Complexation of Amphiphilic Polyelectrolytes with Surfactants of the Same Charge in Water Solutions

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Received August 23, 1994; Revised Manuscript Received January 24, 1995[⊗]

ABSTRACT: Aqueous solutions containing amphiphilic polycations and micelle-forming surfactants of the same charge were examined by potentiometric, fluorescence, sedimentation, and viscometric techniques. Copolymers containing *N*-ethyl-4-vinylpyridinium bromide units and relatively small numbers of either *N*-dodecyl-4-vinylpyridinium bromide or *N*-cetyl-4-vinylpyridinium bromide units were used as amphiphilic polycations. The surfactants were dodecyl- and cetyltrimethylammonium bromides and their pyridinium analogs. The formation of copolymer–surfactant complexes in dilute solution was established, and the complexation behavior was shown to depend upon the copolymer to surfactant concentration ratio in the mixture. At surfactant concentrations lower than or equal to the critical micelle concentration (cmc) complexation leads to compact structures via formation of intrachain aggregates containing several hydrophobic chain units and surfactant molecules. At the cmc, the maximum number of surfactant ions bound per hydrophobic copolymer chain unit increases with increasing length of the polymer side group and decreases for copolymers that are initially in the compact conformation. At surfactant concentrations greater than the cmc the intrachain aggregates are disrupted and copolymer coil expansion occurs. The resultant copolymer–surfactant complexes consist of surfactant micelles, each bound to one hydrophobic chain unit of the copolymer.

Interactions between polymers and low-molecular-weight surfactants have attracted considerable interest during the last several decades.[1–17] Investigation of these reactions is motivated in part by opportunities for the synthesis of new types of polymer–surfactant complexes with novel dispersion, solubilization, or lubrication properties.

The interactions between polyelectrolytes and oppositely charged surfactants are the most thoroughly investigated at present. These interactions lead to complexes in which the polyelectrolyte chain units form salt bonds with the surfactant molecules and in which nonpolar segments of the surfactant chains provide stabilization via hydrophobic interactions in the aqueous medium.[1–7] The reactions resulting in complex formation proceed cooperatively, even at surfactant concentrations significantly lower than the critical micelle concentration (cmc).[1,4,7]

For amphiphilic polymers, one can anticipate complex formation both in water solutions and in low-polarity solvents. We have recently investigated complexation in mixtures of an ionomer and a surfactant in the nonpolar solvent *m*-xylene.[9–11] Ionomers are nonpolar copolymers with a hydrophobic backbone carrying from 1 to 10 mol % of ionogenic (salt) groups. The interactions between ionomers and surfactant molecules have been shown to occur through substitution of the dipole–dipole self-contacts of ionomer salt groups by polymer–surfactant contacts, leading to expansion of the ionomer coil. Ionomer salt groups act as molecular "anchors", binding surfactant micelles and leading to additional aggregation of the molecularly dispersed or weakly aggregated surfactant on the polymer chain.[9–11] Reactions between amphiphilic copolymers and surfactants can also proceed in water solutions. Recent investigation of the interactions between hydrophobically modified copolymers based on poly(*N*-isopropylacrylamide) and various surfactants by fluorescence techniques[12–16] and rheological studies of semidilute solutions of hydrophobically modified poly(sodium acrylate)s[17] provide evidence for the formation of polymer–surfactant aggregates. If the polymer component is an amphiphilic polyion, the low-molecular-weight components should be of the same charge or nonionogenic for the reaction to occur due to hydrophobic interactions only. Otherwise, the interaction between the polymer and surfactant in water solution will occur due to Coulombic attraction or by a more complex mechanism.

In the present paper we describe a systematic study of the role of hydrophobic interactions in the reaction between amphiphilic copolymers and surfactant ions in water solution. We used hydrophobically modified polycations based on poly(*N*-ethyl-4-vinylpyridinium bromide) and low-molecular-weight surfactants of the same charge sign. We applied fluorescence spectroscopy, potentiometry, velocity sedimentation, and viscometry techniques to evaluate the compositions of the complexes formed and to investigate the conformational transitions of the copolymer chains upon interaction with the surfactant molecules. Based on the data obtained on the dependence of complex composition on the hydrophilic–lipophilic balance (HLB) and on the ratio of components in the mixture, we conclude that the character of the complexation changes upon increasing surfactant concentration in the polymer–surfactant mixture. A plausible complex structure is proposed.

Experimental Section

Materials. The amphiphilic polycations contained *N*-ethyl-4-vinylpyridinium bromide units and relatively small amounts of *N*-dodecyl-4-vinylpyridinium bromide or *N*-cetyl-4-vinylpyridinium bromide units:

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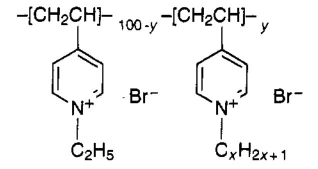
[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1995.



