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Collapse of Polyelectrolyte Networks Induced by Their Interaction with Oppositely Charged Surfactants

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ABSTRACT: The interaction of charged surfactants with oppositely charged polyelectrolyte networks has been investigated. The effective absorption of the surfactant ions by charged gel is observed. The surfactant–network complex formation results in gel collapse. The influence of charge density and mobility, ionic strength, and network topology on complex formation has been studied. It has been shown that the surfactant ions in charged gel form micelle-like aggregates. Due to this fact the surfactant–network complexes are effective absorbers for hydrophobic organic substances.

Introduction

Charged networks swollen in a solvent undergo sudden conformational transitions induced by the change of medium composition (content of poor solvent,[1] salt concentration,[2] and pH values[3]) or temperature.[4] These transitions can be also induced by applying an electric field[5] or mechanical force[6,7] or by introducing charged[8] or uncharged[9] linear polymers in neutral gel. It was shown that gel collapse, i.e., conformational transition of the charged networks from a highly to a slightly swollen state, can proceed as a first-order phase transition.[1,3]

A theoretical approach to the description of the collapse of uncharged networks was proposed in ref 10. The theoretical consideration of phase transitions in charged gels was described in ref 3. The more general case of polyelectrolyte networks which include both cationic and anionic groups taken in different proportion was investigated in refs 11 and 12.

A new type of system where sharp conformational transitions of gels were observed includes polyelectrolyte networks which interact with oppositely charged low molecular surfactants.[13,14] The theory of this phenomenon was described in refs 15 and 16. The present work presents the results of an experimental investigation of the interaction of polyelectrolyte gels with an ionic surfactant. It will be shown that the ions of the surfactant concentrate in the charged network and form micelle-like aggregates. The lowering of the osmotic pressure of counterions in the gel (ions of the surfactant in micelles are partly immobilized) and the presence of hydrophobic groups lead to gel collapse. The complexes of surfactants with networks are good absorbers for different organic compounds, dyes, phenols, etc.; this fact may find interesting practical applications.

Experimental Section

The objects for this investigation were networks of copolymers of sodium methacrylate (SMA) with methacrylic acid (MAA) and the networks of copolymers of SMA with acrylamide (AA) or methacrylamide (MA). Gels were prepared by free-radical copolymerization of monomers in the presence of a cross-linking agent in aqueous solutions. The cross-linking agent was bisacrylamide (BAA). Ammonium persulfate (concentration 4.4×10^{-3} mol/L) and TEMED (*N,N,N′,N′*-tetramethylethylenediamine, concentration 4.4×10^{-3} M) were respectively the initiator and the accelerator of the polymerization reaction. Gelation was performed in cylindrical tubes of diameter 3 mm. The composition of the networks is listed in Table I. After preparation the gels were washed in a large amount of distilled water for 3 weeks, then cut into thin disks, and immersed for 3 weeks in surfactant–water solutions of various compositions. The amount of water was 4×10^5 L/mol of the charged units of the network. The surfactant was cetylpyridinium bromide (CPB).

Table I
Composition of Samples (mol %) and Conditions of Synthesis

sample	AA	MAA	SMA	MA	BAA	monomer concn[a]	T (°C)
1		89.5	10.0		0.5	10	25
2		69.5	30.0		0.5	10	25
3		49.5	50.0		0.5	10	25
4	95.5		4.0		0.5	10	25
5	92.5		7.0		0.5	10	25
6	89.5		10.0		0.5	10	25
7	69.5		30.0		0.5	10	25
8			10.0	89.5	0.5	10	4
9	99.5				0.5	10	25
10	89.0		10.0		1.0	10	25
11	87.0		10.0		3.0	20	25
12	81.0		10.0		9.0	20	25
13	89.0		10.0		1.0	20	25
14	89.0		10.0		1.0	40	25

[a] Total concentration of monomers in polymerization mixture (%).

