

Interaction of Hydrophobically Modified Poly(acrylic acid) Hydrogels with Ionic Surfactants

O. E. Philippova,^{*,†} D. Hourdet,[‡] R. Audebert,[‡] and A. R. Khokhlov

Polymer Physics Laboratory, Physics Department, Moscow State University, 117234, Moscow, Russia, and Laboratoire de Physico-Chimie Macromoléculaire, Université Pierre et Marie Curie, CNRS URA 278, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

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ABSTRACT: The role of the hydrophobic effect in polyelectrolyte gel/ionic surfactant interactions was investigated. A series of hydrophobically modified poly(acrylic acid) gels with well-controlled hydrophobicity was synthesized by free-radical copolymerization of acrylic acid with *n*-alkyl acrylates (*n* = 8, 12, and 18) in the presence of a cross-linking agent. The interaction of the gels with ionic surfactants—*N*-cetylpyridinium chloride and sodium dodecylbenzenesulfonate—was studied. Four gel/surfactant combinations were considered: uncharged gel/cationic surfactant, uncharged gel/anionic surfactant, anionic gel/cationic surfactant, and anionic gel/anionic surfactant. It was shown that the gels absorb cationic surfactant ions via an ion-exchange reaction with network counterions. On the other hand, the absorption of anionic surfactant is governed primarily by hydrophobic interactions, and hence, due to conditions of electroneutrality, anionic surfactant penetrates the gel together with corresponding co-ions. Therefore, the uptake of cationic surfactant ions results in gel shrinkage, while the uptake of anionic surfactant induces gel swelling. In the anionic gel/anionic surfactant system, a significant interaction is observed only for the most hydrophobic gels when hydrophobic interactions overcome the electrostatic repulsion between similarly charged groups.

Introduction

Highly cross-linked polymer networks were used early on a large scale for separative purposes (ion-exchange resins, packings for absorption or size exclusion chromatography, etc.). Later, new fields of interest appeared for lightly cross-linked gels that can absorb a large amount of solvent and undergo sharp conformational transitions. These systems can also be used for the selective absorption (or the progressive release) of organic solutes, including surfactants. These sophisticated separation techniques were proposed, for instance, for the simultaneous flocculation and depollution of raw water¹ and for patches for controlled delivery systems.²

One of the most extensively studied systems involving lightly cross-linked networks are their complexes with ionic surfactants. The results of experimental and theoretical studies of these systems^{3–20} suggest that the polymer gel/ionic surfactant interactions are primarily governed by three effects: translational entropy of counterions and electrostatic and hydrophobic polymer/surfactant interactions. While the first two effects are now usually taken into account in both experimental and theoretical studies, the literature dealing with hydrophobic interactions in polyelectrolyte gels remains very scarce, mainly because of the lack of experimental data on hydrogels of well-controlled hydrophobicity. In this work, we try to partially fill this gap by preparing polyelectrolyte hydrogels with different hydrophobic group contents.

Hydrophobically modified (HM) polyelectrolyte hydrogels were synthesized by the copolymerization of hydrophilic (acrylic acid) and hydrophobic (*n*-alkyl acrylate) monomers in the presence of a small amount of diacrylic monomer as a cross-linking agent. The hydrophobic–hydrophilic balance of the gels was varied by changing the content and the *n*-alkyl chain length of the hydrophobic units.

We describe here the interaction of HM poly(acrylic acid) (PAA) gels with ionic surfactants, *N*-cetylpyridinium chloride (CPC) and sodium dodecylbenzenesulfonate (DBS), at surfactant concentrations ranging from below to above the critical micelle concentration (CMC) in water. The four possible gel/surfactant combinations will be considered according to pH: uncharged gel/cationic surfactant, uncharged gel/anionic surfactant, anionic gel/cationic surfactant, and anionic gel/anionic surfactant. The swelling behavior of the gels in the surfactant solutions and the partition of the surfactant ions between the gel phase and the external solution were examined. We will see that the hydrophobic effect plays a major role in polyelectrolyte gel/surfactant interactions and can even overcome the effect of the presence of charges in the network.

Experimental Section

Materials. The following comonomers were used: acrylic acid (Fluka), *n*-octyl acrylate (Scientific Polymer Products, Inc.), *n*-dodecyl acrylate (Lancaster Synthesis), and *n*-octadecyl acrylate (Scientific Polymer Products, Inc.). *N*-Cetylpyridinium chloride (CMC in water = 9×10^{-4} mol/L)²¹ from Merck and sodium dodecylbenzenesulfonate (hard type; CMC in water = 1.4×10^{-3} mol/L)²¹ from TCI (Japan) were used as surfactants without preliminary purification. Water was purified by a Milli-Q system (Millipore).

Gel Preparation. HM gels were prepared by free-radical copolymerization of acrylic acid and *n*-alkyl acrylates in dimethylformamide (DMF). The fraction of *n*-alkyl acrylate in the monomer mixture was varied from 0 to 20.0 mol %. All copolymerizations were performed at an overall monomer concentration of 3.06 mol/L, with 2,2'-azobis(isobutyronitrile) (1.53×10^{-2} mol/L or 0.5 mol %) as initiator. *N,N*-Methylenbis(acrylamide) (4.6×10^{-2} mol/L or 1.5 mol %) was used as the cross-linker. Gelation was carried out in cylindrical glass tubes (inner diameter = 0.40 cm) under a nitrogen atmosphere at 63 °C for 3 h. The prepared gel was washed in a large amount of absolute ethanol for 3 weeks to remove unreacted components and the sol fraction.

Copolymer gels are identified in terms of the comonomer identities and molar contents. For example, C-8-10% indicates a gel containing 10 mol % of *n*-octyl acrylate (C-8).

[†] Moscow State University.

[‡] Université Pierre et Marie Curie.

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Table 1. Composition of HM Gels and Weight Fraction β of Copolymer in the Networks Swollen in Ethanol

gel sample	<i>n</i> -alkyl chain length	fraction of <i>n</i> -alkyl groups, <i>q</i> (mol %)	β
PAA		0	0.047
C-8-2.5%	C ₈ H ₁₇	2.5	0.044
C-8-5%	C ₈ H ₁₇	5.0	0.045
C-8-10%	C ₈ H ₁₇	10.0	0.035
C-8-20%	C ₈ H ₁₇	20.0	0.043
C-12-2.5%	C ₁₂ H ₂₅	2.5	0.042
C-12-5%	C ₁₂ H ₂₅	5.0	0.047
C-12-10%	C ₁₂ H ₂₅	10.0	0.043
C-18-2.5%	C ₁₈ H ₃₇	2.5	0.040
C-18-5%	C ₁₈ H ₃₇	5.0	0.030
C-18-10%	C ₁₈ H ₃₇	10.0	0.022
PAA*		0	0.034

A PAA gel with a smaller degree of cross-linking, designated as PAA*, was obtained as described earlier, but with a reduced amount of cross-linker (3.5×10^{-2} mol/L).

