6362 *Macromolecules* **2002,** *35,* 6362−6369

Composite Gels of Poly(acrylamide) with Incorporated Bentonite. Interaction with Cationic Surfactants, ESR and SAXS Study

S. G. Starodoubtsev,[†] A. A. Ryabova,[†] A. T. Dembo,[‡] K. A. Dembo,[‡] I. I. Aliev,[§] A. M. Wasserman,[§] and A. R. Khokhlov*,[†]

Physics Department, Moscow State University, Vorobjevy Gory, Moscow 117234, Russia; Institute of Crystallography, Russian Academy of Sciences, 59 Leninsky Pr., Moscow 117333, Russia; and Institute of Chemical Physics, Russian Academy of Sciences, Kosygina 4, Moscow 119991 Russia

Received November 19, 2001; Revised Manuscript Received April 21, 2002

ABSTRACT: The swelling behavior and the structure of composite gels of poly(acrylamide) with incorporated bentonite clay and the products of their reactions with a cationic surfactant, cetylpyridinium chloride, were studied by SAXS and ESR (spin-probe) methods. The ESR data show that the adsorption of CPC on the clay platelets already leads to the formation of the ordered surfactant aggregates with low molecular mobility in the region of surfactant concentrations much below the cmc. A SAXS study demonstrates that further adsorption of the surfactant results in the formation of lamellas, including alternating layers of clay platelets and double layers of CPC. These two steps of the adsorption are accompanied by the strong shrinking of the gel composite. At high concentrations of the surfactant, total overcharging of the surface of the clay particles occurs, resulting in a change in the direction of the electroosmotic transport of water through the gel and in the reswelling of the gel composite. The models of the clay/surfactant complexes in the gel phase are discussed.

Introduction

Slightly cross-linked gels loaded with dispersed clays are a new class of composite materials which combine elasticity and permeability of the gels with high ability of the clays to absorb different substances.[1−3] The clay particles embedded in the cross-linked swollen polymer network strengthen the gel and prevent its collapse in bad solvents. On the other hand, immobilization in the cross-linked network prevents coagulation of dispersed clay particles.[4,5]

Among the other clays montmorillonite (MONT) and bentonite (BENT) (i.e., the clays with a high content of MONT) are the most important and widely used absorbents for organic compounds.[6−9] This property is related to their ability to show extensive swelling in water. By this means, MONT has a large active surface area (700−800 m^2/g).[8] This peculiarity makes MONT and BENT most popular for use in the gel−clay absorbers.

The layer structure of clay minerals was deduced by Pauling.[10] Each layer of MONT consists of two silica sheets and one aluminum sheet between them.[7,8] A silica sheet has two planes of oxygen/hydroxyl ions, one of which consists of the bases and the other of the tips of linked Si(O, OH)$_4$ tetrahedrons. Aluminum sheet contains octahedral plane of Al^{3+} ions, coordinated to the −O− and −OH groups. Because of isomorphic substitution of Si^{4+} for Al^{3+}, the SiO$^-$ groups whose charge is not compensated form salt bonds with their counterions or hydrolyze with the formation of SiOH groups. Figure 1a schematically shows the single platelet of sodium salt of MONT surrounded with counterions.

In a dry state the crystals of MONT are composed of multilayers, schematically shown in Figure 1b. The swelling in water results in the disorder of the layers. Because of attraction forces between the edges of the crystallites and the platelets the clay forms highly

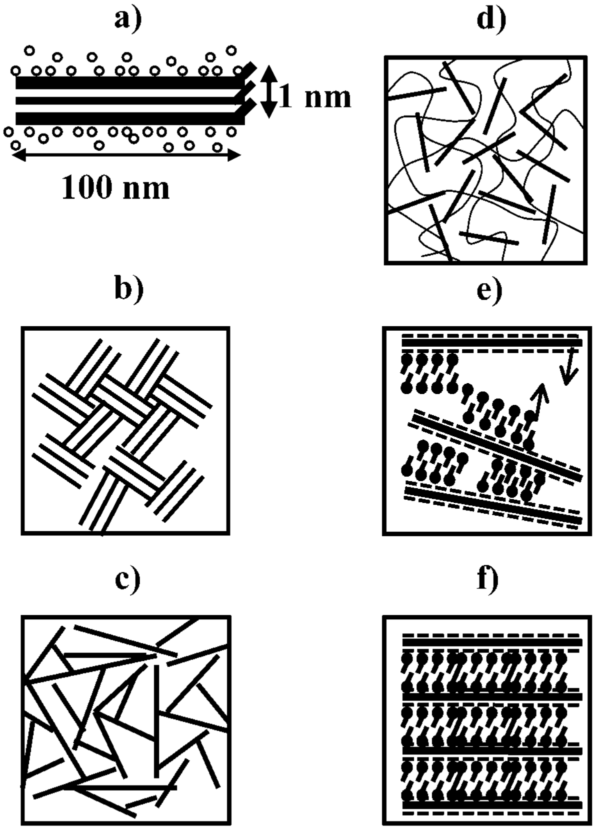


Figure 1. Schematic representation of the structure of BENT suspension in water and in the gel phase: a single platelet (a), the dried clay powder (b),the card-house structure (c), the dispersion of BENT embedded in PAAm gel after ultrasonication (d), the formation of surfactant aggregates on the surface of BENT platelets (e) and the structure of lamellas with intercalated CPC (f). Each line in parts b−f represents a single platelet, which is composed of three layers.

[†] Moscow State University.
[‡] Institute of Crystallography, Russian Academy of Sciences.
[§] Institute of Chemical Physics, Russian Academy of Sciences.