The relative volume of the networks equilibrated with the CPB solution was characterized by the ratio V/V_0, where V is the equilibrium volume of the network and V_0 is the volume of the network after its synthesis. The efficiency of the CPB absorption by the gel phase was characterized by its distribution constant $K = C_g/C_s$, where C_g and C_s are the concentrations of the CPB cations in the gel phase and in solution, respectively. The K value was calculated according to the formula $K = (M - DV_s\epsilon^{-1})\epsilon/VD$, where M is the initial number of moles of CPB in the system, ϵ is the extintion coefficient at $\lambda = 259$ nm, V_s is the volume of the solution, and D is the optical density of the solution. The optical density of the solutions was measured by a Hitachi 150–20 spectrophotometer.

Experimental Results

At first approximation the interaction of the anionic network with CPB cations can be represented by the following scheme:

$$/\text{-COO}^-\text{Na}^+ + \text{Py}^+\text{-C}_{16}\text{H}_{33} + \text{Br}^- \rightleftarrows /\text{-COO}^-\text{Py}^+\text{-C}_{16}\text{H}_{33} + \text{Na}^+ + \text{Br}^- \quad (1)$$

where Py$^+$ is pyridinium cation.

For networks containing carboxylic groups some H$^+$ ions in the gel are replaced by CPB cations from the surrounding solution:

$$/\text{-COOH} + \text{Py}^+\text{-C}_{16}\text{H}_{33} + \text{Br} \rightleftarrows /\text{-COO}^-\text{Py}^+\text{-C}_{16}\text{H}_{33} + \text{H}^+ + \text{Br}^- \quad (2)$$

However, pH measurements have shown that under the

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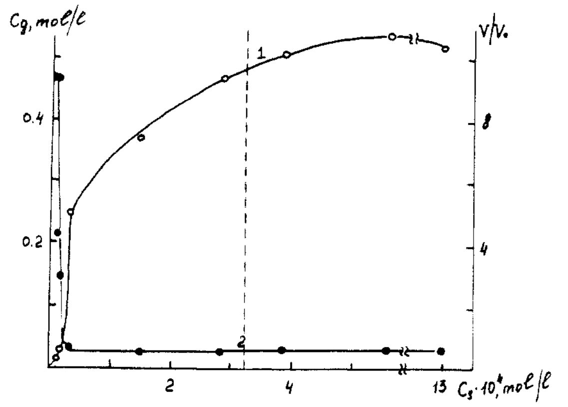

Figure 1. Dependence of the concentration of CPB ions in the gel phase C_g (1) and the ratio V/V_0 (2) on the concentration of CPB in solution C_s for the SMA–MA network (sample 8).

experimental conditions of the present study only 1–2% of the total number of carboxylic groups participate in this process. Therefore reaction 2 will be neglected.

The amount of surfactant ions absorbed by the links of the network will be characterized by the ratio $\gamma = M_{ab}/N$, where M_{ab} is the number of surfactant ions absorbed by the network and N is the total number of monomer units in the sample. In accordance with reaction 1 the number of charged links and the number of surfactant ions in the network are equal when $M_{ab} = N\nu$, where ν is the molar fraction of charged groups in the network.

The parameter K mentioned above characterizes the efficiency of the absorption of surfactants by the gel. It depends strongly on the degree of swelling of the network as well as on the ratio of the volume of the gel to the total volume of the system.

Figure 1 shows the dependence of the equilibrium concentration of cetylpyridinium cations in the anionic gel of MA–SMA, C_g, on the content of CPB in the surrounding solution. At low C_s the C_g values are 10^4 times higher than the value of CPB concentration in the solution and they are much higher than the critical micelle concentration (cmc) of CPB in water (3×10^{-4} mol/L). This fact leads to the assumption that CPB cations in the gel form aggregates.

To prove this assumption particles of water–insoluble dyes (Sudan-1 and Sudan-3) were put upon the gel samples. During the contact the dyes were solubilized by swollen networks, giving a red color to the gels. This result supports the assumption that the surfactant ions in the gel are in aggregated form. For the uncharged polyacrylamide network no solubilization of dyes has been observed for the same region of concentration of CPB in solution, so CPB ions in a neutral network do not aggregate. It should be noted that cmc in the outer solution for the conditions of the present study corresponds to $C_s = 3 \times 10^{-4}$ mol/L (this value is shown by the dotted line in Figure 1). Solubilization of dyes by the gel was observed in the range of much smaller values of C_s ($C_s \sim 3 \times 10^{-5}$). Analogous results were obtained for all charged networks investigated in this work.