Gel Characterization. The weight fraction of the polymer in the swollen network, β , was determined using the formula $\beta = m_0/m_{sw}$, where m_0 is the mass of the dry gel and m_{sw} is the mass of the swollen gel. The values of β for the prepared gels are summarized in Table 1. It can be seen that most of the gels have similar values of β in ethanol.

The composition of the prepared HM gels was characterized by ¹H NMR. NMR measurements were performed on a Bruker WP 250 spectrometer. A mixture of deuterium oxide (99.9 atom % D, Spectrometrie Spin et Techniques) and deuterated methanol (99.6 atom % D, Spectrometrie Spin et Techniques) was used as solvent. The NMR spectral bands of swollen gels are poorly resolved, which hampers the precise calculation of the network composition. To avoid this problem, NMR measurements were performed with linear HM copolymers synthesized under the same conditions as used for the HM gel, but without a cross-linking agent. It was shown that, for all of the copolymers under investigation, the composition of the copolymer is identical to the composition of the initial monomer mixture. Related experiments on HM gels show that the same relationship holds true for cross-linked copolymers. The compositions of the networks are listed in Table 1.

The distribution of hydrophobic units along the polymer chains was characterized by ¹³C NMR. It was shown that the *n*-alkyl acrylate units are randomly distributed along the polymer chains.

Swelling Experiments in Gel/Surfactant Systems. The swelling experiments were performed at pH 2.5 for uncharged gels and at pH 9.0 for ionized gels. Stock solutions of surfactants (10^{-2} mol/L) at pH 2.5 and 9.0 were first prepared and subsequently diluted with HCl (pH 2.5) or NaOH solution (pH 9.0) to achieve the desired concentration.

To study the gel/surfactant interactions, the gel samples (with mass m_{sw} of ca. 0.15 g) previously equilibrated at the desired pH were put in solutions of surfactant of a definite concentration (3 mL of solution per 10^{-5} mol of network repeating units, including *n*-alkyl acrylate units). The gel samples remained in the surfactant solutions at 25 °C for the time required to attain equilibrium (3 weeks). When equilibrium was established, the gel samples were weighed and the surfactant concentration in the exterior solution was measured.

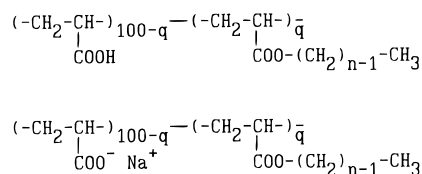
The degree of swelling of the gel samples equilibrated with the surfactant solution was characterized by the m/m_0 ratio, where m is the mass of the sample at the equilibrium state in surfactant solution and m_0 is the mass of the dried gel sample. The mass of the dry sample was calculated as $m_0 = m_{sw}\beta$, where β is the weight fraction of polymer in the initial gel equilibrated in aqueous solution at the desired pH.

The absorption of the surfactant by the gel leads to a decrease in surfactant concentration in the external solution. The surfactant concentration in the solution was measured by UV spectroscopy. UV spectra were recorded on a Perkin-Elmer 552 UV-vis spectrophotometer, using a quartz UV cell of 1 cm optical path length. The optical densities at $\lambda_{max} = 258$ nm ($\epsilon = 4.47 \times 10^3$ L/mol·cm) and $\lambda_{max} = 223$ nm ($\epsilon =$

1.31×10^4 L/mol·cm) were used to calculate the concentrations of CPC and DBS, respectively. The surfactant content in the gel phase was evaluated by subtraction of the equilibrium concentration of surfactant in the surrounding solution from the initial concentration of surfactant. The amount of surfactant in the gel was characterized by the surfactant/gel monomer unit molar ratio in the gel θ (hydrophobic units are included in the gel molar mass in the case of an uncharged gel, but not included in the case of a charged gel). The efficiency of the surfactant absorption by the gel was characterized by the distribution constant $K = C_g/C_s$, where C_g and C_s are the concentrations of the surfactant ions in the gel phase and in solution, respectively.

Results and Discussion

Swelling of HM Gels in Aqueous Medium. The objects of the present investigation were the HM PAA gels containing up to 20 mol % of *n*-alkyl acrylate units of different alkyl chain lengths ($n = 8, 12, \text{ and } 18$). Thus, the gels consist of hydrophobic (*n*-alkyl acrylate) and hydrophilic (acrylic acid) units. Since PAA is a weak acid, its degree of ionization can be varied over a wide range by changing the pH of the medium. We consider two extreme cases: uncharged acrylic acid units and completely ionized acrylic acid units.



The copolymerization reaction in DMF produces the gel in the uncharged acidic form. The immersion of this gel in water results in a partial dissociation of carboxy groups. To suppress this dissociation, all of the experiments with the uncharged gel in aqueous medium were performed at pH 2.5. To obtain completely ionized gel in the form of poly(sodium acrylate) (NaPAA), a calculated amount of NaOH required to neutralize all acrylic acid units was added to the solution containing a gel sample. The pH of the solution surrounding a completely ionized gel was 9.0.

The dependence of the degree of swelling of the HM PAA gels in the acid form on the fraction of hydrophobic units in the network is presented in Figure 1. The corresponding dependence for a HM NaPAA gel in the salt form is displayed in Figure 2. One can see, first of all, that the degree of swelling of the ionized gel is much higher; this is known to be the consequence of the osmotic pressure exerted by counterions.⁸ Figure 2 also depicts that the relative mass of HM NaPAA gels depends weakly on the fraction of hydrophobic groups in the network, except the C-18-10% gel for which we observe a 2-fold decrease in the degree of swelling in comparison with the unmodified gel. As would be expected, C-12 gels seem to exhibit the same tendency to shrink, but at a higher content of hydrophobic groups than C-18 gels. One can suggest that the degree of swelling of the HM gel in aqueous medium is mainly determined by an interplay between two opposite-acting forces: the osmotic pressure exerted by the counterions and the attractive hydrophobic forces between alkyl groups. The competitive balance between these two forces depends on the degree of ionization and the hydrophobicity of the gel. For most of the completely ionized HM gels, the effect of the osmotic pressure exerted by the counterions prevails over the hydrophobic association. The hydrophobic attraction leading to the