$x = 12$; $y = 3, 6, 10, 18$
$x = 16$; $y = 3, 7, 7.5, 10$

We will refer to such copolymers as P4VP-$C_x(y)$, where x is the number of carbon atoms in the hydrocarbon segment of the hydrophobic chain unit and y is the molar percentage of hydrophobic units in the copolymer chain. For comparison we used a polycation which did not contain such hydrophobic chain units, poly(*N*-ethyl-4-vinylpyridinium bromide), P4VPQ, which we will call the reference polycation. The viscosity-average degrees of polymerization (DP_η) of the copolymers were approximately 500. We also used samples of P4VP-C_{16}(2.5) and P4VPQ with $DP_\eta = 3000$.

P4VPQ was synthesized from poly(4-vinylpyridine) (Polysciences Inc.) by quaternization with a 5-fold molar excess of ethyl bromide in an argon atmosphere at 60 °C for 36 h using methanol as solvent.[18] The polymer was precipitated by dropping the methanolic solution into absolute diethyl ether, washed with ether, filtered, and dried in vacuum.

The P4VP-$C_x(y)$ copolymers were obtained by a two-stage synthesis. First, P4VP was quaternized by either dodecyl bromide or cetyl bromide (Aldrich) under conditions similar to those used for P4VPQ. In the case of P4VP-$C_{12}(y)$ and P4VP-C_{16}(3) equimolar ratios of P4VP units and the corresponding alkyl halides were used. In the case of P4VP-$C_{16}(y)$, $y > 3$, a 3-fold excess of cetyl bromide was used. Partially quaternized P4VP was precipitated by dropping into ether, with subsequent filtering, drying, and quaternization by ethyl bromide. The degree of quaternization of P4VP was estimated using IR and UV spectroscopy, as described in ref 18 and 19. The degree of quaternization of the samples by ethyl bromide was 90–95 mol %.

Cationic surfactants with the formula $R\text{-}N^+(CH_3)_3Br^-$ (where R = dodecyl (DDTMABr) or cetyl (CTMABr)), dodecylpyridinium chloride (DDPCl), and cetylpyridinium bromide (CPBr)) were used as received from Aldrich.

1-Pyrenecarboxyaldehyde (PyCHO) (Aldrich) was used as a fluorescence probe.

Solution Preparation. All solutions were made in doubly distilled water, deionized with a Millipore water purification system. Polymer and surfactant solutions were prepared by magnetic stirring of the samples in 0.01 M NaCl for 24–48 h. This salt concentration was held constant in all of the experiments reported herein. The polymer–surfactant solutions were mixed for 24 h prior to measurement. Copolymer concentration was 0.0137 M (in chain units).

Fluorescence Spectroscopy. The application of PyCHO as a fluorescent probe for investigating the formation of hydrophobic aggregates in aqueous solutions is based on the known dependence of the fluorescence spectrum of PyCHO on the dielectric permittivity of the solvent.[20] Micelle formation in surfactant solutions containing PyCHO (the concentration of the saturated solution is about 10^{-6} M) results in probe solubilization by the micelles and a blue shift of the emission maximum. To observe aggregate formation, 4–6 μL of PyCHO solution in acetone was added to the sample solutions with subsequent stirring for about 30 min. The probe concentration in the solutions investigated was 5×10^{-7} M. PyCHO spectra were recorded on a Hitachi F-3000 fluorescence spectrometer at room temperature with excitation at 363 nm and excitation and emission slitwidths equal to 5 nm.

Potentiometry. The concentration of free surfactant ions in the copolymer–surfactant mixtures was measured using surfactant-ion selective electrodes. The surfactant-ion selective electrode was a galvanic half-element with an ion selective membrane. The inner side of the ion selective membrane was brought in contact with a surfactant solution of a certain concentration below the corresponding cmc (2.5×10^{-3} M for DDPCl and 2.5×10^{-4} M for CPBr). The standard silver chloride electrode acting as an inner reference electrode was immersed in the surfactant solution. The indicator membrane electrode contained a film of poly(vinyl chloride) (PVC) made through dissolution in THF of a plasticizer (*o*-nitrophenyloctyl ether) and the surfactant ion transfer agent bis(diphenylphosphinylmethyl ether) of oligo(ethylene oxide) with subsequent solvent evaporation. The details of the membrane preparation and the electrode characteristics have been described previously.[21,22] The second galvanic half-element was a silver chloride electrode immersed in a saturated KCl solution, and contact between the two half-elements was maintained through a salt bridge.

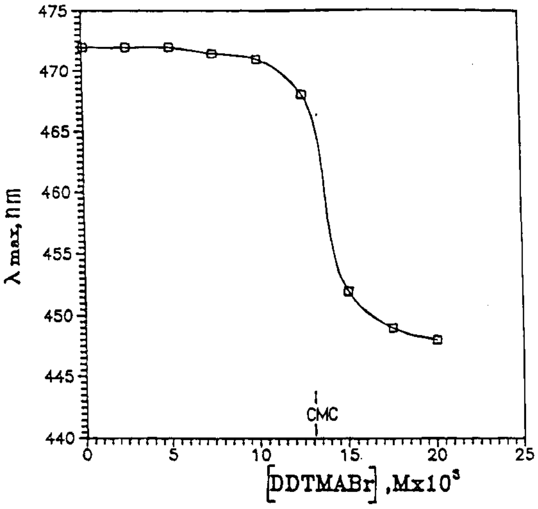


Figure 1. Dependence of the PyCHO fluorescence λ_{max} on the concentration of DDTMABr. The cmc marked on the concentration axis corresponds to the inflection point in the curve.