10.1021/ma012021z CCC: $22.00

viscous liquid (gel) with a structure schematically shown in Figure 1c (the card-house structure).[7,8] Further dilution leads to complete disorder of the clay platelets and to the formation of the stable colloid dispersion with low viscosity.

Previously we have shown that the particles of BENT suspension embedded in poly(acrylamide) gel (PAAm) adsorb a cationic surfactant, cetylpyridinium chloride (CPC).[4,5] Adsorption is accompanied by the shrinking of the gel composite. However, at high surfactant concentration, the reentrant transition to a swollen state takes place.

The goal of this paper is the study of the conformational and structural changes in the gel−clay composites induced by the interaction with cationic surfactant. We investigated the composites based on the cross-linked PAAm with embedded BENT. CPC was used as the cationic surfactant. The concentration of the cross-links in the networks was 1/100 and 1/500 monomer units of the polymer chains. The dimensions of the clay platelets in the composite were large in comparison with the mesh size of the network; therefore, they are unable to diffuse out of the gel.

Experimental Section

Sample Preparation. The clay, BENT, acrylamide (AAm), *N*,*N*′-methylenebis(acrylamide) (BAA), and ammonium persulfate were purchased from Fluka Chemika. CPC was obtained from Koch-Light Lab. Ltd. Chemical composition of BENT was as follows. Anal. Calcd: Na, 4.35; Ca. 1.7; Fe, 1.6; Al, 11.4, Si, 29.8, O, the rest. The chemical composition of BENT was determined in the Laboratory of the Microanalyses of the Institute of Elementoorganic Compounds of Russian Academy of Science.

Two gels with different prehistory and concentration of the cross-links were prepared. Gel I was prepared as follows. A 0.24 g sample of BENT was added to 9.76 g of a 6 wt % solution of monomers with a molar ratio of AAm to BAA of 100:1. The obtained suspension was mixed by a magnetic stirrer for 1 h. After this the suspension was kept for one night. The next day the suspension was mixed for 4 h. Then it was heated to 40 °C. Then 5 μL of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and 50 μL of a 10 wt % solution of ammonium persulfate in water were added to the heated suspension. Polymerization was carried out in the glass tubes of diameter 3.8 mm at 40 °C for 2 h and then at 25 °C for 24 h. The tubes were isolated from the air by Parafilm. The obtained gel was removed from the tubes, cut into cylinders of height ca. 4 mm, and washed with a large excess of distilled water for 2 weeks. The water was changed every 2−3 days. After that the gel samples were equilibrated in an air thermostat in closed vials containing a known amount of water and surfactant at 25 °C for 1 month.

The suspension of BENT for gel II was prepared in the same manner as for the gel I, but without monomers. Finally it was sonicated for 1 h. For the sonication the Sonorex Super RK255 system (Volkswagen, Wolfsburg, Germany) was used. After the suspension was heated, the monomers were added, and after intensive stirring, TEMED and PS were injected into the mixture. In the gel II, the molar ratio of AAm to BAA was 500:1. The time of intercalation of the monomers between the particles of BENT for the gel II was small (about 10 min) in comparison with the gel I (24 h.).

The swelling of the gels was characterized by the ratio F = m_{eq}/m_d, where m_{eq} is the weight of the gel at equilibrium and m_d is the weight of the dried composite. Since the swelling ratio of the gels was not stable in time, it was specially measured before each set of experiments.

The content of mobile sodium ions in BENT was determined by flame photometry using wavelength 589 nm at maximum of transmission. The measurements were performed using a Carl Zeiss Jena AAS1 atomic absorption spectrometer by the method of external standard. Comparison samples were prepared by dilution of standard Merck solution. As it was estimated, the concentration of sodium in BENT was 4,35 wt %. The composition of the complexes of the gels with surfactants was characterized by the ratio *Q* between the total number of the surfactant ions in the gel phase, $[\mathrm{CPC}]_g$, and the number of Na^+ cations, $[\mathrm{Na}^+]$, contained in BENT that were inside the gel sample before the interaction with surfactant. The amount of the surfactant absorbed by the gel was determined using spectrophotometry after the replacement of the surfactant ions from the gel by sodium ions of NaCl in water−ethanol mixtures.[4] Extraction was performed in 50 vol % of aqueous ethanol saturated with sodium chloride (concentration about 2 M) for 3 days. Previously we have shown that under these conditions one extraction is enough to remove more than 95% of the surfactant from the gel.[11] Thus, taking into account the weight content of sodium in BENT (0.0435) and the weight fraction of BENT in dry gels (0.024/0.084), the values of *Q* were calculated by the formula

$$Q = [\mathrm{CPC}]_g/[(m_{eq}/F) \times 0.0124] \qquad (1)$$

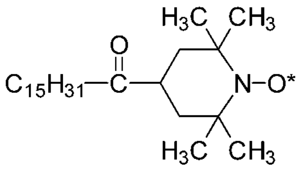
Optical density was measured by a Hewlett-Packard 8452 spectrophotometer. In the preliminary study it was shown that PAAm gel without BENT does not absorb the excess of the surfactant in comparison with water. The calculations show that at a concentration of CPC below ca. 0.01, BENT adsorbs practically all of the surfactant contained in the gel.

SAXS Study. The small-angle X-ray scattering (SAXS) measurements were carried out at the Institute of Crystallography, Russian Academy of Sciences, using a SAXS diffractometer AMUR-K[12] with a linear position-sensitive detector.[13] The detector had a window of 10 × 100 mm, and the range of measured q is $0.1 \leq q \leq 10$ nm^{-1} with $q = 4\pi(\sin\theta)/\lambda$ and 2θ being the scattering angle. The monochromatization was achieved with a crystalline monochromator; the incident beam wavelength was tuned at 0.1542 nm. The thickness of samples was ca. 1 mm. The experimental data were corrected for background scattering and sample transmission. The collimation smearing effect was also corrected for this setup.