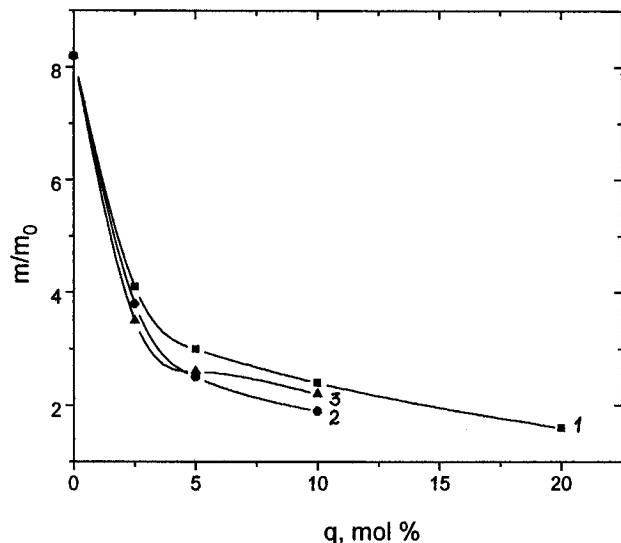


Figure 1. Dependence of the degree of swelling of uncharged HM PAA gels (pH 2.5) on the content, q , of hydrophobic repeating units in the network for the C-8 (1), C-12 (2), and C-18 series (3).

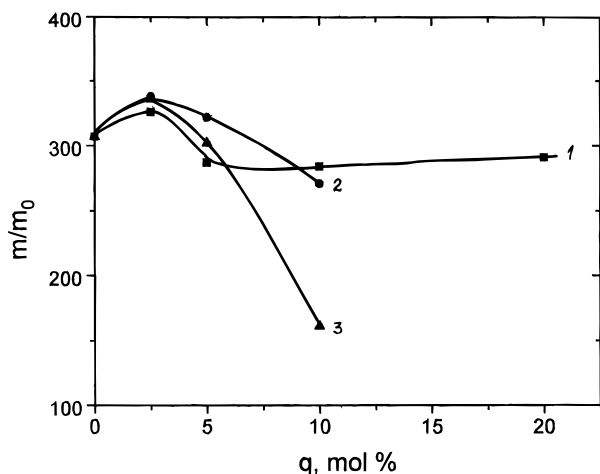


Figure 2. Dependence of the degree of swelling of anionic HM NaPAA gels (pH 9) on the content, q , of hydrophobic repeating units in the network for the C-8 (1), C-12 (2), and C-18 series (3). The lines are only a guide for the eyes.

shrinkage of the strongly charged gel mainly emerges for the most hydrophobic C-18-10% gel (Figure 2).

A similar situation holds for the corresponding linear HM NaPAA copolymers.^{22,23} By fluorescence spectroscopy and viscosity measurements, it was established that, at linear copolymer concentrations close to the concentration of polymer units in the swollen HM NaPAA gels, only the C-18-10% linear copolymer forms hydrophobic aggregates; less hydrophobic linear copolymers behave as the unmodified polymer.²²

In contrast to the ionized NaPAA gel, the shrinkage of the uncharged PAA gel with the increase in the content of hydrophobic units (Figure 1) is observed even at very small hydrophobic group contents ($q < 5$ mol %). In the uncharged gel there is no osmotic pressure exerted by the counterions, and the hydrophobic attraction between n -alkyl side chains becomes the most important effect. One can suggest that hydrophobic interactions tending to shrink the gel are realized through the formation of hydrophobic clusters including n -alkyl side groups belonging to different network chains.

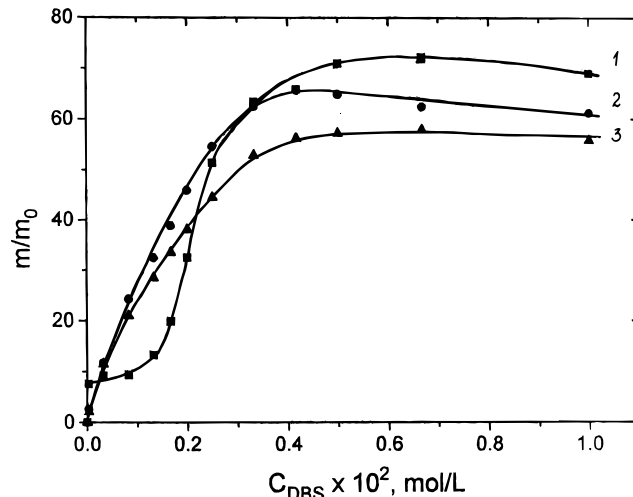


Figure 3. Dependence of the degree of swelling of uncharged PAA gel (1) and HM C-12-5% (2) and HM C-12-10% (3) PAA gels on the initial concentration of the anionic surfactant DBS in solution (pH 2.5).

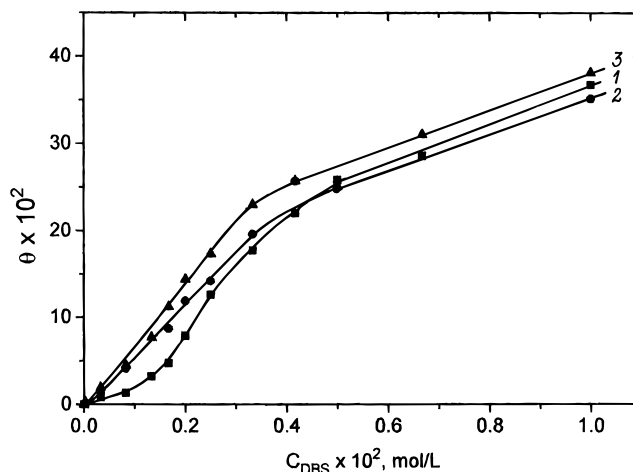


Figure 4. Fraction of the anionic surfactant DBS in uncharged PAA gel (1) and HM C-12-5% (2) and HM C-12-10% (3) PAA gels as a function of the initial concentration of DBS in solution (pH 2.5).