In this work, indicator electrodes containing DDPCl or CPBr solutions as the inner solutions were used. For the electrode employed, a plot of the observed potential (E) vs the logarithm of the surfactant concentration was linear at surfactant concentrations below the cmc, with a slope of 59 ± 12.5 mV/M, over 1 decade of variation in surfactant concentration, in agreement with the Nernst equation. All measurements were carried out at 20 °C.

Sedimentation Velocity. Sedimentation measurements were performed using a Beckman-E analytical ultracentrifuge. The sedimentation of either the polymer or the polymer–surfactant complex was monitored by recording the absorption spectra of the pyridinium groups of the polymer at $\lambda_{max} = 250$ nm as a function of time. The sedimentation coefficients were calculated according to the formula:

$$S = \mathrm{d}\ln r/(\omega^2\,\mathrm{d}t)$$

r being the distance between the center of the sedimentation profile and the bottom of the cell at different time points.[23] The rotor rotation speed (ω) was 60 000 rpm. All measurements were performed at 20 °C.

Viscometry. All measurements were carried out using a standard Ubbelohde viscometer, at 20 °C. The polymer and the polymer–surfactant solutions were equilibrated for 10–15 min before each measurement. All measurements were repeated four to five times.

Results and Discussion

Fluorescence Spectroscopy and Potentiometry. Figure 1 shows the dependence of the maximum wavelength, λ_{max}, of the fluorescence emission spectrum of PyCHO on the concentration of DDTMABr in aqueous solution.

At surfactant concentrations below the cmc, the PyCHO spectra in pure water and in the surfactant solution are identical. As the cmc is reached, an abrupt blue shift of the λ_{max} is observed, caused by solubilization of PyCHO molecules in surfactant micelles. The

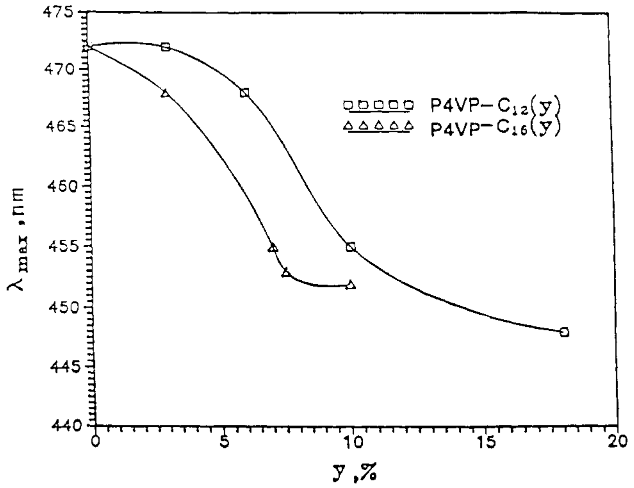


Figure 2. Dependence of the PyCHO fluorescence λ_{max} on the content of hydrophobic groups in the copolymer chains in aqueous solutions of P4VP-$C_x(y)$.

cmc observed is in good agreement with that reported in the literature *(vide infra)*.[24]

Figure 2 illustrates the dependence of the λ_{max} of the same probe in P4VP-$C_x(y)$ solutions on the mole percent of the hydrophobic chain units in the copolymers.

The fluorescence spectrum of the probe in solutions of the reference polycation, P4VPQ, is identical to that in water. Introduction of 3 mol % of cetyl groups in the polycation chains leads to a slight decrease in λ_{max}. Further increase in the number of hydrophobic chains results in an abrupt decrease of λ_{max}, with subsequent saturation of the effect at about 7 mol % of cetyl groups. The behavior of the copolymers quaternized with dodecyl groups is analogous to that of P4VP-$C_x(16)$, but saturation is observed at higher extents of alkylation. The "s"-shaped character of the curves in Figure 2 is attributed to the formation of predominantly intrachain clusters of the hydrophobic side groups of the copolymers in the dilute solution. It has been shown previously by viscometric methods that these amphiphilic polycations can form intramolecular aggregates stabilized by interactions of the hydrophobic chain units in aqueous solution. The saturation of the dependence of λ_{max} on the content of hydrophobic groups correlates with the approach to the most compact conformation of the copolymer chain according to the viscosity data.[25]

Figures 3 and 4 illustrate the dependence of the PyCHO emission maximum on the surfactant concentration in solutions containing a series of polycations and either DDTMABr or CTMABr.

The dependence of λ_{max} on the surfactant concentration in polymer-free solutions is presented for comparison. In these experiments, copolymers bearing 3−6 mol % of dodecyl or cetyl groups were used, which in the absence of surfactant affords PyCHO spectra characterized by relatively high λ_{max} values. The following general trends are observed in the polymer−surfactant mixtures. At low surfactant concentrations, the PyCHO emission spectra of the P4VP−surfactant mixtures are identical to the spectrum of PyCHO in 0.01 M NaCl. At surfactant concentrations 2−3 times lower than the cmc, an abrupt blue shift is observed, followed by saturation at concentrations near the cmc. The variations of λ_{max} with the surfactant concentration in solutions of P4VPQ and P4VP-$C_{12}(3)$ are essentially identical. Increasing the length or the content of hydrophobic groups in the copolymer results in a decrease in the surfactant concentration corresponding to the blue shift of the PyCHO fluorescence spectrum.