The detailed study of the structure of aggregates of ionic surfactants in polyelectrolyte gels is still lacking. For example, one can assume either of the structures shown in Figure 2a,b. The further reasoning in the present paper does not depend on the specific structure of the aggregates. When C_s reaches the cmc in the outer solution, the gel is already saturated with a surfactant, and at higher surfactant concentration in solution, the values of C_g become somewhat lower than its maximal value. It should be also mentioned that the interaction of network with ionic surfactant results in a change of the gel structure, and samples with high C_g values become opaque.

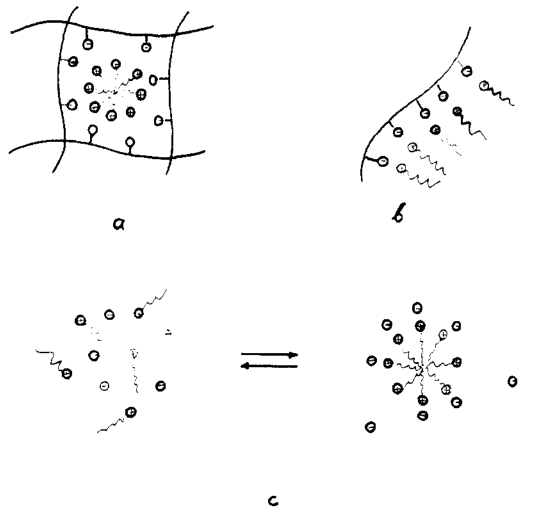

Figure 2. Schematic representation of possible structure of CPB aggregates in the gel phase (a and b). Micelle formation in the solution (c).

Theoretical consideration of the interaction between a polyelectrolyte network and oppositely charged surfactants was developed in refs 15 and 16. In the present paper we will discuss only the main physical reasons for the preferential formation of micelles or aggregates in a polyelectrolyte gel.

Micelle formation in water leads to strong counterion binding due to the high charge density on the surface of the micelles (Figure 2c). In polyelectrolyte networks the charge of the micelles or aggregates is neutralized by the ions of a network which are initially immobilized due to their connection in polymer chains (Figure 2). In addition to this, the network–surfactant complex formation is accompanied by diffusion of counterions of network chains in the outer solution, so formation of micelles or aggregates in the gel leads to a large gain in entropy in comparison with micelle formation in solution.

The interaction of charged gel with ionic surfactants leads to a rapid decrease of the volume of the sample (Figure 1, curve 2). The observed conformational transition resembles collapse of charged gels in a poor solvent. In both cases the conformational changes are the result of volume interactions. For the gels that contain charged counterions of surfactants the volume interactions between hydrophobic hydrocarbon groups of surfactant ions cause their aggregation. Due to this fact (i) the concentration of mobile counterions inside the gel decreases, leading to the essential decrease of the internal osmotic pressure of the gel, and (ii) strongly charged micelles are attracted to the oppositely charged network chains, inducing their additional effective cross-linking. As a result we observe pronounced collapse of the gel.

It is well-known that there are numerous factors that influence the gel collapse (charge density, topological structure of the network, medium composition, etc.). The same factors are present in the case under study as well. The influence of these factors on equilibrium properties of network–surfactant complexes will be discussed below.