Uncharged Gel/Anionic Surfactant. Figure 3 depicts the typical dependence of the degree of swelling of the HM PAA gel on the initial concentration of DBS in solution. Figure 4 illustrates the absorption of DBS by the gel as a function of the initial concentration of DBS in solution. Figures 3 and 4 show that the uncharged gels absorb anionic surfactant, and this process results in gel swelling. The distribution constants of DBS between the gel phase and solution are presented in Table 2. The data show that the concentration of DBS in the gel phase is substantially higher than that in the external solution. The accumulation of ionic surfactant in the uncharged network is apparently due to hydrophobic interactions. Owing to the conditions of electroneutrality, the uncharged network must absorb the anionic surfactant, together with its counterions. The osmotic pressure exerted by mobile counterions within the network causes gel swelling.

An analogous effect was observed in ref 24, where the interaction of uncharged linear PAA with the anionic surfactant sodium dodecyl sulfate (SDS) was studied by fluorescence spectroscopy. It was shown that the binding of the surfactant to the polymer results in an expansion of the poly(acrylic acid) chain. However, this was attributed in ref 24 to the repulsion among the

Table 2. Distribution Constants of the Anionic Surfactant DBS between the Uncharged Gel and Solution

initial concentration of DBS, C ($\times 10^{-3}$ mol/L)	K					
	PAA	C-8-2.5%	C-8-5%	C-8-20%	C-12-5%	C-18-5%
0.33	0	49	56	95	53	78
0.83	16	36	33	39	31	38
1.33	28	25	26	27	21	23
1.67	22	22	26	25	20	19
2.00	20	23	22	21	20	19
2.50	17	16	21	23	16	15
3.33	14	15	18	18	15	13
4.27	14	15	14	15	15	11
5.00	12	12	14	13	12	10
6.67	10	10	11	10	9	8
10.0	9	7		8	8	7

bound surfactant molecules. From our experience on polyelectrolyte systems,⁸ we believe that the effect of the repulsion is much weaker than the osmotic pressure of the counterions.

Let us now compare the experimental results for HM and unmodified gels. An essential difference is observed at low DBS concentrations. Figure 4 shows that, in contrast to HM gels, the unmodified PAA gel does not absorb the surfactant and does not change the degree of swelling at DBS concentrations below a certain critical concentration C^* equal to 1.3×10^{-3} mol/L. This concentration C^* is only slightly lower than the CMC of DBS in water (1.4×10^{-3} mol/L).²¹ The same behavior is observed for unmodified PAA* gels with smaller cross-linking density (Figure 5). It was found that the decrease in the cross-linking density does not influence the value of C^* .

The fact that the uncharged gel interacts with anionic surfactant only at surfactant concentrations above a certain critical concentration C^* has come to light for various uncharged gel/surfactant systems. It was shown¹⁸ that anionic surfactant SDS at concentrations below 5×10^{-3} mol/L does not cause the conformational changes in the poly(acrylamide) gel with pendant poly(ethylene glycol) chains; at higher SDS concentrations the gel swells sharply. The critical concentration C^* required for the onset of surfactant-induced swelling agrees well with the critical concentration for the formation of polymer-bound micelles and is slightly lower than the CMC of SDS in water (8×10^{-3} mol/L).²¹ The analogous behavior was observed for poly(acryloyl-L-proline alkyl ester) gels interacting with SDS.¹⁹ It was shown that the anionic surfactant begins to influence the swelling behavior of the gels only at the concentration ca. 7×10^{-4} mol/L, which is very similar to the critical aggregation concentration (CAC).

In the absence of charges on the gel chains for single surfactant molecules below the CAC, it is unfavorable to be inside the network. In this case, the surfactant molecules do not gain any considerable energy due to contact with the uncharged network chains; on the other hand, being confined inside the gel, they lose some conformational entropy.

A different situation arises at surfactant concentrations above the CAC. For surfactant molecules aggregated in micelles, the loss in conformational entropy resulting from confinement with the network is negligible in comparison to confinement due to the incorporation into micelles. Besides, surfactants can start to self-associate in the network at concentrations below the CMC in water. According to the thermodynamic theory developed by Nagarajan,²³ in nonionic polymer/anionic

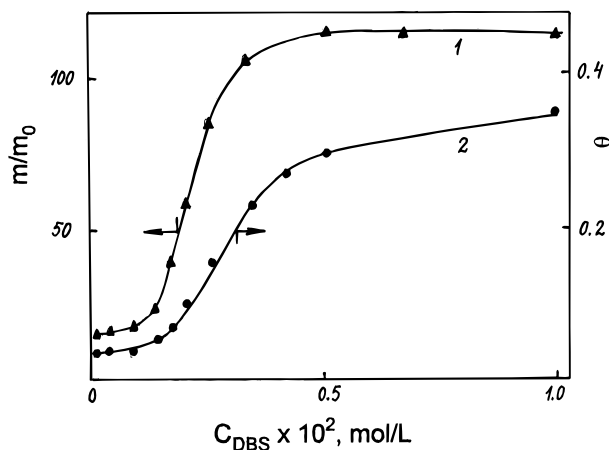


Figure 5. Dependence of the degree of swelling (1) and the fraction of the anionic surfactant DBS in the gel (2) on the initial concentration of DBS in a solution of uncharged PAA* gel.

surfactant systems, irrespective of the polymer hydrophobicity, the free energy of the polymer-bound micelles is lower than that for the free micelles in solution. The gain in energy due to the self-association of surfactant molecules in the gel compensates for the entropy losses.

In contrast to unmodified PAA gels, the HM gels absorb the anionic surfactant even at very low surfactant concentrations. This may be due to hydrophobic interactions between network hydrocarbon chains with surfactant alkyl tails. As was mentioned earlier, the hydrocarbon side chains of the uncharged HM gels can self-associate. It is conceivable that DBS surfactant molecules incorporate into these associates, thus forming mixed micelles.

Thus, the hydrophobic modification enhances the interactions between the uncharged gel and the anionic surfactant in dilute solutions of the surfactant. The binding of surfactant molecules to the HM gel starts at much lower surfactant concentrations than for the corresponding unmodified gel.

Some differences in the behavior of HM and unmodified gels are also observed at high DBS concentrations. Figure 3 shows that, at initial concentrations of DBS = 5×10^{-3} to 10^{-2} mol/L, the relative mass of the HM gel is smaller than that of the unmodified gel. The greater the fraction of hydrophobic units, the smaller the relative mass of the gel. At the same time, the fraction of DBS in the network is the same for both HM and unmodified gels. This can be partially ascribed to the increase in m_0 with an increasing degree of modification (for a constant number of repeating units). However, this fact cannot completely explain the observed values of relative mass for HM gels. Another reason could be the additional cross-linking of the gel due to the formation of mixed hydrophobic aggregates containing surfactant tails and *n*-alkyl side chains of the network. The greater the relative content of hydrophobic network alkyl chains in mixed aggregates in the network, the greater the contraction of the gel.