ESR Study. ESR spin-probe spectra were recorded by a RADIOPAN X-band ESR spectrometer for unsaturated conditions at 20 °C. Rotational correlation times of spin-probe (τ) in fast rotational motion region were determined by the relation

$$\tau = 6.65\Delta H_{(+1)}\left(\sqrt{\frac{I_{(+1)}}{I_{(-1)}}}\text{-}1\right) \times 10^{-10}\ \mathrm{s} \qquad (2)$$

where $I_{(+1)}$ and $I_{(-1)}$ are the intensities of spectrum components in low and high fields, respectively, and $\Delta H_{(+1)}$ is the width of the spectrum components in the low field.[14] As a spin-probe the amphiphilic stable nitroxide radical containing 15 carbon atoms in the hydrocarbon chain was used:



The typical ESR spectrum of the spin-probe probe is shown in Figure 6a.

The samples containing the spin-probe were prepared by addition of 0.06 M solution of CPC ($c \gg$ cmc) with solubilized radical (50/1) to the gels in aqueous media.

Experimental Results

Swelling of the Composites. The swelling of the gel−clay composites is strongly affected by the osmotic pressure of the counterions of the clay particles. Because of this, the swelling ratio of the composites demonstrates

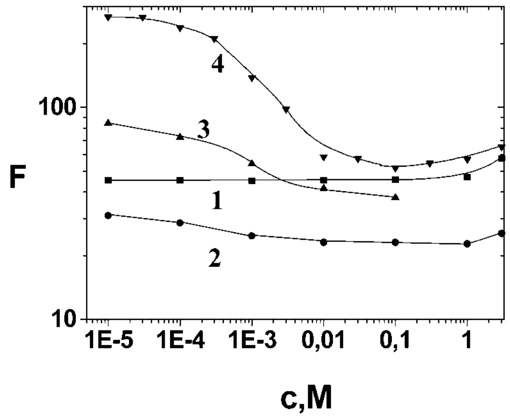


Figure 2. Dependencies of the swelling ratio, *F*, on the concentration of sodium chloride *c* for PAAm gel without BENT (concentration of the cross-links 1/500) (1) and for gels I (2) and II (3, 4) taken from water (2, 3) and from the concentrated salt solution (4).

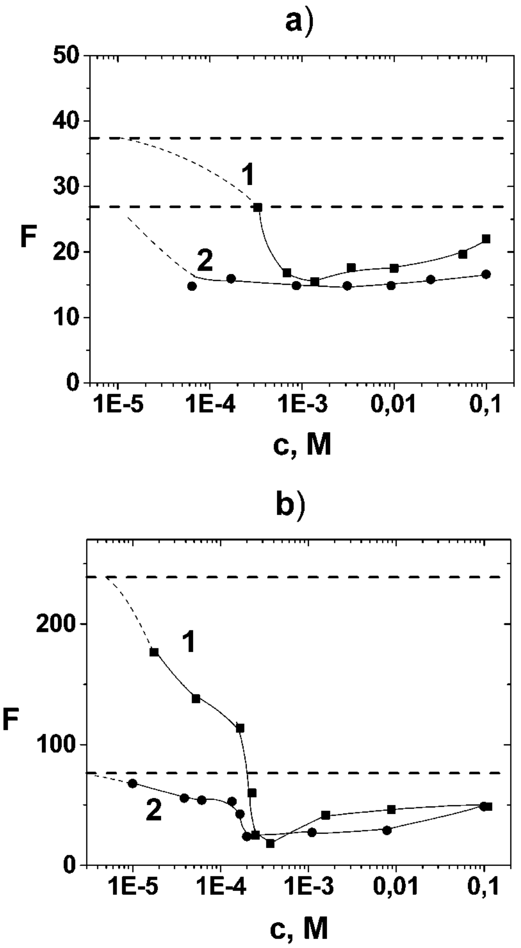


Figure 3. Dependencies of the swelling ratio *F* on the concentration *c* of CPC (a) for gel I in water (1) and in 0.01 M sodium chloride (2) and (b) for gel II in water (1) and in 0.01 M NaCl (2). The dotted lines show the swelling ratio of the gels in water and in 0.01 M sodium chloride.

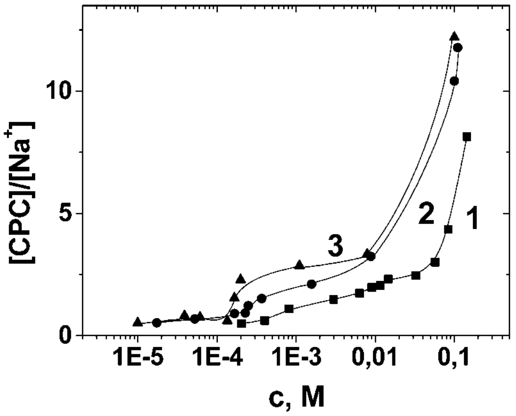


Figure 4. Isotherms of absorption of CPC by the gel composites for gel I in water (1) and for gel II in water (2) and in 0.01 M NaCl (3).

a strong pH dependence.[2] The osmotic pressure of the counterions is most pronounced in the absence of salt, while at a high ionic strength it is strongly decreased and the degree of swelling of the network with embedded clay particles approaches that of the neutral gel.[5,6]

Figure 2 shows the plot of the swelling ratio *F* vs the concentration of sodium chloride, *c*, for the gels. The swelling ratio of the neutral PAAm gel without BENT does not depend on the concentration of salt up to the region of a very high concentration of sodium chloride where the density of aqueous salt solution increases (Figure 2, curve 1). The swelling ratio of PAAm gels containing BENT decreases with *c* (Figure 2, curves 2−4). The effect is more pronounced for gel II with a smaller content of the cross-links (0.2 instead of 1.0 mol %).