It has been shown that an increase of charge density of polyelectrolyte networks results in an increase of the amplitude of the collapse.[3] Figure 3 illustrates the influence of charge density on collapse of SMA–MAA and SMA–AA gels in the presence of CPB. The introduction of cationic surfactant in the networks causes a strong decrease of the volume of the sample. For gels containing only 10% charged groups tenfold volume changes are

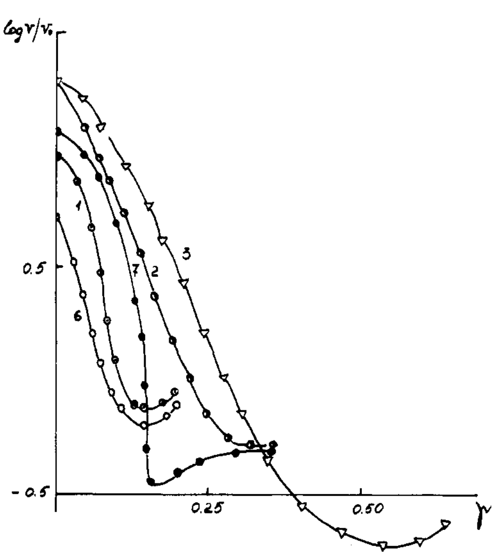

Figure 3. Dependence of the ratio V/V_0 on γ. The numbers of the samples correspond to the numbers of the curves.

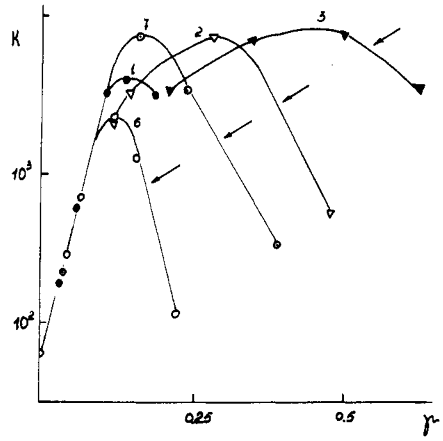

Figure 4. Dependence of the distribution constant K on γ. The numbers of the samples correspond to the numbers of the curves. Arrows correspond to critical micelle concentration.

observed. Comparison of curve 1 with curve 3 and curve 6 with curve 7 shows that the increase of the charge density results in stronger volume changes of the networks.

The degree of charging of MAA gel can be changed also by addition of sodium hydroxide. We have performed such experiments and have shown that the qualitative picture is analogous to that presented in Figure 3.

Now let us compare two types of networks with the same degree of charge (Figure 3). One is formed by ionic monomer units which can migrate along the chains (SMA–MAA copolymers) and the other contains immobile (quenched) ionic groups (SMA–AA copolymers). The data shown in Figure 3 indicate that for networks of the second type the transition to the collapsed state is sharper and that it proceeds at lower concentrations of surfactants. The observed difference can be explained by the fact that in the latter case the charged groups of the network are divided by nonionizable fragments so that their attaching to charged aggregates causes more essential changes of the gel volume than in the former case, where the gel adjusts to the structure of the aggregates.

The charge density and the mobility of charges in the networks influence essentially the efficiency of absorption of surfactant. The results illustrated by Figure 4 show that at low values of γ the ratio K increases sharply. At concentrations higher than the point at which the charge of the micelles is neutralized by the ions attached to the network (this point is not achieved exactly at equimolar content of CPB cations and SMA links in the gel phase because of the presence of mobile surfactants inside the network) the efficiency of absorption drops and micelle formation in solution is observed. It should be also noted that the networks with fixed charges (SMA–AA copolymers) absorb less surfactant ions than those with mobile charges (SMA–MAA copolymers). Thus the presence of mobile charges in polyelectrolyte network facilitates neutralization of micelles and complex formation.

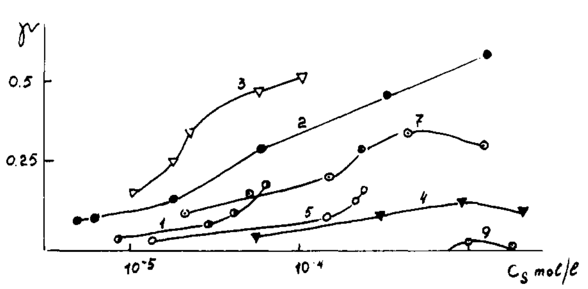

Figure 5. Relationship between γ and C_s for the gels. The numbers of the samples correspond to the numbers of the curves.