Uncharged Gel/Cationic Surfactant. The immersion of the uncharged HM PAA gels in an aqueous solution of the cationic surfactant CPC results in the absorption of the surfactant by the gel. Typical plots of the fraction of the surfactant in the network as a function of the initial concentration of the surfactant in the solution are presented in Figure 6. It was shown that the concentration of the surfactant in the gel phase is typically 2 orders of magnitude higher than that in

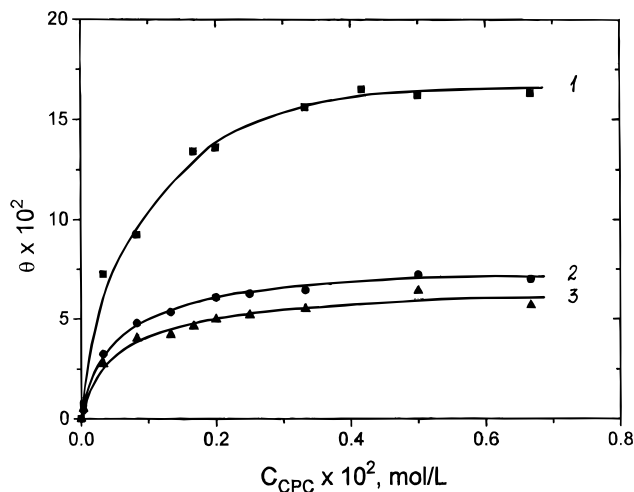


Figure 6. Fraction of the cationic surfactant CPC in uncharged PAA gel (1) and HM C-12-5% (2) and HM C-12-10% (3) PAA gels as a function of the initial concentration of CPC in solution.

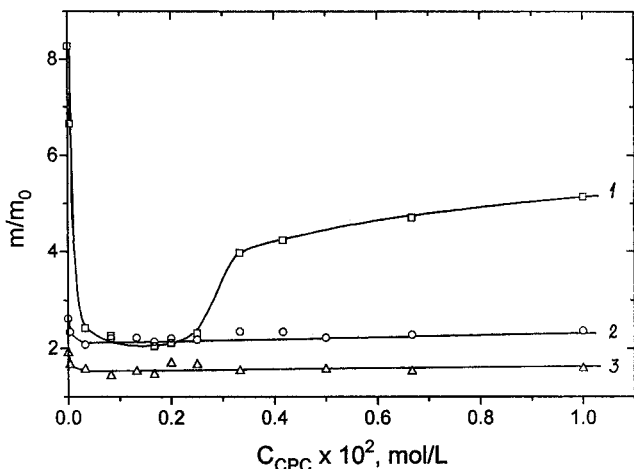


Figure 7. Dependence of the degree of swelling of uncharged PAA gel (1) and HM C-12-5% (2) and HM C-12-10% (3) PAA gels on the initial concentration of the cationic surfactant CPC in solution.

the external solution. These data provide evidence that the cationic surfactant is effectively concentrated within the network.

The absorption of the surfactant leads to gel shrinkage (Figure 7). It is seen from Figure 7 that the contraction occurs even at very low CPC concentrations.

Thus, the conformational behavior of uncharged PAA gel in the solution of ionic surfactant strongly depends on the sign of the charge of the surfactant. The absorption of anionic surfactant results in gel swelling, while the absorption of cationic surfactant induces gel shrinkage. To explain this, it is worthwhile to note that, for the uncharged PAA network/cationic surfactant system, one more mechanism of network/surfactant interaction is possible. This mechanism is the ion-exchange reaction between H^+ ions of carboxy groups of the gel and the cationic surfactant. One can suppose that at pH 2.5 a very small fraction of PAA carboxy groups is dissociated. The replacement of these H^+ ions by surfactant cations can be followed by the release of the substituted H^+ ions in the surrounding solution. The ion-exchange reaction displaces the dissociation equilibrium of weak PAA toward the dissociation of carboxy groups. Unfortunately, we cannot measure, with reasonable accuracy, the change in pH of the external

solution because of the high initial concentration of H^+ ions. Rough calculations suggest that the release of 10% H^+ ions into the exterior solution results in a decrease in pH only from 2.50 to 2.46.

At higher pH (>3.00), the interaction of PAA gels with the cationic surfactant dodecylpyridinium chloride (DPC) via an ion-exchange reaction, with the release of H^+ in the exterior solution, was proven by potentiometric titration.¹⁴ It was shown that the amount of DPC ions absorbed by a network is equal to the amount of H^+ released in the external solution. From these data, it was concluded that almost all absorbed DPC ions are bound to the charged network units due to electrostatic forces.

The absorption of cationic surfactant via an ion-exchange reaction does not result in gel swelling since the counterions of the network as well as the counterions of the surfactant are released into the external solution and cannot cause the osmotic pressure exerted in the network, as in the case of the uncharged network/anionic surfactant system. On the other hand, it is reasonable to suggest that the hydrophobic tails of the surfactant absorbed by a gel aggregate with each other, forming hydrophobic clusters. The surfactant aggregation in the network can be responsible for the contraction of the gel in the solution of CPC. The aggregation of surfactant ions results in a decrease in osmotic pressure in the gel; moreover, the charged surfactant clusters attract oppositely charged network units. Both of these factors promote gel shrinkage. As for the HM gel, it stands to reason that *n*-alkyl side chains of the network would form mixed aggregates with the absorbed surfactant ions.

The HM PAA gels in the absence of surfactant contain hydrophobic clusters covalently bound to a network. Unmodified PAA gels with cationic surfactant absorbed via an ion-exchange reaction contain hydrophobic clusters bound to a network electrostatically. Let us compare the degree of swelling for the gels with both types of bonding of hydrophobic clusters to the network. From Figures 6 and 7, it was calculated that the unmodified PAA gel with 10% absorbed CPC ions per one network repeating unit has a degree of swelling equal to 2.1. The HM PAA gels containing 10 mol % of *n*-alkyl side chains in the absence of CPC have almost the same value of the degree of swelling (Figure 1). This fact seems to demonstrate that, in both cases, the gel contraction is associated with hydrophobic aggregation.

Let us compare the experimental results for HM and unmodified gels. As is evident from Figure 6, the unmodified PAA gel absorbs more surfactant than the gel containing hydrophobic units. This can be explained by the more expanded conformation of the unmodified gel compared to the HM gels (Figure 1). Since the more expanded gel contains a more polar solvent (water), the dielectric constant in this gel is higher than that in compact HM gels (cf. ref 26). This is favorable for PAA ionization and, hence, for the ion-exchange reaction.