The swelling ratio of the gels strongly depends on their prehistory. In Figure 2, the values of *F* for the curves 2 and 3 were obtained for the different pieces of the gels which were put in salt solutions after washing (see Experimental Section). The values of *F* for curve 4 were also obtained for gel II. For the case of curve 4, the gel was at first put in the solution of sodium chloride with a concentration of 3 M and then sequentially put in lower concentration salt solutions. The values of *F* for this gel are significantly higher, especially in the region of low concentration of sodium chloride. This result can be explained by the ion exchange of Ca^{2+} ions of BENT for Na^+ ions of salt[7] and probably by a partial replacement of H atoms in the SiOH groups by sodium cations. In both cases, the osmotic pressure created by the clay counterions should significantly increase.

The complete drying of the gel composite followed by its swelling results in the decrease of the values of *F* due to the formation of the additional bonds between the edges and the clay platelets in the dry state (Figure 1c). These bonds partly remain after the gel swelling. For instance, in water, the value of *F* for gel II decreases from 84 to 40 after drying. We have shown that ultrasonication of the swollen gel which was undergoing the drying destroys the new contacts between the clay crystals and initiates its additional swelling. The more detailed study of the effect of sensitivity of the gels to the ultrasound is now in progress.

The decrease of the swelling ratio of the composite gels is also observed after a long stay of the sonicated samples in water (if during the observations water is not changed). For gel II the value of *F* in water decreased from 84 to 56 after 3 months of observation. Before polymerization, the contacts between the clay particles in the clay suspension were destroyed by the ultrasound, and this state was fixed during the network formation (Figure 1d). However, despite the small mesh size of the network, some fraction of the bonds between the clay particles is slowly restored, and the gel slightly shrinks for this case as well.

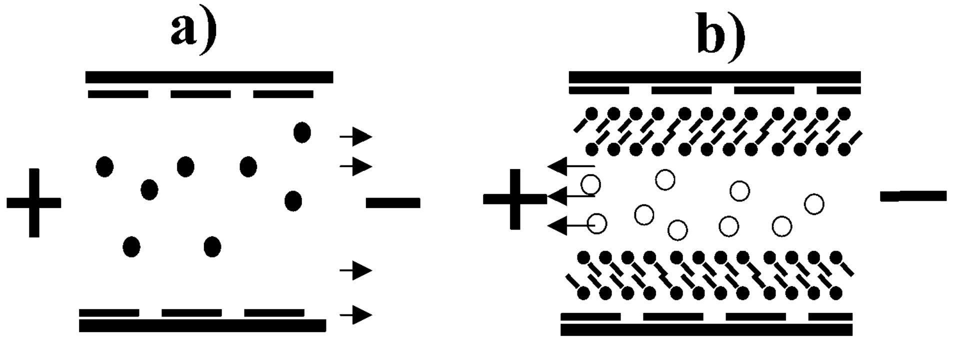


Figure 5. Scheme of electroosmotic transport of water in the composite gels before (a) and after (b) their modification with CPC.

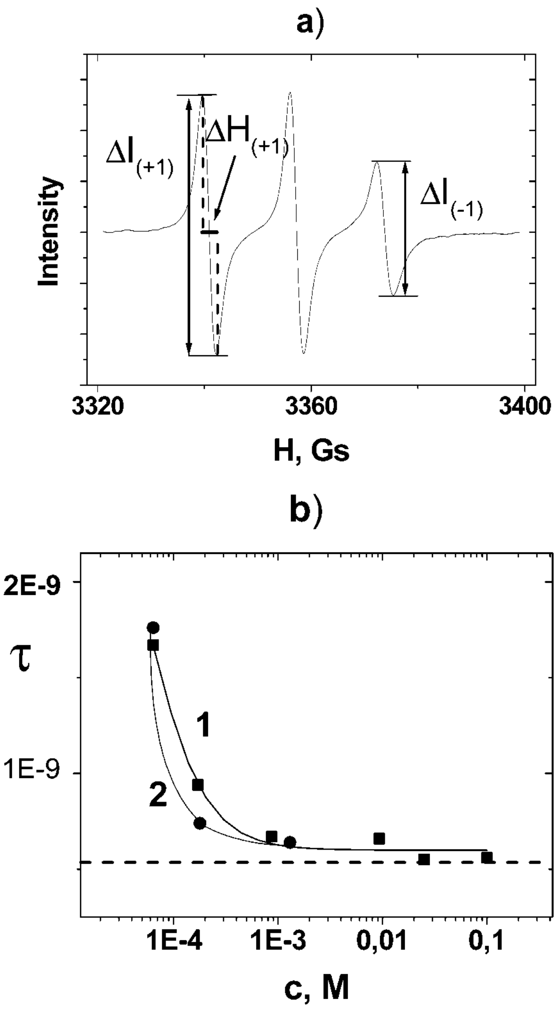


Figure 6. (a) Typical ESR spectrum of the spin-probe in gel I ($c = 8.7 \times 10^{-4}$ M) (see explanations in the Experimental Section). (b) Dependencies of the correlation time of the spin-probe in gels I and II on the concentration, *c* of CPC.

