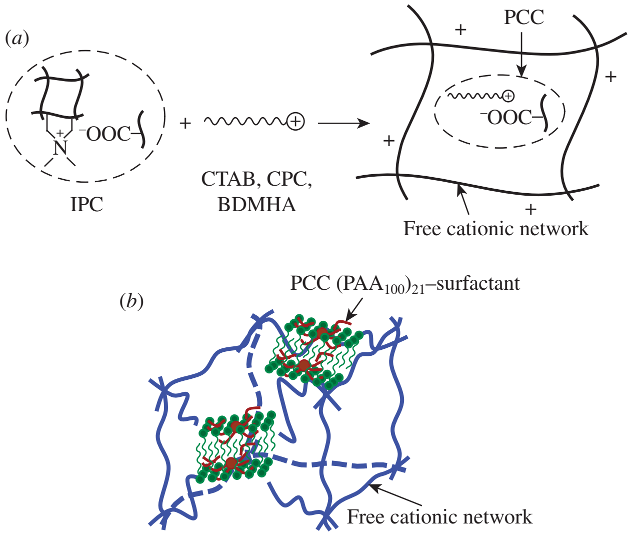


Figure 2 The kinetic curves of surfactant sorption by [cPDADMAC–$(PAA_{100})_{21}$] interpolyelectrolyte complexes for (*1*) CPC, (*2*) BDMHA, and (*3*) DPC, gel sample mass was 1 g, $T = 20\,°\mathrm{C}$.

In the system discussed, the X-ray patterns of both the products of surfactants sorption by IPCs and the products of interaction in binary systems $(PAA_{100})_{21}$–surfactant revealed the identical parameters of crystalline structure for PCCs formed. This fact indicates the formation of polyanion star-surfactant PCC in the network phase.

According to the above experimental results, one can conclude that the surfactants sorbed by the IPC [cPDADMAC–$(PAA_{100})_{21}$] displace the cationic gel in IPC with the star-shaped polyacrylic acid and form a new PCC with star polyanion, while the network releases from the interactions with $(PAA_{100})_{21}$. The reaction carried out in the system (*a*) and the resulting product (*b*) are shown in Scheme 2.



Scheme 2

As a result of interaction of IPC [cPDADMAC–$(PAA_{100})_{21}$] with CPC, CTAB or BDMHA, the triple composite consisting of free cationic network filled with PCC [$(PAA_{100})_{21}$–cationic surfactant] particles is formed. The increase in swelling ability of the samples is provided by the contribution of the small counter ions within the free fragments of the cationic gel to the osmotic pressure. However, it should be noted that the swelling ability of the samples after surfactant sorption did not achieve the value for the initial free gel. One can assume that entanglements are formed between the network units and newly formed PCC particles, which restricts the gel swelling ability and prevents the release of the PCC from the swollen gel sample. Earlier the similar kind of transformations was observed for the interactions of ionic surfactants with IPC of charged gels and oppositely charged linear polyanions.[9] So, the possibility of the substitute reaction in our system is in a good agreement with the known data.

By contrast, in the case of the systems containing IPC [cPDADMAC–$(PAA_{100})_{21}$] and DPC or DTMAB, after immersing of the IPCs into surfactant solutions no changes were observed. As it is seen from Figure 1 (curves *4* and *5*) and Figure 2 (curve *3*), the mass of the IPCs after interaction with DPC or DTMAB solutions did not change and the surfactant concentration in the solutions remained constant. Thus, in this case the sorption of surfactants by IPC samples did not proceed.

Previously, upon studying the interactions in the triple systems containing oppositely charged linear polyelectrolytes and different kinds of ionic surfactants, the influence of several parameters, such as the nature of the competitive polyion and surfactant, as well as pH, temperature, and the nature of counter ions, on the direction of the substitution reactions were discussed.[7] In the systems under consideration, the substitution reaction with the formation of PCC proceeds only for the surfactants with relatively long hydrophobic tail (CTAB, CPC, BDMHA). One can see that the alteration of the surfactant ionic group does not change the reaction course. This fact confirms a considerable contribution of the non-polar interactions in stabilization of the PCCs formed.

Thus, the hydrophobicity of a surfactant is proved to be the main factor determining the equilibrium of the substitution reaction in the test triple system. Previously,[7] the ability of alkylcarboxylated surfactants to replace polymethacrylate ions in their complexes with linear polycations was found to decrease in the following order: $C_{11} > C_9 > C_8$ according to the changes in the critical micelle concentration, which confirms the role of hydrophobic interactions in this reaction.

In conclusion, the obtained results revealed the possible character of interactions in the multicomponent mixture containing lightly cross-linked polycation, star-shaped polyanion, and the series of cationic surfactants with different hydrophobic tail lengths. The capability of star-shaped polyanions to be involved into the substitution reactions yielding a triple composite, in which PCC particles are formed in the swollen cationic gel, was established. By changing the nature of a surfactant it is possible to control the direction of the process in this triple system. The substitution reaction described could be used for the development of novel complex composites incorporating PCC of anionic stars with cationic surfactants trapped in the charged swollen network.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.09.031.

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