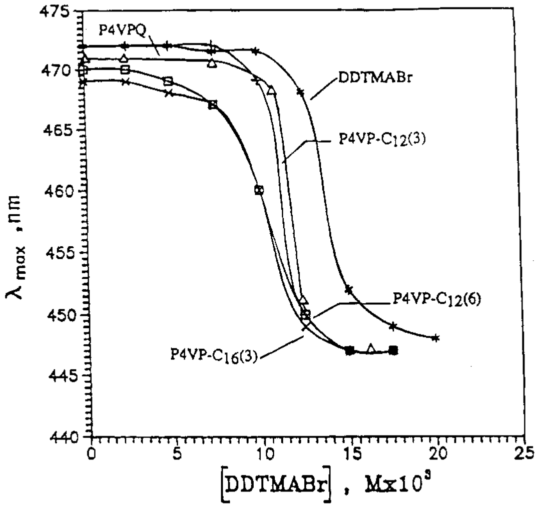


Figure 3. Dependence of the PyCHO fluorescence λ_{max} on DDTMABr concentration in aqueous solutions of DDTMABr and in DDTMABr−P4VP-$C_x(y)$ or DDTMABr−P4VPQ mixtures.

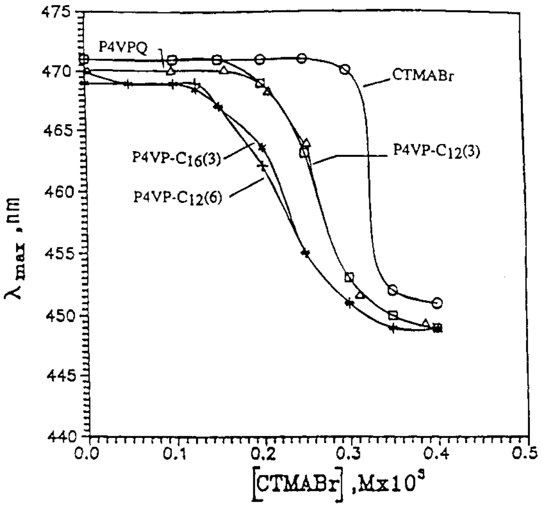


Figure 4. Dependence of the PyCHO fluorescence λ_{max} on the concentration of the CTMABr in aqueous solutions of CTMABr and in CTMABr−P4VP-$C_x(y)$ or CTMABr−P4VPQ mixtures.

These data provide clear evidence of interaction between the cationic copolymers P4VP-$C_x(y)$ and surfactant ions of the same charge sign in dilute aqueous solutions. The interactions result in the formation of hydrophobic domains, which solubilize PyCHO. Such interactions are not expected in the case of P4VPQ, a simple polycation without long hydrophobic side groups. The slight shift in concentration required for surfactant aggregation in the presence of P4VPQ can be attributed to a decrease in the cmc due to the increase in the ionic strength of the solution. For example, introduction of NaCl causes a decrease in the cmc of DDTMABr from 1.6×10^{-2} M (without added salt) to 8.7×10^{-3} M for [NaCl] = 7×10^{-2} M, according to ref 24. This effect is more pronounced for bromide salts, e.g., KBr or NaBr.[24]

The fluorescence probe technique does not provide information on the interactions of surfactants with the copolymers containing more than 3−6 mol % of hydrophobic side groups. These copolymers alone form hydrophobic domains in water solutions, and the emission maximum for PyCHO is strongly blue-shifted even in the absence of added surfactant (compare Figures

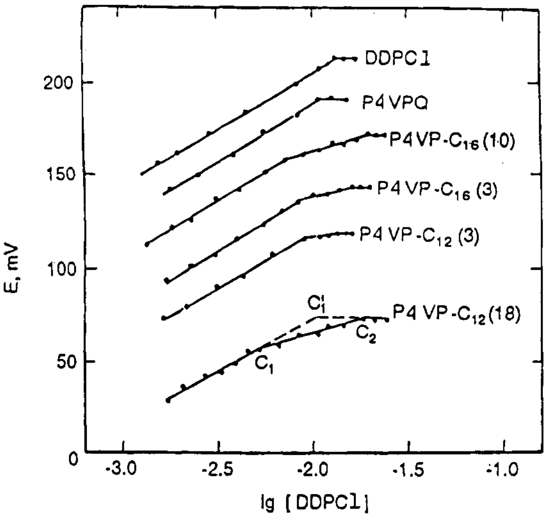


Figure 5. Dependence of the electrode potential on the logarithm of DDPCl concentration in aqueous solutions of DDPCl and P4VP-$C_x(y)$−DDPCl or P4VPQ−DDPCl mixtures. The experimental curves are shifted along the *E* axis, in order to avoid overlap. The initial position of each curve corresponds to the position of the lowest curve in each figure.