Interaction of the Composites with CPC. Figure 3 shows the effect of CPC on the swelling ratio of the composites. At low concentrations of CPC, much less than its cmc in water (cmc $\sim 9 \times 10^{-4}$ M), a pronounced contraction of the gels is observed. Further increase of the surfactant concentration leads to the gel swelling. This effect is more pronounced for gel II with a smaller concentration of the cross-links. In the presence of CPC, even in the region of very low surfactant concentrations, the gel shrinking is much more significant than that in a solution of salt with a high ionic strength. The osmotic effects due to the clay counterions cannot explain the latter observation.

It is well-known that the anionic particles of clays can absorb organic substances due to the ion exchange and also due to the intercalation of the organic substance between the platelets of the clays.[6−9] In the case of the gel−clay composites, there is a third pathway for absorption of the cationic surfactant, namely free penetration of the surfactant ions in the space of the neutral swollen network, which is not occupied by the clay particles. The calculations show that at low concentrations of CPC (ca. below 0.01 M), its amount in the network due to free penetration is negligibly small and the absorption is a result of the interaction of the surfactant with the clay particles embedded in the neutral gel.

The isotherms of absorption of CPC by the PAAm−BENT composites are shown in Figure 4. The dependencies of *Q* on *c* have a tendency to intermediate saturation (plateau region) at rather high concentration of the surfactant. The number of surfactant ions absorbed by the gel can be higher than the initial number of sodium ions which were contained in the clay. The amount of the surfactant absorbed by the gel in the plateau region can be as much as two times higher than the number of sodium ions contained in the clay.

The comparison of curves 1 and 2 in Figure 4 shows that for the same surfactant concentration, gel II absorbs more CPC than gel I. The observed difference in absorption properties of the gels can be explained by several reasons. First, the suspension of BENT for gel II (in contrast to gel I) was ultrasonicated. Because of this the aggregation of the platelets in gel II should be lower and their effective surface higher than in gel I. Second, in our previous study it was shown that the increase of the cross-link density in the composite gels containing the same ultrasonicated suspension of BENT can itself lead to the decrease of the efficiency of the absorption.[11] Third, the time of intercalation of BENT with the solution of monomers in the case of gel I was much higher in comparison with gel II. It can be assumed that the intercalation of BENT by the PAAm after polymerization with the formation of gel I is more complete. As a result, polymer chains hinder the adsorption of CPC by the clay platelets due to steric reasons. An analogous effect of the marked decrease of absorption of neutral organic substances was observed by us in the previous paper.[11]

The comparison of curves 2 and 3 in Figure 4 shows that the absorption ability of the composite gel II in the presence of 0.01 sodium chloride is higher than in water. By analogy with linear polyelectrolyte networks,[15] this effect can be explained by the incorporation of the ions of the low molecular weight salt to the clay−surfactant complex. This effect will be studied in detail in another publication.

Electroosmotic Transport of Water in the Composite Gels Modified by CPC. Electroosmotic transport of water in the composite gels was used as a tool for the study of the sign of the charge of the mobile ions in the gel phase. Experiments were performed as described elsewhere.[16,17] It is known that at low ionic strength each of the mobile ions moving in the phase of polyelectrolyte gel can transport as much as 10^3-10^4 molecules of water due to the electroosmotic effect.[17]

Figure 5 shows the scheme of the electroosmotic transport of water in the composite gels. The gels are represented as capillaries with the walls composed of the BENT platelets. Under the action of the electric field in the composite gels free of CPC the ions of sodium move from anode to cathode. The measurements of the gel weight show that the action of DC results in significant release of water from the gel. The calculations show that in pure water for gel II the number of water molecules N transported by one sodium ion is equal to $N = 360$. Obviously, this number is much higher than the number of water molecules in the hydrate shell of the ion; therefore, this effect can be attributed to the electroosmotic transport in porous medium.[16] After modification of the composite by the cationic surfactant in 0.01 M CPC the inversion of the charge of the mobile ions occurs and the release of water is observed near anode. In the latter case, the value of N is smaller, $N = 40$. These experiments demonstrate that in the solutions of the cationic surfactants the surface charge of BENT is reversed.

The marked difference between the amounts of water transported by the single ion in the surfactant-free and the surfactant modified composites can be explained by the large difference in their swelling ratios. As it was demonstrated above, the addition of CPC results in significant shrinking of the gels. The decrease of the gel swelling leads to the decrease of the effective dimensions of the pores of the gel and hence to lower values of N.

Rotational Mobility of the Amphiphilic Spin-Probe in the Composites Modified by CPC. The solubility of the spin-probe in water is very small and its molecules cannot be recorded by the ESR spectrometer. Thus, in the ESR study were recorded only those radicals which were solubilized by the surfactant micelles or other types of the surfactant aggregates.

Figure 6b shows the dependencies of τ on the concentration of CPC in the outer solution for gels I and II. Despite the significant difference in the prehistory, concentration of the cross-links, the presence of salt, etc., both experimental curves are practically coincident. At a low concentration of CPC, the values of τ are high and the mobility of the probe is small. However, the increase of the concentration of the the surfactant leads to a fast decrease of τ. Finally the values of τ become the same as for the probe in the solutions of CPC at the concentrations higher than cmc, i.e., the same as in the free micelles in water (the dashed line in Figure 6b).