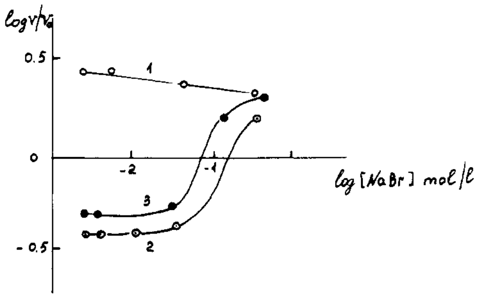

Figure 6. Influence of the concentration of sodium bromide on the ratio V/V_0 for the complexes of CPB with the SMA–AA network (sample 7). The values of γ are 0.5 (1), 0.6 (2), and 1.2 (3).

The dependence of γ on C_s characterizes the efficiency of CPB cation adsorption on network chains. From the analysis of the experimental curves shown in Figure 5, it can be concluded that the efficiency of interaction of anionic networks with CPB increases with the increase of charge density. For neutral PAA gel the amount of absorbed molecules of CPB is within the experimental error. Comparing curves 2 and 7, one can see that networks with mobile charges absorb more surfactant than those with fixed charged groups.

From Figure 5 it can be seen that when the concentration of surfactants increases, the efficiency of CPB cation adsorption by anionic gels grows and reaches its maximum level after which a decrease of γ is observed in some cases (see curves 4 and 7). This decrease was predicted theoretically.[15,16] This can be explained by the fact that in this region of surfactant concentrations the ionic strength of the solution is already high enough to suppress the gain in translational entropy in the course of the network–surfactant complex formation.

Figure 6 illustrates the influence of addition of a low molecular weight salt on the swelling of the network–surfactant complexes. The SMA–MAA gels were equilibrated with CPB solutions of different concentrations, and the obtained complexes with different values of γ were immersed in aqueous solutions of sodium bromide. Curve 1 illustrates the dependence of the relative volume V/V_0 on the concentration of KBr for the sample with $\gamma = 0.13$. Due to the high content of sodium counterions in the network, the initial degree of swelling of this gel is rather high. The increase of salt concentration leads to a decrease of the sample volume due to a lowering of the osmotic pressure of the counterions in the network.

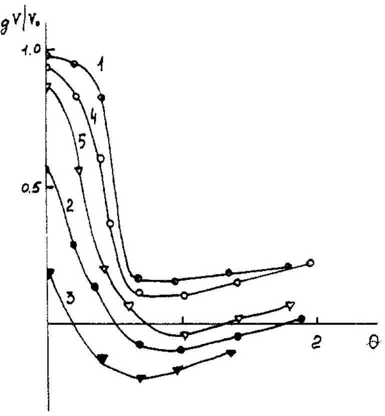

Figure 7. Dependence of the ratio V/V_0 on γ for networks with different concentrations of cross-links (curves 1–3 correspond to samples 10, 11, and 12) and with different concentrations of monomers at synthesis conditions (curves 1, 4, and 5 correspond to samples 10, 13, and 14).

The analogous dependencies for gels with high values of γ ($\gamma = 0.6$ and 1.2) are illustrated by curves 2 and 3. In both cases at low concentrations of salt the anionic networks are in the collapsed state due to the high content of CPB cations (in contrast to the case of curve 1). The increase of salt concentration results in the complex dissociation and in the swelling of the gels. At high salt concentration the relative volume of the gel only slightly depends on the initial content of the surfactant in the polyelectrolyte network (all three curves in Figure 6 are close each other).

The investigation of collapse phenomena has shown that the topological structure of the network plays an essential role in the process of gel collapse.[17,18] The lowering of the number of chemical cross-links or topological entanglements results in a sharper gel collapse. To check the influence of network topology on equilibrium properties of the structure of micelle–network complexes, a set of experiments with gels differing in cross-link content or in the conditions of synthesis was performed.