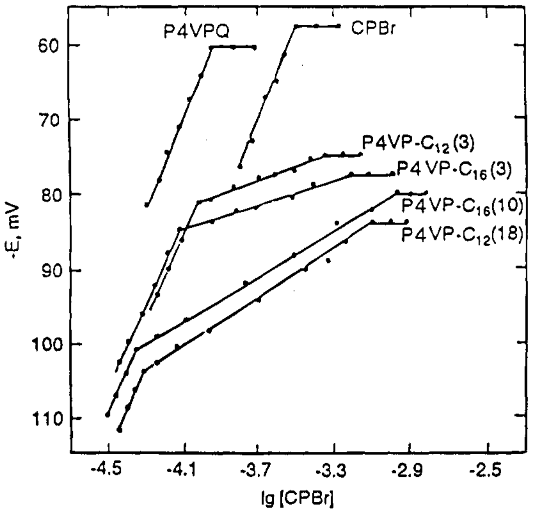


Figure 6. Dependence of the electrode potential on the logarithm of CTMABr concentration in CTMABr solutions and in CTMABr−P4VPC$_x$(y) or P4VPQ−CTMABr mixtures. The experimental curves are shifted along the *E* axis, in order to avoid overlap. The initial position of each curve corresponds to the position of the lowest curve in each figure.

2−4). For this reason we applied a potentiometric technique, which allows one to measure directly the concentration of surfactant ions which are not bound to the copolymer chains (if the surfactant concentration in the solution is lower than the cmc). The variation of the observed potential, *E*, with the concentration of surfactant ions in P4VP-$C_x(y)$-surfactant and P4VPQ−surfactant mixtures and in surfactant solutions is illustrated in Figures 5 and 6. In polymer-free solutions of the surfactant, *E* exhibits a linear increase with increasing surfactant concentration below the cmc and then saturates at the cmc. Similar behavior is observed in the presence of the reference polycation. The slope of the linear part of the *E* vs log [surfactant] plots remains nearly the same, while the cmc is shifted toward lower concentrations. Thus, P4VPQ does not interact with the surfactant investigated, and the observed decrease in the cmc can be attributed to an increase in the ionic strength of the solution in the presence of the polycation. In copolymer solutions, one observes three regimes in the variation of the potential with the surfactant concentration. At surfactant concentrations below C_1 (Figure 5) a linear increase in *E* is observed, the slope of the curve being equal to that in the water solution of the corresponding surfactant.

Table 1. Surfactant Molecules Bound per Hydrophobic Chain Unit (*f*) in Copolymer−Surfactant Mixtures

experiment	surfactant	copolymer	f^a
1	DDPCl	$P_4VP\text{-}C_{12}(3)$	8
2	DDPCl	$P_4VP\text{-}C_{12}(18)$	3
3	DDPCl	$P_4VP\text{-}C_{16}(3)$	14
4	DDPCl	$P_4VP\text{-}C_{16}(10)$	6
5	CPBr	$P_4VP\text{-}C_{12}(3)$	0.8
6	CPBr	$P_4VP\text{-}C_{12}(18)$	0.8
7	CPBr	$P_4VP\text{-}C_{16}(3)$	1.3
8	CPBr	$P_4VP\text{-}C_{16}(10)$	0.7

[a] The experimental error in the evaluation of *f* values did not exceed 10%.

At surfactant concentrations greater than C_1 (but still lower than the cmc) *E* increases with surfactant concentration, but with a reduced slope of the curve. At concentrations equal to C_2 (with C_2 greater than the cmc) one observes no further concentration dependence of the potential, corresponding to the formation of surfactant micelles in the aqueous solution. This behavior is observed in all copolymer−surfactant mixtures investigated and supports the conclusion that a complexation reaction occurs in the water solutions of P4VP-$C_x(y)$ and cationic surfactants when a certain critical surfactant concentration is reached (Figures 5 and 6).

As the content of the hydrophobic groups in the copolymer chains is increased, the point (C_2) at which free micelles form in the copolymer−surfactant mixtures shifts to higher surfactant concentrations.

We have estimated the compositions of the complexes formed on the basis of the potentiometric data. The quantity of surfactant bound to the copolymer chains was calculated as the difference between the point corresponding to the formation of the free micelles in the mixture (C_2) and the effective cmc in the presence of copolymer (C'_1).[18] The concentration C'_1 was obtained by extrapolation of the initial linear dependence of *E* on log [surfactant] to the *E* value corresponding to saturation (Figure 5). The compositions of the complexes thus obtained, i.e., the maximum number of the surfactant molecules bound to the copolymer chains at the cmc point in surfactant−copolymer mixtures, are presented in Table 1.

One can discern the following features of the copolymer−surfactant complexation. The number of surfactant molecules bound per hydrophobic group of the copolymer increases with increasing length of the polymer-bound alkyl group for a fixed number of hydrophobic groups in the chain (compare experiments 1 and 3, and 5 and 7). On the other hand, an increase in the alkyl chain length of the *surfactant* molecule results in an order of magnitude *decrease* in the number of surfactant molecules bound. This result can be attributed to the cmc difference of the surfactants investigated, which causes a difference in the concentration of monomolecular surfactant in the reaction mixture. We estimated the fraction of surfactant molecules bound to the copolymer chains as $\alpha = (C_2 - C'_1)/C_2$, using the data given in Figures 5 and 6. The resulting values are presented in Table 2. As is evident from Table 2, the fraction of surfactant molecules bound to a given copolymer is greater in the case of CPBr than DDPCl.