SAXS Study. Figure 7a shows SAXS profiles obtained from initial dry BENT powder (curve 1), from the surfactant-free composites (curves 2 and 3), and from the BENT−CPC complex (curve 4). The complex was obtained at a 2-fold excess of the surfactant in a 0.5 wt % dispersion of BENT. The scattering curve obtained from BENT powder shows rather broad maximum located at the scattering vector $q = 4.67$ nm. The peak location corresponds to the d spacing $d = 1.34$ nm. After dispersion in water and the preparation of the gels, the scattering curves significantly change. Because of the intercalation of PAAm between the clay layers during the gel preparation a strong broadening of the

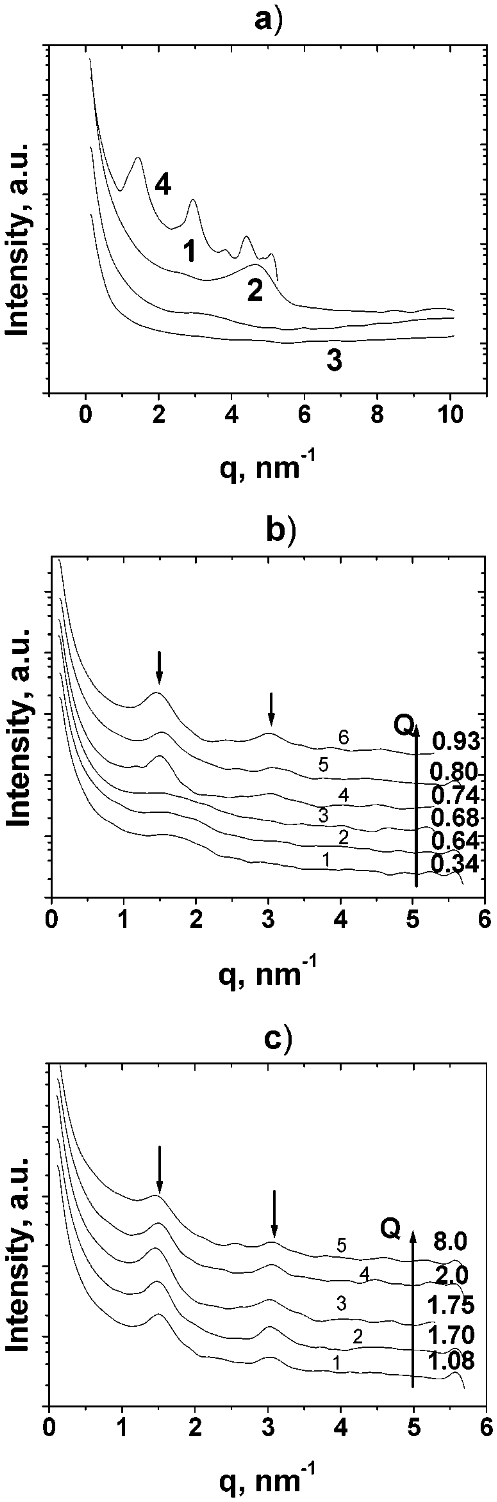


Figure 7. (a) SAXS profiles of BENT powder (1), dried PAAm−BENT gel II (2), swollen PAAm−BENT gel II in 0.01 M solution of sodium chloride (3), and swollen BENT−CPC complex obtained at $Q_0 = 2.0$ (4). (b) SAXS profiles of PAAm−BENT gels I and II at low values of Q (gel I, $Q = 0.34$ (1), $Q = 0.64$ (2), and $Q = 0.80$ (5); gel II, $Q = 0.68$ (3), $Q = 0.74$ (4), and $Q = 0.93$ (6)). (c) SAXS profiles of PAAm−BENT gels I and II at high values of Q (gel I, $Q = 1.08$ (1), $Q = 1.70$ (2), $Q = 2.0$ (4), and $Q = 8.0$ (5); gel II, $Q = 1.75$ (3)).

maximum is observed for gel II even in the dried state (Figure 7a, curve 2). The maximum is positioned at $q \sim 3.2$ nm^{-1}, and the d spacing corresponds to the characteristic size between 1.9 and 2.0 nm. For the gel composites in the swollen state, no maxima are observed on the scattering curves obtained from gel II (Figure 7a, curve 3). The scattering curve obtained from the BENT−CPC complex shows three maxima at $q = 1.45$, 2.90, and 4.37 nm^{-1}. The location of the peaks indicates the lamella structure of the complex. The positioning of the first maximum corresponds to $d = 4.33$ nm. The length of the fully stretched single ion of CPC is about 2.5 nm. The characteristic size of 4.33 nm demonstrates the formation of lamellas built of the clay platelets with intercalated double layers of the surfactant between them.

Figure 7b shows the scattering curves obtained from the gel−surfactant complexes with low values of Q, i.e., obtained in rather diluted solutions of CPC. The absorption of CPC by the composites at low surfactant concentrations, c ($c = 2-4 \times 10^{-5}$) leads to the appearance of the weakly pronounced broad maximum at $q \sim 1.6$ nm corresponding to $d = 3.9$ nm (curves 1, 2, 3). This value is significantly higher than the characteristic d value for the length of the fully stretched single ion of CPC. Further absorption of the surfactant by BENT leads to the appearance of two maxima at $q = 1.53$ and 3.06 nm^{-1} corresponding to $d = 4.1$ and 2.05 nm (curves 4, 5, and 6). The location of the peaks has a ratio of 1:2 and indicates the lamellar structure of the scattering elements.

Curves 1−5 in Figure 7c show the scattering curves obtained from the gels with a higher content of CPC. Their important feature is a very weak dependence of the positioning and of the relative width of the peaks on Q. Moreover, the significant variation in the methods of the preparation of the composite gels I and II, the difference in their swelling ratio and, hence, in the concentration of the clay particles in the gel phases, practically do not affect the positioning and the relative intensity of the scattering curves. The results obtained show that the structure of the clay/surfactant complex, once formed, practically does not change with the increase of the surfactant concentration.