The contraction caused by the absorption of CPC is more pronounced for the unmodified PAA gel. The greater the fraction of hydrophobic units in the gel, the less the contraction of the gel.

The role of hydrophobic substituents of the polymer was studied in ref 27, describing the interaction of linear polymers PAA and poly(methacrylic acid) (PMAA) and the copolymer of methacrylic acid and methyl methacrylate (MAA-MMA) with the cationic surfactant cetyltrimethylammonium bromide (CTAB). The extent

to which the ion-exchange reaction proceeds, calculated from the increase in H^+ concentration in the solution, was found to be equal to 13.5, 6.0, and 4.0% for PAA, PMAA, and the copolymer MAA-MMA, respectively. Thus, the interaction with the cationic surfactant falls off with the increase in the hydrophobicity of the polyelectrolyte. This effect was attributed to the shrinkage of macromolecular coils due to hydrophobic interactions, which results in a decrease in the electrostatic charge density and the permeability of polymer coils to surfactant ions.

The addition of CTAB causes the decrease in the reduced viscosity of the polyelectrolyte solution.²⁷ Thus, the binding of CTAB to polyelectrolyte leads to the contraction of polyelectrolyte chains. This effect is analogous to the contraction of PAA gel in the cationic surfactant solution.

Another difference between HM and unmodified gels is observed at high concentrations of CPC. The relative mass of HM gels does not change with CPC concentration, while the unmodified PAA gel remains in the collapsed state up to concentrations of CPC equal to 2.5×10^{-3} mol/L and then reswells (Figure 7). In contrast to HM gels, the unmodified PAA gel probably absorbs a small amount of CPC with counterions, with the osmotic pressure exerted by these mobile counterions being responsible for the reswelling of the gel. The unmodified gel contains surfactant aggregates that are bound to the network by electrostatic forces. These aggregates are more labile than the mixed clusters in HM gels, and they can easily be modified to include additional surfactant molecules.

Anionic Gel/Cationic Surfactant. The interaction of a polyelectrolyte gel with an oppositely charged surfactant has been studied extensively in recent years.^{3-14,20} After the immersion of a swollen polyelectrolyte gel in the solution of an oppositely charged surfactant, the surfactant ions penetrate in the network and replace the network counterions. This process is extremely favorable from the point of view of translational entropy of the counterions.⁶ If the volume charge density in the network is much higher than that in the external solution, the surfactant ions are effectively concentrated within the network as a result of this ion exchange. Absorption of a considerable amount of the surfactant ions leads to a transition of the swollen network to the collapsed state. The main reason for this conformational transition consists of the aggregation of surfactant ions within the gel due to hydrophobic interactions between their hydrocarbon chains. This aggregation is responsible for the decrease in the concentration of mobile counterions in the network, leading to a significant decrease in the internal osmotic pressure in the gel. Besides, the attraction between the charged surfactant aggregates and the oppositely charged network chains acts as additional effective cross-linking.⁷

The aggregation of an ionic surfactant in the polyelectrolyte network starts at a concentration that is much lower than the CMC of the surfactant in water.¹⁰ This is because micelle formation in solution requires the immobilization of a significant number of counterions neutralizing the charge of the micelle, while in the gel the neutralizing charges are initially immobilized since they belong to the network chains.⁷

Thus, both electrostatic and hydrophobic forces seem to control the interaction of polyelectrolyte gels with oppositely charged surfactants. The hydrophobic modi-

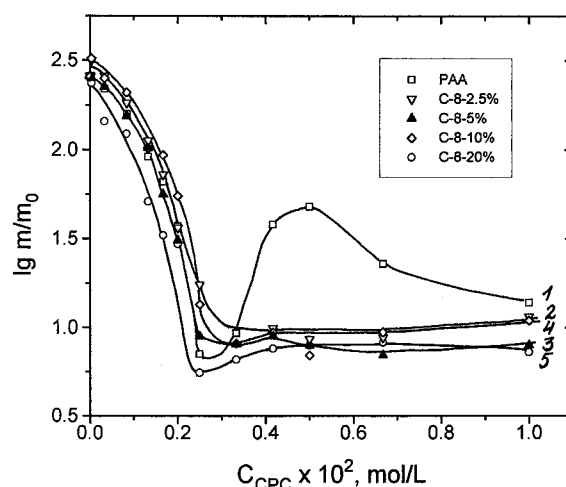


Figure 8. Dependence of the degree of swelling of anionic NaPAA gel (1) and HM C-8-2.5% (2), HM C-8-5% (3), HM C-8-10% (4), and HM C-8-20% (5) NaPAA gels on the initial concentration of the cationic surfactant CPC in solution.

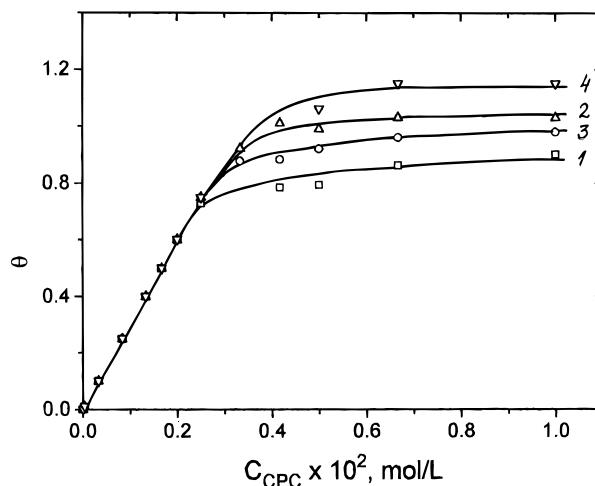


Figure 9. Fraction of the cationic surfactant CPC in anionic NaPAA gel (1) and HM C-8-2.5% (2), HM C-8-5% (3), and HM C-8-20% (4) NaPAA gels as a function of the initial concentration of CPC in solution.

fication of a polyelectrolyte gel permits one to make an estimate of the role of hydrophobic forces.

