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Conformational Changes of Poly(vinylcaprolactam) Macromolecules and Their Complexes with Ionic Surfactants in Aqueous Solution

Elena E. Makhaeva,[†] **Heikki Tenhu,**[‡] **and Alexei R. Khokhlov***[,†]

Physics Department, Moscow State University, Moscow, 117234 Russia, and Laboratory of Polymer Chemistry, University of Helsinki, PB 55, FIN-00014 HY, Helsinki, Finland

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ABSTRACT: Dynamic light scattering measurements have been performed for aqueous solutions of linear poly(vinylcaprolactam) (PVCa) at several polymer concentrations and over a wide range of ionic surfactant concentration. The intermolecular aggregation of PVCa accompanied by a sharp increase of the light scattering intensity is observed in pure water at 33 °C. The effect of ionic surfactants (cetylpyridinium chloride (CPC) and sodium dodecyl sulfate (SDS)) on the behavior of solutions of linear PVCa was studied as a function of temperature. For polymer concentrations below the overlap concentration (2.5 mg/mL) a decrease of the macromolecular hydrodynamic diameter is observed upon the addition of ionic surfactant (SDS, CPC) at low surfactant concentrations. This effect is in contrast to the behavior of the complexes of surfactant with another thermosensitive polymer, poly(*N*-isopropylacrylamide) (PNIPA). A further increase of the surfactant concentration leads to the reentrant swelling of macromolecules. In the presence of ionic surfactant the temperature increase results in the sharp drop of the hydrodynamic diameter of the particles at some critical temperature. This critical temperature becomes higher with increasing surfactant concentration. For higher polymer concentrations (5 mg/mL) the particle size always increases upon the addition of ionic surfactants, because of intermolecular aggregation.

Introduction

One of the interesting phenomena occurring in polymer systems is the coil−globule transition, which has been extensively studied for the last three decades.[1,2] The coil−globule (or collapse) transition of macromolecules is observed in dilute solution when the solvent quality becomes poorer. In this case, due to the increasing attraction between monomer units, the intramolecular collapse of macromolecular coils can take place. The transition normally occurs within a small interval of the variation of external parameters. One of the most important situations corresponds to the case when the change in the solvent quality is achieved via the variation of temperature. For example, for the solutions of poly(*N*-isopropylacrylamide) (PNIPA) in water the coil−globule transition is observed with increasing temperature.[3−6] This system has been extensively studied in the last years. The shrinking of polymer coils above the critical temperature is explained by the increase of the hydrophobic interactions of the nonpolar PNIPA groups with the increase of temperature.

The thermosensitive behavior of polymers in aqueous solutions generally depends on the hydrophobic−hydrophilic balance of macromolecular groups, which can be easily varied by the addition of surfactant molecules. Therefore, polymer−surfactant−water systems are attracting significant current interest. A number of papers deals with the investigation of the surfactant effect on the conformational state of the thermosensitive macromolecules (mainly PNIPA).[7−13] One of the main effects obtained is the strong influence of the addition of ionic surfactants on the swelling behavior of PNIPA. At low surfactant concentration, intermolecular solubilization prevents aggregation. Increasing surfactant concentration results in intramolecular solubilization: the conformational transition from a compact globule to an expanded coil.[13] This intramolecular solubilization is consistent with the elevation of the critical temperature of collapse transition of the sodium dodecyl sulfate (SDS)−PNIPA solutions as compared to a surfactant-free system.[10−12] The increase of the critical temperature, absence of the cloud point for SDS concentration larger than 10 μM and the enhanced aggregation of the surfactant due to the presence of the polymer were explained by the formation of polymer−surfactant aggregates. However, it was shown[14] that these mixed polymer−surfactant aggregates may adopt different conformations depending on temperature, surfactant concentration, hydrophobicity and flexibility of the polymer chains. It should be emphasized once again that in all studied systems the main object for investigation was PNIPA.[7−15]

Therefore, it is necessary to study new thermosensitive polymers and their complexes with surfactants in order to judge the universality of the observed phenomena. In the present paper we report on the studies of a new ternary system containing poly(vinylcaprolactam) (PVCa), which is another thermosensitive polymer. The properties of PVCa are not so well-studied as those for PNIPA, although recently a number of papers devoted to this polymer have been published.[16−20] The interest in PVCa is connected with the combination of very interesting features of this polymer: it is thermosensitive, water and organic soluble, and biocompatible and possesses a high absorption ability. Therefore, PVCa finds applications in medicine and biochemistry.