Discussion

PAAm gels with embedded particles of BENT show a polyelectrolyte behavior. The decrease of the ionic strength of the solution results in a significant increase of swelling ratio of the gels due to osmotic pressure of counterions. On the other hand, the slow process of the recovery of the “card house” structure of the composite gels leads to the decrease of the swelling ratio. However, within the time of the observation, ca. 2 weeks (the time needed for the equilibration with the surfactant), the second process can be neglected. The free energy of the composite gel may be written as[4]

$$\Delta G = \Delta G_{\text{el}} + \Delta G_{\text{int}} + \Delta G_{\text{tran}} + \Delta G_{\text{c}} \tag{3}$$

where ΔG_{el} describes the change in the elastic free energy; ΔG_{int} is the change in the free energy of the interactions between polymer segments, solvent molecules and the surface of the clay particles; ΔG_{tran} is related to the change in the translation entropy of the counterions of the clay and 1,1-salt; and ΔG_{c} describes the change in the free energy of Coulomb interaction between the ions. For the case when the ionic surfactant is added to the solution, the expression for the free energy should include additional terms, the most essential being the term describing the free energy of the formation of hydrophobic aggregates of the surfactant ΔG_{m}.[16]

The comparison of the swelling curves obtained from the gels in the solutions of salt (Figure 2) and the surfactant (Figure 3) shows that the addition of the cationic surfactant, CPC, results in much stronger shrinking of the gels than in the case of sodium chloride. The dependence of F on the surfactant concentration, c, passes through a minimum after which the swelling ratio begins to increase. Finally the swelling ratio of the gel approaches that in the solution of 1,1-salt with a high ionic strength. Below we will analyze separately the three regions of the surfactant concentration namely, the region of the slight decrease of the swelling ratio, the region of the gel collapse and the region of the reentrant transition in the swollen state.

Region of Low CPC Concentration. From the SAXS data listed in Figure 7, it follows that the clay platelets in the gel composites without surfactant are very disordered. The maximum at $q \sim 3.2$ nm^{-1} is very broad even for the dried gels while for the swollen gels it is not observed at all. The adsorption of CPC by the composites at low concentrations of the surfactant, c ($c = 2-4 \times 10^{-5}$), leads to the appearance of a weakly pronounced broad maximum at $q \sim 1.6$ nm^{-1}, corresponding to $d = 3.9$ nm. From the isotherms of absorption of the surfactant by the composites it follows, that the appearance of the maxima on the SAXS curves occurs already at Q~0.3. The value of $d = 3.9$ nm is significantly higher than the characteristic d value for the dried composite or the length of the fully stretched single ion of CPC (about 2.5 nm). In the same region of CPC concentration, the swelling ratio of the gels decreases much more strongly in comparison with the gels in salt solution.

The data presented in Figure 6 show that in the region of low concentrations of CPC the values of τ of the spin-probe solubilized by CPC are the highest. The increase of the surfactant concentration results in the decrease of the values of τ. Finally, the rotational mobility of the probe becomes as high as that for the “free” micelles of CPC in the solution.

The obtained data can be explained on the basis of the assumption that at low surfactant concentrations the ordered aggregates of the surfactant are already formed and they solubilize the amphiphilic molecules of the spin-probe. The low mobility of the probe together with SAXS data manifests the formation of highly packed double layers of the surfactant molecules in the composite gels due to adsorption of the surfactant molecules on the particles of BENT. The structure of the double layer is strongly different from that of the micelles. In the latter the mobility of the spin-probe is much higher.

How can one imagine the structure of these aggregates? The charge density on the surface of MONT crystals is about 1.0×10^{-7} mequiv/cm^2.[8] The square occupied by the single ion of CPC is about 0.25 nm^2. The calculations show that the ions of CPC packed closely on the surface of BENT crystal have a charge density ca. 6-fold higher than the density of the negatively charged groups of the clay.

The physical reasons for the adsorption of the cationic surfactant on the anionic clay platelets resemble those for the absorption of the ionic surfactants by oppositely charged polyelectrolyte networks.[16] The driving force for the interaction is the release of the counterions of the clay and the aggregation of the hydrophobic "tails" of the surfactant together with the electrostatic interaction between the charges of the surfactant and of the clay surface. The additional stabilizing of such contacts comes from the low local "dielectric constant" in the area of the contacts between the surfactant aggregate and the clay platelet. The release of the counterions results in the large gain in translational entropy. Hence, even few electrostatic contacts between the surfactant aggregate and the platelet should be enough to make the aggregate stable enough from the thermodynamic point of view.

However, at low surfactant concentration, such aggregates will occupy only some small areas on the platelets of the clay. The reason for the instability of continuous layer of the surfactant on the surface of the platelets comes from a strong difference in the charge density of the layer of the closely packed surfactant ions and the surface of the clay. Besides, due to high hydrophobicity of the cetyl groups of CPC the surfactant's tails should be packed inside the aggregates and form double-layer structure. We assume that the ordered aggregates of CPC on the surface of BENT particles in the gel phase can be represented as "flat micelles" or double layer fragments schematically shown in Figure 1e. From this schematic representation it follows that the appearance of the double layers of the surfactant should result in a strong Coulomb attraction between the platelets because negatively charged areas of platelets will be attracted to the overcharged areas of platelets with double layers on them. This conclusion is supported by the fact that the gels begin to shrink in the region of CPC concentration where no lamellar structure is observed by SAXS.