The experimental results of the study of the interaction of anionic HM NaPAA gels with cationic surfactant CPC are presented in Figures 8 and 9. Figure 8 depicts the typical dependence of the degree of swelling of the HM NaPAA gels on the initial concentration of CPC in solution. Figure 9 illustrates the absorption of CPC by the gels as a function of the initial concentration of CPC in solution. From Figure 9, it is seen that the fraction of cationic surfactant CPC in the anionic network increases monotonically with the increase in the initial concentration of CPC in solution and reaches a limiting value. At initial CPC concentrations of less than 2.5×10^{-3} mol/L (which corresponds to initial CPC/network unit molar ratios of less than 0.75), the anionic gel absorbs all of the cationic surfactant from aqueous solution. The amount of cationic surfactant absorbed per anionic NaPAA repeating unit is the same for HM and unmodified gels and does not depend on the degree of hydrophobic modification of the gel. At higher initial CPC concentrations, the fraction of CPC in the network increases slightly and approaches a value close to 1. Thus, the anionic gel absorbs an equimolar amount of cationic surfactant per charged network unit.

The absorption of oppositely charged surfactant results in gel collapse (Figure 8), accompanied by a 30-fold decrease in the degree of swelling of the gel. These results are consistent with data previously obtained for other polyelectrolyte network/oppositely charged surfactant systems.^{5,14}

Figure 8 shows that, at low CPC concentrations, the degrees of swelling of the unmodified gel and of almost all HM gels fall on the same curve. This result implies that, at low CPC concentrations, the hydrophobic modification does not influence the swelling behavior of the gel/surfactant complex (Figure 8). Thus, the interaction of an anionic hydrogel with a cationic surfactant is governed by electrostatic interactions and does not rely on hydrophilic–hydrophobic balance of the gel.

A small difference between HM and unmodified gels arises only for the gels with high *n*-alkyl group content: C-8-20%, C-12-10%, and C-18-10%. The transition to the collapsed state for these very hydrophobic gels proceeds more sharply than for the unmodified gel. This effect can be attributed to the additional cross-linking due to the formation of mixed hydrophobic aggregates between surfactant molecules and network alkyl side chains.

The formation of mixed micelles was shown for linear anionic HM NaPAA polymers interacting with the cationic surfactant dodecyltrimethylammonium chloride (DTAC).²⁸ Depending on the polymer and surfactant concentrations, the mixed micelles contain alkyl groups belonging to one or more polymer chains. In the latter case, cross-linking between polymer chains occurs, leading to the gelation of the system.²⁸ The aggregation number of the mixed micelles was estimated by steady-state and time-resolved fluorescence methods.²⁸

A difference in the behavior of HM and unmodified gels is also observed at high surfactant concentrations. The increase in the initial surfactant concentration does not affect the degree of swelling of the collapsed HM gels, while it does induce a small reswelling of the unmodified gel. The reswelling takes place when the equilibrium concentration of surfactant in the external solution reaches the CMC. At a further increase in surfactant concentration, the degree of swelling of the unmodified gel decreases and approaches the degree of swelling of HM gels. The gel reswelling at CPC concentrations in the external solution close to the CMC is not observed for HM gels, probably because the mixed micelles in HM gels more effectively stabilize the collapsed state of the gel compared to the electrostatically bound CPC micelles in the unmodified gel.

Thus, one can conclude that the major reason for the binding of surfactant molecules to an oppositely charged polyelectrolyte gel is the electrostatic interaction. The hydrophobic interactions influence only some secondary features of the conformational transition of the gel in the collapsed state.

Anionic Gel/Anionic Surfactant. The interaction of polyelectrolyte gels with a surfactant of similar charge is poorly understood. However, there are some papers^{24,29–33} describing the interaction of a linear polyelectrolyte with a surfactant of the same charge. Fluorescence and conductivity data provide evidence^{24,29} that there are no interactions on the molecular level between linear NaPAA and similarly charged surfactant SDS, but if the polymer concentration is high enough, an increase in ionic strength results in the aggregation of the surfactant, even at concentrations much lower than the CMC. Hence, similarly charged polyelectrolyte

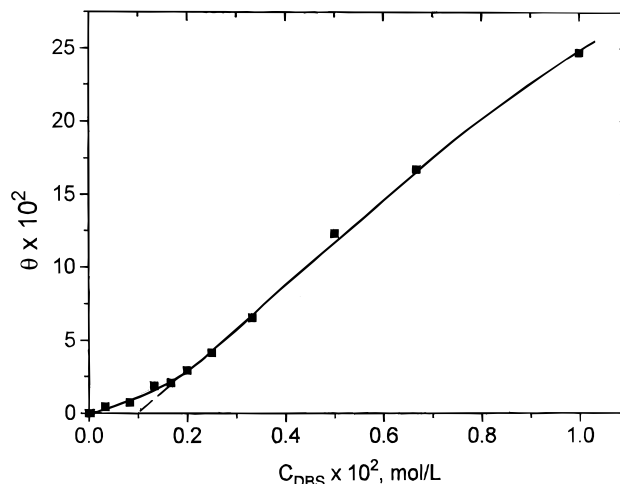


Figure 10. Fraction of the anionic surfactant DBS in anionic NaPAA gel as a function of the initial concentration of DBS in solution.

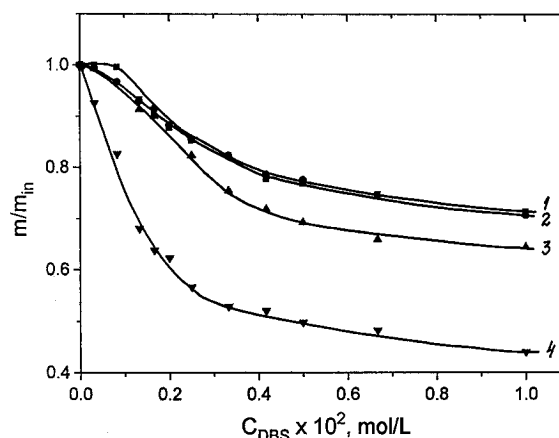


Figure 11. Dependence of the swelling ratio of anionic NaPAA gel (1) and HM C-8-5% (2), HM C-8-10% (3), and HM NaPAA gels (4) on the initial concentration of the anionic surfactant DBS in solution.

acts as a salt decreasing the CMC of SDS through electrostatic effects.