This testifies to the fact that the abrupt decrease in the number of bound surfactant molecules with increas-

Table 2. Fraction of Bound Surfactant Molecules (α) in the Copolymer–Surfactant Mixtures Estimated by Potentiometry

	α	
copolymer	DDPCl	CPBr
P$_4$VP-C$_{12}$(3)	0.20	0.70
P$_4$VP-C$_{12}$(18)	0.45	0.90
P$_4$VP-C$_{16}$(3)	0.30	0.80
P$_4$VP-C$_{16}$(10)	0.40	0.90

Table 3. Sedimentation Coefficients (*s*) of Dilute Aqueous Solutions of P$_4$VP-C$_x$(*y*) Copolymers. [P$_4$VP-C$_x$(*y*)] = 0.0137 base-mol/L

P$_4$VP-C$_x$(*y*)	*s*,[a] S	P$_4$VP-C$_x$(*y*)	*s*,[a] S
P$_4$VP-C$_2$(100)	1.5	P$_4$VP-C$_{12}$(18)	3.2
P$_4$VP-C$_{12}$(3)	1.5	P$_4$VP-C$_{16}$(3)	1.5
P$_4$VP-C$_{12}$(6)	1.5	P$_4$VP-C$_{16}$(7.5)	2.0
P$_4$VP-C$_{12}$(10)	2.1	P$_4$VP-C$_{16}$(10)	2.7

[a] The experimental error of *s* evaluation is within 6–12%.

ing length of the alkyl group of the surfactant molecule is, indeed, a result of the decrease in the concentration of the monomeric surfactant in the solution. The previously noted regularity in the dependence of the number of bound surfactant molecules on the length of the hydrophobic side groups is maintained if α values are compared. Thus, α for P4VP-C$_{16}$(3) is greater than that for P4VP-C$_{12}$(3) for both surfactants.

These data also suggest an effect of the conformation of the copolymer chain on the number of surfactant molecules bound: For the sparsely alkylated copolymers characterized by relatively open conformations, the number of surfactant molecules bound per hydrophobic chain unit is somewhat greater than that for the more compact, highly alkylated copolymers (compare successive experiments in Table 1).

Thus, fluorescence spectroscopy and potentiometry indicate the formation of polymer–surfactant complexes in aqueous solutions of amphiphilic polycations and surfactants of the same charge sign. In order to investigate the structure of the complexes and the possibility of conformational transitions of the copolymer chains upon complexation, we applied velocity sedimentation and viscometry techniques.

Velocity Sedimentation and Viscometry. As noted previously, the amphiphilic polycations P4VP-C$_x$(*y*) undergo progressive aggregation of their hydrophobic groups in water solutions as the number of hydrophobic groups in the chain is increased (Figure 2). Since the formation of hydrophobic clusters in dilute aqueous solutions occurs predominantly through intrachain association of the alkyl side groups of the copolymers, it should result in compaction of the copolymer chains, as has been shown previously for similar copolymers by viscometry.[25] Sedimentation velocity data confirm the compaction of P4VP-C$_x$(*y*) chains in water solutions (Table 3).

In dilute solutions the sedimentation coefficient (*s*) of the copolymers containing 3–6 mol % of hydrophobic groups is identical to that of P4VPQ of the same degree of polymerization (DP$_\eta$ = 500). Further increase of the hydrophobic group content leads to an increase in *s*, supporting the suggestion of a more compact conformation of P4VP-C$_x$(*y*) chains compared to P4VPQ.

Addition of surfactant to P4VP-C$_x$(*y*) solutions results in an increase in *s*, with subsequent saturation, as shown in Figures 7 and 8.

This kind of variation in *s* is observed for all of the copolymer–surfactant mixtures. In the case of the reference polycation, P4VPQ, on the other hand, *s* is essentially independent of the surfactant concentration in the mixture (Figure 7), which confirms the absence of complexation in this case. The greatest increase in *s* is observed for those compositions which lie in the range characterized by the transition from the expanded state to the compact form. In the case of the P4VP-C$_{12}$(3) copolymer, for example, the conformation of which is essentially identical to that of P4VPQ, and in the case of P4VP-C$_{12}$(18), which has already adopted a collapsed conformation in the absence of surfactant, the increase in *s* upon complexation is substantially less (Figure 7).