The aim of the present work is to study the behavior of PVCa in water using the dynamic light scattering technique with the main emphasis on the effect of the association of PVCa with the ionic surfactants (SDS and cetylpyridinium chloride (CPC)). The investigation of the new thermosensitive polymer and comparison with known experiments performed on PNIPA offers a clearer

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[†] Moscow State University.

[‡] University of Helsinki.

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view of the universal features for the ternary systems including a neutral thermosensitive polymer, ionic surfactant, and water. Dynamic light scattering measurements have been performed for aqueous solutions of linear poly(vinylcaprolactam) at several polymer concentrations and over a wide range of ionic surfactant concentration. By this method we were able to study the properties of isolated macromolecular coils and their complexes with ionic surfactants.

Experimental Section

Monomer vinylcaprolactam (VCa) was distilled under reduced pressure. The middle fraction was collected (refractive index equal to 1.5133). The initiator 2,2′-azobis(2-methylpropionitrile) was recrystallized three times from methanol and dried in a vacuum at room temperature.

The polymer was prepared by free-radical polymerization of VCa in benzene solutions. The polymerization at 30 °C was carried out in ampules for 96 h. Monomer solutions were prepared shortly before use by the addition of specified amounts of VCa, initiator, and benzene. The initial VCa content was 50 vol %, and the initiator concentration was 0.001 wt %. After degassing by four successive freeze−thaw cycles using liquid nitrogen and a reduced pressure of 10^{-3} mmHg (10^{-1} Pa), the ampules were torch sealed.

After the reaction, the polymer was precipitated into diethyl ether, decanted, and dried at 50 °C. The polymer was fractionated by standard solvent/nonsolvent techniques involving the addition of diethyl ether to a benzene solution of the polymer. In the present work the high molecular weight fraction of polymer was used ($M_w = 4.08 \times 10^6$).

The surfactants cetylpyridinium chloride (CPC) (Aldrich) and sodium dodecyl sulfate (SDS) (Aldrich) were used without further purification.

The solvent for PVCa was deionized water, which was purified by an Elgastat UHQ-PS purification system. The polymer−surfactant solutions were prepared at least 1 day before the dynamic light scattering measurements.

Dynamic Light Scattering. Dynamic light scattering (DSL) measurements were performed with a Brookhaven Instruments BI-200SM goniometer and a BI-9000 digital correlator. The light source was a Spectra Physics Model 127 helium/neon laser (633 nm, 35 mW). Time correlation functions were analyzed with a Laplace inversion program (CONTIN).

The intensity−intensity time correlation functions $g_2(t,q)$ in the self-beating mode were measured at a scattering angle 90° as a function of temperature. Temperature ranged from 20 to 70 °C. At each temperature the sample was allowed to equilibrate 30 min before the measurement. The equilibrium state was controlled by following the intensity of scattered light as a function of time (stability test).

Before use the solutions were clarified by filtering through Millipore membranes with 0.22 μm pore size.

Static light scattering measurement (Zimm method) was used for determination of M_w. M_w of the polymer studied in the present paper was determined to be 4.08×10^6. The gyration radius was equal to 86 nm.

Results and Discussion

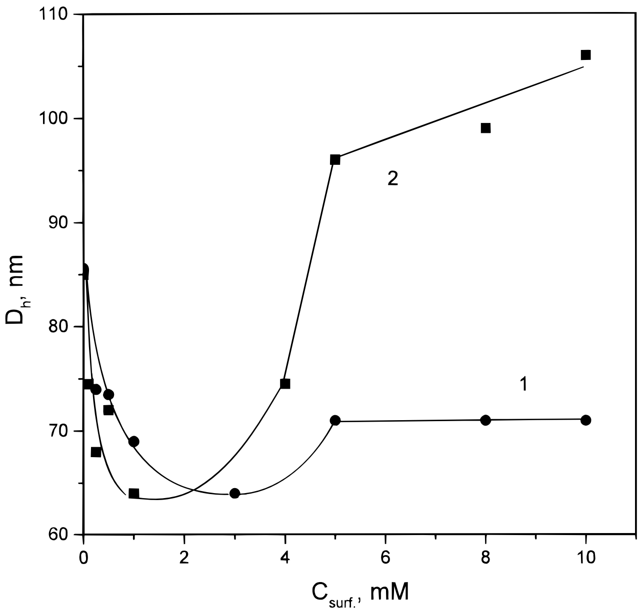

Figure 1. Dependence of the hydrodynamic diameter of PVCa macromolecules (D_h) on SDS (curve 1) and CPC (curve 2) concentration at 20 °C. PVCa concentration: 0.5 mg/mL.