Figure 7 illustrates the collapse of the SMA–AA networks induced by the addition of CPB for gels with equal charge densities but differing cross-link densities (curves 1, 2, and 3) or differing monomer concentrations at the preparation conditions (curves 1, 4, and 5). It can be seen that the increase of the degree of cross-linking results in smoother gel collapse. Comparison of curves 1, 4, and 5 shows that the increase of the concentration of monomers at the preparation conditions which results in appearance of additional topological entanglements (refs 17 and 18) also leads to smoothening of the collapse. Thus, both the increase of the content of chemical cross-links and of topological entanglement affect the collapse in the same manner.

The data listed on Figure 7 show that after collapse a slight increase of gel volume is observed. This increase might be a result of an increase in the internal osmotic pressure of the network due to introduction of the excess of surfactant molecules within the network. However, analysis of data shown in Table II does not confirm such an assumption because the water content of the gels decreases when the samples absorb the excess of CPB cations in relation to the number of SMA anions of the network. Thus it is natural to assume that the effect mentioned above is a result of the introduction of the bulky surfactant ions in the gel, most of which participate in the formation of micelles or aggregates (and thus do not contribute to osmotic pressure). In fact, the presence of hydrophobic surfactants in the collapsed gel can be very essential. For example, by comparing curves 1, 2, and 3 in Figure 3, one can see that at high values of γ the water content of gels with high charge density is less than the water content of slightly charged gels. This is due to the fact that all charges of the network participate in the complex formation with hydrophobic surfactants, and therefore more charged network is more hydrophobic in this regime.

Table II
Dependence of the Water Content (Weight Fraction) of the Samples α on the Value of γ

sample	γ	α	sample	γ	α
10	0.066	0.82	13	0.096	0.70
	0.090	0.81		0.142	0.69
	0.139	0.76		0.190	0.65
	0.179	0.80	14	0.068	0.65
11	0.097	0.77		0.096	0.63
	0.143	0.75		0.135	0.61
	0.189	0.74	7	0.070	0.47
12	0.069	0.78		0.101	0.45
	0.098	0.71		0.174	0.46
	0.142	0.70			
	0.178	0.69			

Table III
Influence of the Content of Cross-Linking Agent in the Networks and of the Concentration of Monomers at the Conditions of Network Formation on the Value of γ at Fixed Concentration of CPB in Solution[a]

BAA[b]	10[c]	20[c]	40[c]
1	0.136	0.194	0.160
3		0.142	
9		0.128	

[a] Concentration of CPB in solution $C_s = 3 \times 10^{-4}$ mol/L. [b] Content of BAA in the network (mol %). [c] Concentration of monomers at the conditions of network formation (%).

The topological structure of the network affects the efficiency of absorption of the surfactant ions by the gel.[14] Comparison of the amount of CPB ions absorbed for a set of networks which have the same charge density but differ in their topological structure has been performed, using the results of the ref 14. In Table III the γ values are listed for the SMA–AA gels for the conditions when the concentration of free CPB is constant for all samples. These values were obtained by the extrapolation from the corresponding γ–C_s dependences obtained in ref 14. The networks listed in Table III differ in cross-link density or concentration of monomers at the preparation conditions. The obtained results indicate that an increase of cross-link density results in lower γ values, i.e., in lower absorption ability of the networks. One can assume that introduction of cross-links retards the neutralization of micelle charges in the gel due to steric hindrances.

Comparison of γ values for the gels obtained in dilute and concentrated solutions of monomers shows that there is some optimal region of concentration of monomers at the network preparation conditions where the final gels have maximum absorption ability. The gel obtained in 20% solution of monomers absorbs more CPB cations than the gels which were synthesized in 10% or 40% solutions of monomers.

In conclusion it should be noted that complexes formed by polyelectrolyte networks with oppositely charged surfactants are very effective absorbers for organic compounds dissolved or dispersed in water. Our experiments have shown that for some regimes they take as much as 95–99% of phenols from water and can find practical applications for cleaning of water, for concentrating hydrophobic compounds, etc. These aspects of the problem will be considered in separate publications.

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Registry No. (SMA)(MAA) (copolymer), 9035-87-4; (SMA)(AA) (copolymer), 24991-37-5; (SMA)(MA) (copolymer), 29755-80-4; CPB, 140-72-7.