Thus, polymer–surfactant complexation in dilute solutions results in an increase in the sedimentation coefficient of the copolymers. What is the reason for such an increase in *s*? The effect cannot be ascribed simply to a change of the copolymer molecular weight upon complexation, since the contribution of the increased molecular weight can account for no more than 5–7% of the observed change in *s*. The expected increase in the partial specific volume of the copolymer upon complexation with the surfactant should lead to a decrease in *s*, which is not observed. Thus, we believe that the increase in *s* can only be attributed to a contraction of the copolymer chain due to the formation

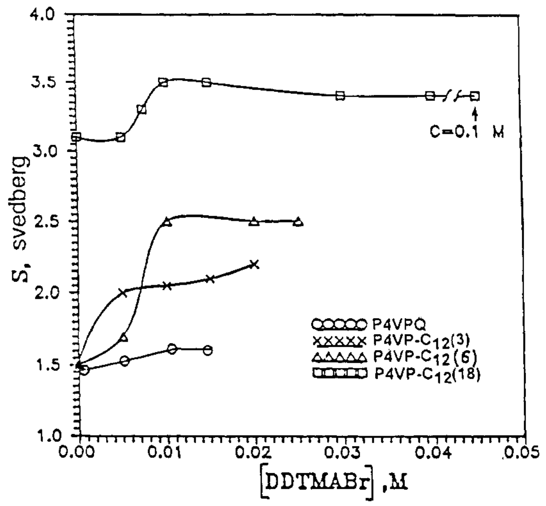


Figure 7. Dependence of the sedimentation coefficient on the DDTMABr concentration in DDTMABr–P4VPQ and DDTMABr–P4VP-C$_x$(*y*) mixtures.

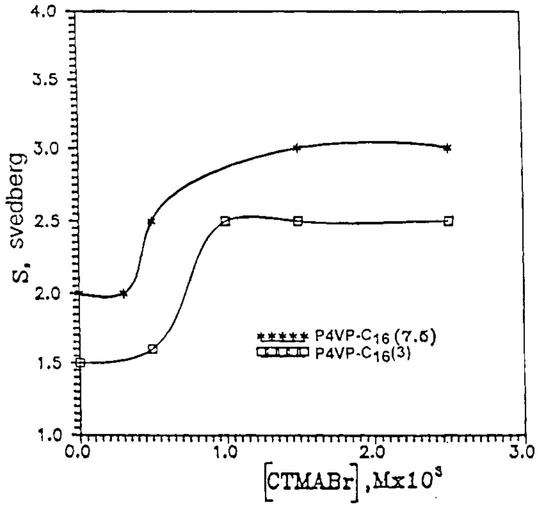


Figure 8. Dependence of the sedimentation coefficient on the CTMABr concentration in CTMABr–P$_4$VPQ and CTMABr–P4VP-C$_x$(*y*) mixtures.

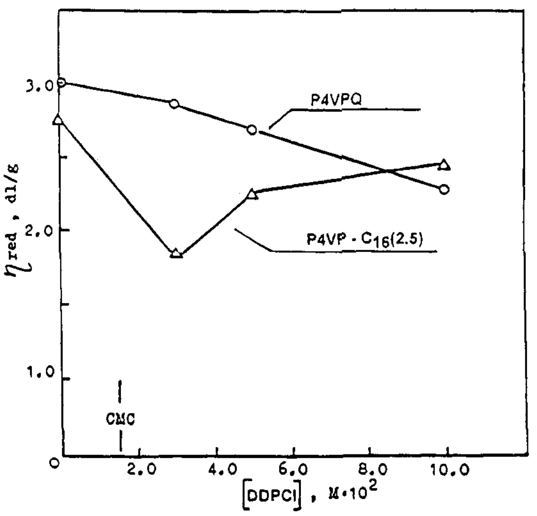


Figure 9. Dependence of reduced viscosity on the DDPCl concentration in P4VPQ–DDPCl and P4VP-$C_{16}(2.5)$–DDPCl mixtures. [P_4VPQ] = [P_4VP-$C_{16}(2.5)$] = 0.007 (base·mol/L); DP_η(polymer) = 3000.

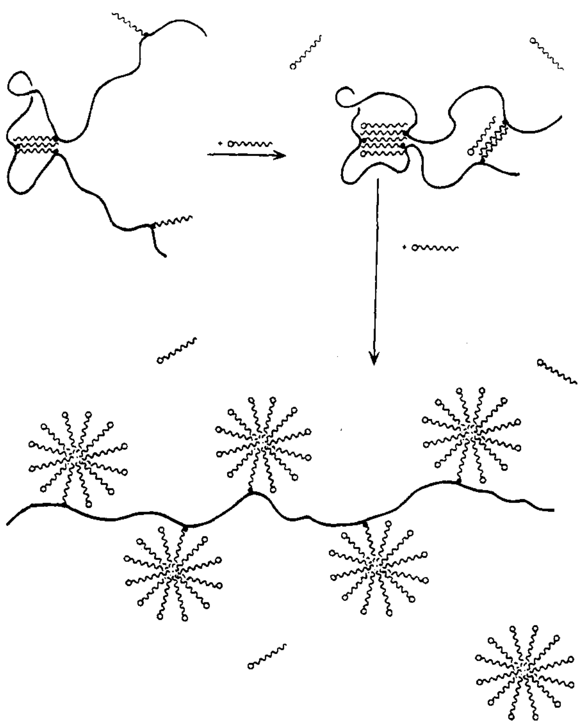
of the mixed intrachain aggregates of the hydrophobic side groups of the copolymer and the surfactant molecules, acting as intrachain cross-links.