Figure 1 demonstrates the dependence of the hydrodynamic diameter (D_h) for the polymer particles in a ternary system PVCa−surfactant−water on the surfactant concentration at 20 °C. The polymer concentration was 0.5 mg/mL. D_h is the diameter obtained using the CONTIN program. In the presence of the anionic surfactant SDS (curve 1) as well as for the cationic surfactant CPC (curve 2), nonmonotonic changes of D_h are observed upon the increase of the surfactant concentration. First (at the surfactant concentration below ca. 3 mM) D_h is decreased. In this case we observe a decrease of D_h from 85 to 64 nm at 20 °C. Here it should be noted that the critical temperature of the polymer collapse for PVCa in water is 34 °C.[17,19] So, even at the temperatures below this critical temperature the addition of ionic surfactant (anionic as well as cationic) induces some shrinking of PVCa macromolecules. This transition could be caused by the enhancement of the intramacromolecular hydrophobic attractions resulting from the complexation of surfactants and PVCa macromolecules. This attraction reduces the hydrophilicity of PVCa, and water becomes a poor solvent for PVCa.

With a further increase of the surfactant concentration above ca. 3 mM the shrunken polymer molecules expand again and the hydrodynamic diameter eventually reaches the same value as for the surfactant-free system, or even exceeds this value. This effect can be explained by the swelling of polymer macromolecules due to the osmotic pressure of the surfactant counterions, which penetrate inside the polymer−surfactant aggregates. The influence of this osmotic pressure should be especially pronounced at high surfactant concentrations. Additional effects may be connected with the effective weakening of the hydrophobic interactions for surfactant tails due to the repulsion of the similarly charged surfactants in the self-assemblies inside macromolecular coils, as well as with the increase of the excluded volume due to the binding of surfactants to the polymer chains.

All dynamic light scattering measurements reported above have been performed in dilute solutions. This is confirmed by unimodality of the correlation functions. Also from Figures 2 and 3 it can be seen that the angle or concentration dependencies of D_h are practically absent.

Assuming that PVCa coils behave in dilute water solutions as hard spheres,[16] the approximate overlap concentration can be estimated as $c^* \sim M_w[N_A(4\pi/3)R_g^3]^{-1}$, where M_w is the molecular weight of the polymer and R_g is the radius of gyration of the coil. In our case $M_w = 4.08 \times 10^6$, $R_g = 86$ nm (see the Experimental Section), therefore $c^* = 2.6$ mg/mL. We will perform

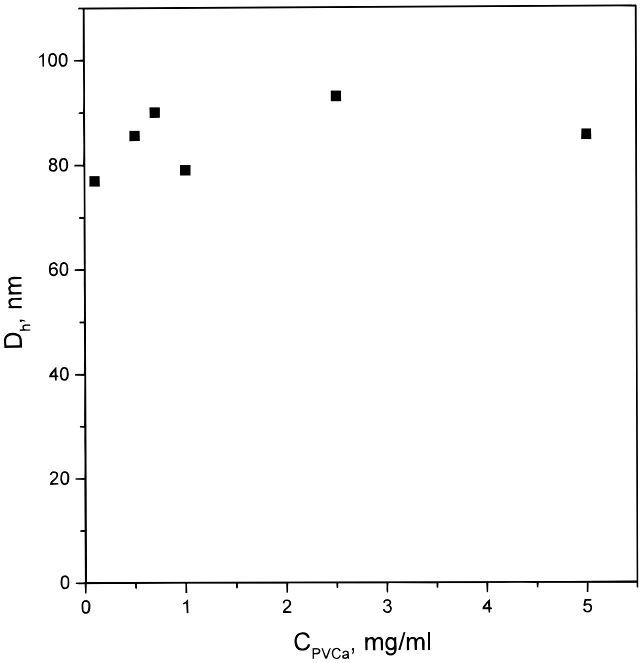

Figure 2. Dependence of the hydrodynamic diameter of PVCa macromolecules (D_h) on polymer concentration.