Let us consider the experimental results for an unmodified anionic NaPAA gel interacting with anionic surfactant DBS. The data obtained are illustrated in Figures 10 and 11. The fraction of anionic surfactant DBS in the anionic NaPAA network is plotted against the initial concentration of DBS in solution in Figure 10. The absorption of anionic surfactant by the gel is observed at DBS concentrations above a certain critical concentration C^* equal to 8.3×10^{-4} mol/L. This concentration is only slightly lower than the CMC of DBS in water.²¹ At DBS concentrations below C^* , the surfactants almost do not penetrate the network at all (Figure 10). This may be due to significant losses in the conformational entropy of single surfactant molecules confined within the network. These entropy losses are reduced when the surfactant micelles are formed (cf. Uncharged Gel/Anionic Surfactant section). At higher DBS concentrations, the anionic surfactant penetrates the anionic gel. To estimate the efficiency of the absorption, the distribution constants of the surfactant between the gel phase and solution have to be considered. It was shown that the distribution constants K increase monotonically with increases in the initial concentration of DBS and reach a limiting value of close to 1. Hence, at relatively high DBS

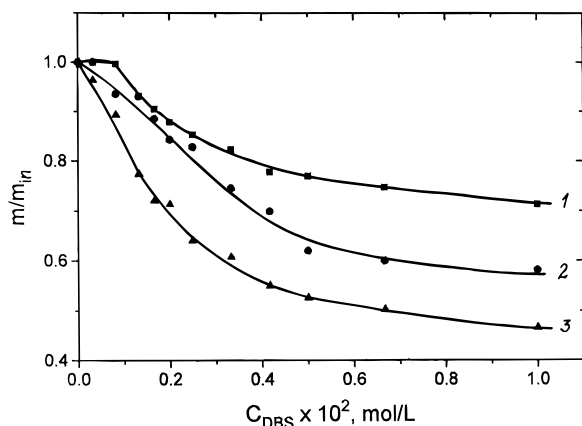


Figure 12. Dependence of the swelling ratio of anionic NaPAA gel (1) and HM C-18-2.5% (2) and HM C-18-5% (3) NaPAA gels on the initial concentration of the anionic surfactant DBS in solution.

concentrations, the anionic surfactant is distributed evenly between the gel phase and solution. This fact may indicate that there are no specific interactions between the anionic gel and the anionic surfactant, which is consistent with the above-mentioned results for the anionic linear polymer/anionic surfactant system.

The immersion of anionic NaPAA gel in a solution of the anionic surfactant DBS results in a small contraction of the gel (Figure 11, curve 1). As we do not expect any specific interactions between the gel and the surfactant of the same charge, one can suggest that the main reason for the contraction of the gel is the usual osmotic deswelling, i.e., surfactants mainly act like low molecular weight salts.^{34–36} The contraction starts to appear at DBS concentrations above a certain critical concentration C^* equal to 8.3×10^{-4} mol/L. Below this concentration the surfactant does not penetrate the network (Figure 10). At the same time the increase in the external osmotic pressure is insignificant because the concentration of DBS is too small. The contraction of the gel is more pronounced in the range of DBS concentrations from 8.3×10^{-4} to 5×10^{-3} mol/L when the surfactant penetrates the network. At these DBS concentrations, the values of the distribution constant K are less than 1, which means that the concentration of anionic surfactant in the exterior solution is higher than in the gel phase and can induce the contraction of the gel due to the external osmotic pressure compression.

We do not expect any appreciable association of polyelectrolyte gels with a surfactant of similar charge unless the gel is markedly hydrophobic. The most interesting systems in this category are those of hydrophobically modified polyelectrolyte gels.

The conformational behavior of anionic HM NaPAA gels in a solution of the anionic surfactant DBS is illustrated in Figures 11 and 12. In contrast to the unmodified gel, the shrinkage of HM gels is observed even at very low surfactant concentrations. At DBS concentrations higher than C^* , the degree of contraction of less hydrophobic HM NaPAA gels is almost the same as that for the unmodified NaPAA gel (Figure 11). The difference between HM and unmodified gels arises only for the gels bearing long enough n -alkyl side chains or having a high content of n -alkyl groups. In C-8 and C-12 series gels, the difference is observed only for the gels with the highest contents of n -alkyl side chains: C-8-20% and C-12-10%. The other C-8 and C-12 gels behave similarly to the unmodified NaPAA gel. For the

HM gel series with the longest n -alkyl side chains ($n = 18$), the introduction of only 2.5% hydrophobic groups results in more pronounced gel shrinkage than for the unmodified gel (Figure 12). Thus, only the more hydrophobic anionic gels (C-8-20%, C-12-10%, C-18-2.5%, C-18-5%, and C-18-10%) undergo a significant contraction in a solution of the anionic surfactant that exceeds the contraction of the unmodified gel.

To explain the conformational behavior of the gels, the distribution constant K of DBS between the gel phase and solution should be considered. The limiting values of distribution constant K higher than 1 are obtained for C-8-20%, C-12-10%, C-18-2.5%, C-18-5%, and C-18-10% gels. Hence, for these more hydrophobic gels, the concentration of DBS in the gel phase is higher than in the external solution. Instead of the electrostatic repulsion between similarly charged groups, anionic surfactant is concentrated within the anionic network, probably due to the hydrophobic aggregation of surfactant tails and HM gel alkyl side chains. Hydrophobic interactions can overcome the electrostatic repulsion between similarly charged groups only at a high enough degree of hydrophobic modification. The analogous effect was observed for linear anionic HM NaPAA polymers interacting with the anionic surfactant SDS.³²

The hydrophobic interactions inside the network can result in the formation of mixed hydrophobic clusters, including surfactant tails and polymer alkyl chains. These aggregates may be responsible for more considerable shrinkage of HM gels because they act as additional cross-links. Thus, the anionic surfactant can bind to the anionic network and induce additional gel shrinkage only if the anionic network contains a sufficient amount of hydrophobic side chains. In this case, the hydrophobic interactions can prevail over the electrostatic repulsion between similarly charged network units and surfactant ions.

Conclusions

Uncharged PAA gels absorb anionic as well as cationic surfactants. But the results of the absorption are quite different: anionic surfactant induces gel swelling, while cationic surfactant induces gel shrinkage.

Hydrophobic modifications can improve the gel/surfactant interactions. In the uncharged gel/anionic surfactant system, binding of surfactant molecules to HM gels starts at a lower surfactant concentration than for the corresponding unmodified gel. In the anionic gel/anionic surfactant system, the gel generally does not associate with similarly charged surfactant, and it is only for quite hydrophobic gels that a significant interaction is observed. Hence, due to hydrophobic forces, surfactant binding takes place even when the unmodified hydrogel/surfactant interactions are strongly repulsive. In the anionic gel/cationic surfactant system, the presence of hydrophobic groups facilitates the cross-linking between different polymer chains that results in the increased sharpness of the gel collapse compared to the corresponding unmodified gel/oppositely charged surfactant system.

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