It should be noted that these results differ from those obtained in studies of complexation in solutions of ionomers (amphiphilic *oil-soluble* copolymers) and surfactants in nonpolar solvents. It has been shown recently[9] that such reactions lead to a loosening of the ionomer coil in dilute solution, due to disruption of the ionomer chain aggregates and the formation of contacts with the aggregated surfactant. In such systems *s* decreases upon surfactant addition in *m*-xylene.

The question arises as to whether there is a possibility of formation of polycation–surfactant complexes similar to those formed by ionomers and surfactants in nonpolar solvents. In the experiments discussed above, the surfactant concentration was relatively low, never exceeding the cmc in the copolymer–surfactant mixture. In the ionomer solutions examined in ref 9, however, disruption of intrachain aggregates occurs at surfactant concentrations corresponding to one surfactant micelle per ionomer salt group. In order to answer the question raised above, we investigated complexation in mixtures of amphiphilic polycations and surfactants at higher surfactant concentrations. Unfortunately, the velocity sedimentation method is not straightforward at surfactant concentrations greater than the cmc. For this reason we used viscometry to study the conformational transitions of the copolymer chains over a broad range of surfactant concentrations. For this purpose we synthesized higher molecular weight copolymer (DP_η = 3000). Figure 9 illustrates the dependence of the reduced viscosity (η_{red}) on DDPCl concentration in dilute aqueous solutions containing P4VP-$C_{16}(2.5)$ or P4VPQ.

In the case of the reference polycation, a slight monotonic decrease in η_{red} is observed, as a result of the compaction of the polycation chains due to screening of the electrostatic repulsion of the cationic chain units and the low-molecular-weight counterions. The copolymer behavior is quite different. One observes an abrupt decrease in η_{red} upon surfactant addition, until the surfactant concentration reaches approximately twice the cmc. Further increase in the surfactant concentration results in an increase in η_{red}, and then the dependence levels off at about three to four surfactant micelles per one hydrophobic chain unit.

Scheme 1



The difference in the behavior of the reference polycation and its hydrophobically modified analog may be ascribed to the complex character of copolymer–surfactant interactions in this broad range of surfactant concentrations. At concentrations below the cmc, as has been pointed out above, copolymer–surfactant interactions result in compaction of the copolymer chain due to the formation of aggregates consisting of hydrophobic polymer side groups and surfactant molecules. Such aggregates act as intrachain cross-links. When the surfactant concentration is increased up to three to four surfactant micelles per hydrophobic chain unit, the complexation character changes. The intrachain hydrophobic aggregates are disrupted, and mixed clusters of separate hydrophobic side groups are formed, as shown in Scheme 1.

The hydrophobic side groups of the copolymer play the role of molecular anchors which bind the surfactant molecules in a manner similar to that of ionomers and surfactants in nonpolar solvents.[9-11] Complexation results in loosening of the copolymer coil and an increase in η_{red}. Similar behavior has been observed for an amphiphilic polyanion and surfactant molecules of opposite charge.[17]

Concluding Remarks

The data obtained allow us to conclude that hydrophobic interactions between amphiphilic polycations containing up to 10–18 mol % of hydrophobic chain units, and surfactant molecules of the same charge sign, may result in the formation of copolymer–surfactant complexes in aqueous solutions. At surfactant concentrations lower than the cmc, complexation leads to the formation of hydrophobic clusters consisting of surfactant molecules and copolymer alkyl side groups. Such interaction results in the formation of new intrachain cross-links (and in an increase in the size of the original cross-links) and leads to copolymer chain compaction. The maximum number of surfactant molecules bound to each hydrophobic copolymer chain unit depends on the monomolecular surfactant concentration in the mixture. This number decreases by an order of magnitude from 8.0 ± 0.4 surfactant molecules per hydrophobic copolymer chain unit in the mixture P4VP-C_{12}(3)−DDPCl to 0.8 ± 0.05 surfactant molecules in the mixture P4VP-C_{12}(3)−CPBr. The number of surfactant molecules bound to each hydrophobic copolymer chain unit increases with the alkyl side group length and depends on the copolymer chain conformation. This number is lower for copolymers that spontaneously adopt a compact conformation as a result of intrachain interactions of the hydrophobic chain units. At intermediate copolymer compositions when the initial conformation of the copolymer chain is not essentially different from that of reference polycation, complexation may result in a conformational transition, i.e., in a contraction of the copolymer chains.

At surfactant concentrations much greater than the cmc, when more than one micelle is present per hydrophobic chain unit, the complexation character is changed. In this range of surfactant concentration, disruption of intrachain hydrophobic aggregates and expansion of the copolymer coils occur. Individual hydrophobic groups act as molecular anchors binding the surfactant micelles and forming mixed clusters. In this range of surfactant concentration the interaction between the water-soluble copolymer and the surfactant becomes similar to that observed in mixtures of ionomers and surfactants.[9]

Acknowledgment. We thank N. V. Shvedene (Department of Analytical Chemistry, Chemistry Faculty, Moscow State University) for help with the potentiometry technique. We thank the Russian Fund for Fundamental Research (Project Code 93-03-5998) and NSF (additional grant to Grant DMR-8914359) for financial support of this work.

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MA946017H