Region of Intermediate CPC Concentration. The increase of CPC concentration leads to further shrinking of the gels. The amount of CPC adsorbed on the clay platelets increases and the attraction between the platelets becomes stronger. Finally some fraction of the platelets collapses with the formation of the densely packed lamellas built of the clay platelets with intercalated double layers of the surfactant between them. Schematic representation of such structure is shown in Figure 1f. However, due to low ordering of the platelets in the initial gels and their immobilization in the polymer network only a smaller fraction of them forms ordered multilayers. This conclusion is confirmed by the SAXS data. The comparison of the SAXS profile obtained from the BENT−CPC complex embedded in the gel (curve 4 in Figure 7c) with that obtained from the BENT−CPC complex prepared without a polymer network at a ratio Q_0 of CPC to Na of $Q_0 = 2.0$ (curve 4 in Figure 7a) demonstrates the much higher self-ordering in the latter.

SAXS profiles obtained from the samples with different Q in the range of $Q = 0.9-8.0$ are very similar (Figure 7b,c). Thus, the fraction of the ordered lamellar structure, once formed, does not increase with further growth of the CPC concentration.

The rotational mobility of the spin-probe increases in the concentration regime of CPC where lamellas are formed. This result can be explained by the parallel formation of micelles (which structure is not so ordered) together with ordered lamellas in the gel phase. Because of the difference in the chemical structure of the surfactant and of the probe, the latter can be excluded from the ordered lamellas formed by CPC and the clay platelets and solubilized by micelles. Hence, the mobility of the probe does not reflect the local mobility in the lamellas.

Region of High CPC Concentration. The adsorption of the cationic surfactant on the surface of the clay particles between the platelets shown in Figure 1e,f induces the appearance of the contractive forces which shrink the gel. However, a large fraction of the clay platelets forms aggregates. The formation of the double layer of CPC on the outer surface of such aggregates is less favorable in comparison with their formation on the inner surfaces. In the first case, the gain in the free energy of the electrostatic interaction is smaller (only one side of the surfactant double layer participates in the Coulomb interaction with negatively charged surface). However, as follows from the electroosmotic data, at high CPC concentration, these outer surfaces are covered by the CPC double layers, thus overcharging the aggregates of BENT−CPC complexes (lamellas and the structures of the type schematically shown in Figure 1e). The overcharging leads to Coulomb repulsion between the particles to their partial separation and, hence, to the reentrant swelling of the composite gel.

Conclusion

The interaction of the composite gels of poly(acrylamide) with incorporated bentonite clay with cationic surfactant, CPC is a multistep process depending on the surfactant concentration. At low surfactant concentration, much smaller than its cmc surfactant already forms ordered aggregates on the surface of clay particles. The ESR data show that the rotational mobility of the spin-probe solubilized in these aggregates is low in comparison with its mobility in the micelles of the surfactant in the solution. SAXS study demonstrates that at higher CPC concentration adsorption of the surfactant results in the formation of lamellas including alternating layers of clay platelets and double layers of CPC. The strong shrinking of the gel composite occurs during these two steps of the adsorption. At high concentration of the surfactant the surface of most of the clay particles in the gel phase becomes overcharged. This overcharging results in the reentrant transition of the gel in the swollen state. The overcharging also results in the change of the direction of the electroosmotic transport of water through the gel composite.

References and Notes

(1) Gao, D. *Preparation and Property Improvements of a Superabsorbent Polymer Composite*; Alberta Research Council: Edmonton, Canada, 1992; Chapter 1.

(2) Gao, D.; Heimann, R. B. *Polym. Gels Networks* **1993**, *1*, 225.

(3) Churochkina, N. A.; Starodoubtsev, S. G.; Khokhlov, A. R. *Polym. Gels Networks* **1998**, *6*, 205.

(4) Starodoubtsev, S. G.; Churochkina, N. A.; Khokhlov, A. R. *Langmuir* **2000**, *16*, 1529.

(5) Starodoubtsev, S. G.; Churochkina, N. A.; Khokhlov, A. R. *Macromol. Symp.* **1999**, *146*, 193.

(6) Grim, R. E. *Clay Mineralogy*; McGraw-Hill Series in Geology: New York, London, and Toronto, Canada, 1953.

(7) Hoffmann, U. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 681.

(8) Theng, B. K. G. *Formation and Properties of Clay−Polymer Complexes*; Elsevier: Amsterdam, 1979; Chapter 1.

(9) Kukovsky, E. G. *Structure and Properties of Clay Minerals*; Naukova Dumka: Kiev, 1966.

(10) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1930**, *16*, 578.

(11) Evsikova, O. V.; Starodoubtsev, S. G.; Khokhlov A. R. *Vysokomolek. Soed.*, in press.

(12) Mogilevsky, L. Yu.; Dembo, A. T.; Svergun, D. I.; Feigin, L. A. *Kristallografia* **1984**, *29*, 587.

(13) Aultchenko, V. M.; Baru, S. E.; Sidorov, V. A.; Savinov, G. A.; Feldman, I. G.; Khabakhpashev, A. G.; Yasenev, M. V. *Nucl. Instrum. Methods* **1983**, *208*, 443.

(14) Osada, Y.; Hasebe, M. *Chem. Lett.* **1985**, 1285.

(15) Mironov, A. V.; Starodoubtsev, S. G.; Khokhlov, A.R.; Dembo, A. T.; Yakunin, A. N. *Macromolecules* **1998**, *31*, 7698.

(16) Starodoubtsev, S. G.; Khokhlov, A. R.; Makhaeva, E. E. *Polym. Bull. (Berlin)* **1991**, *25*, 373.

(17) Khokhlov, A. R.; Starodoubtsev, S. G.; Vasilevskaya, V. V. *Adv. Polym. Sci.* **1993**, *109*, 123.

MA012021Z