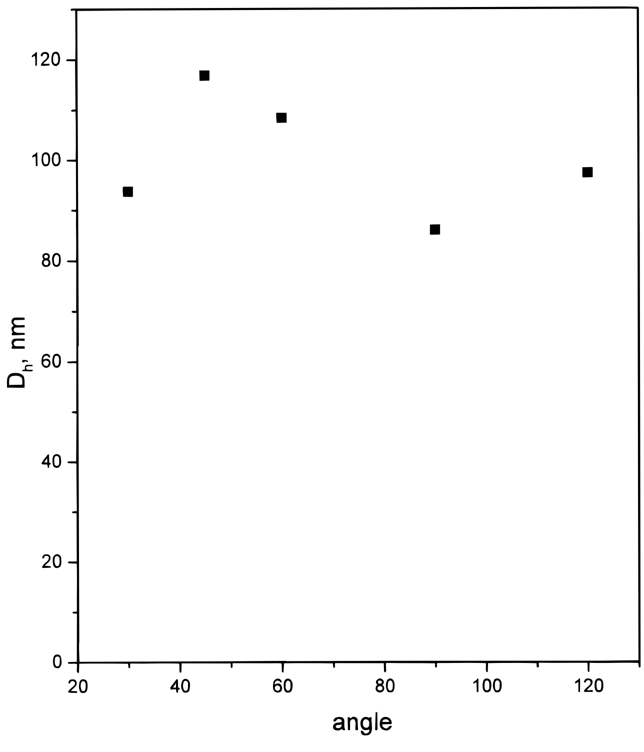

Figure 3. Dependence of the hydrodynamic diameter of PVCa macromolecules (D_h) on scattering angle at 20 °C. Polymer concentration: 0.5 mg/mL.

further analysis for different polymer concentrations. From this set one concentration (5 mg/mL) is above *c**.

Figure 4 shows the dependencies of D_h on CPC concentration at 20 °C for the different polymer concentrations. For all polymer concentrations corresponding to the interval from 0.5 to 2.5 mg/mL (that is below *c**), the addition of CPC leads to a decrease of D_h at the low surfactant concentrations (Figure 4, curves 1−3). The increase of polymer concentration up to 5 mg/mL (that is above *c**) leads to the opposite effect: the effective hydrodynamic diameter essentially increases upon the addition of ionic surfactant. For example, after the addition of 3 mM CPC the hydrodynamic diameter of polymer particles increases from 85 to 488 nm (Figure 4, curve 4) The most obvious explanation of this effect is the aggregation of macromolecules. At high polymer concentrations above *c** = 2.6 mg/mL the mixed aggregates of the surfactant molecules and PVCa macromolecules are apparently formed in the solution because the surfactant molecules included in joint micelles with polymer chains can act as effective intermolecular cross-links. The formation of these intermacromolecular aggregates leads to the increase of the hydrodynamic diameter of polymer particles.

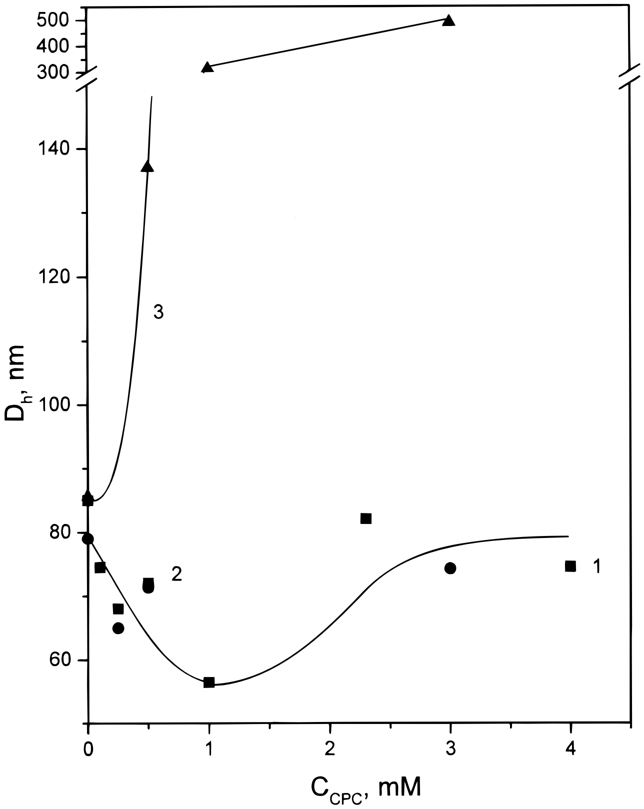

Figure 4. Dependence of the hydrodynamic diameter of PVCa macromolecules (D_h) on CPC concentration at 20 °C. Polymer concentration: 0.5 mg/mL (1), 1 mg/mL (2), 5 mg/mL (3).

So the conformational behavior of PVCa−surfactant complexes is a function of the polymer concentration. In the studied polymer concentration range, at least two different concentration regimes can be distinguished. In the dilute regime, below 2.6 mg/mL, the polymer coils are well separated and behave like more or less independent particles. Upon increasing the polymer concentration, the onset of aggregation of macromolecules can be observed.

Temperature Effect. Figures 5 and 6 show the dependencies of the hydrodynamic diameter of PVCa on temperature in the presence of SDS (Figure 5) and CPC (Figure 6). We can see that in pure water the temperature increase to 30 °C leads to the weak temperature dependence of the particle size (Figure 5, curve 1). At 33 °C the aggregation of PVCa macromolecules is observed, as a sharp increase of the scattered light intensity. In this case it is difficult to characterize the particle sizes. Above 33 °C PVCa is water insoluble and tends to form large aggregates due to the collapse of macromolecules and the association of the globules via hydrophobic interactions. The temperature 33 °C is

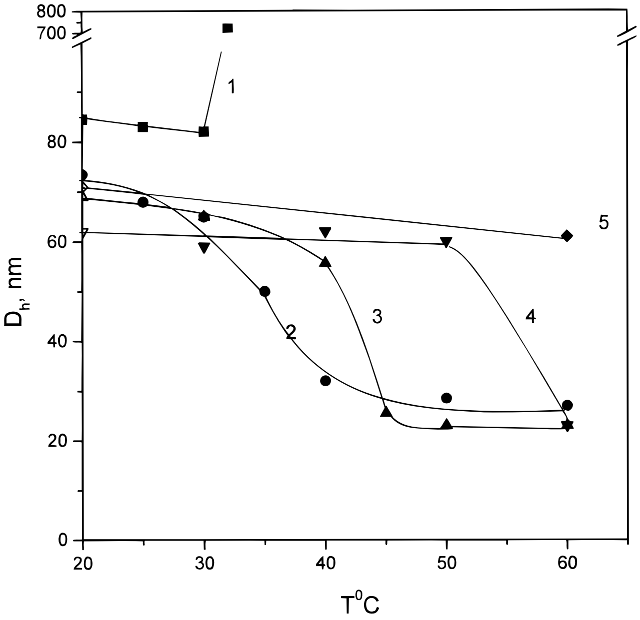

Figure 5. Temperature dependence of the hydrodynamic diameter of PVCa macromolecules (D_h) in the presence of SDS. SDS concentration: 0 (1), 0.25 (2), 0.5 (3), 1 (4), 3 mM (5).

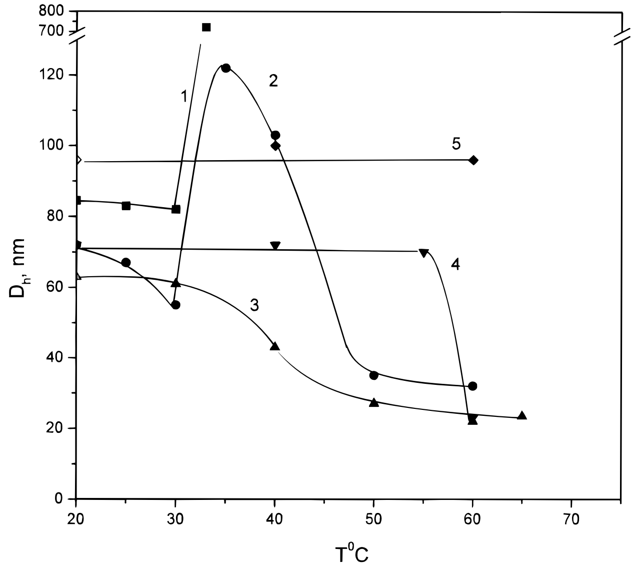

Figure 6. Temperature dependence of the hydrodynamic diameter of PVCa macromolecules (D_h) in the presence of CPC. CPC concentration is 0 (1), 0.25 (2), 0.5 (3), 1 (4), and 2.3 mM (5).

close to that obtained in our previous work where we have detected the temperature at which the collapse of the PVCa gel is taking place.[17]

The situation changes in the presence of ionic surfactants. At temperatures above the precipitation temperature of the pure polymer solution, the conformation of the macromolecules strongly depends on the surfactant concentration. Without surfactant the large polymer aggregates of PVCa globules are formed. Already the amount of 0.25 mM of surfactant is sufficient to greatly reduce the aggregation. If either anionic surfactant (SDS) or cationic surfactant (CPC) at the concentration above 0.5 mM is added to the solution, the polymer aggregation upon the temperature increase is completely suppressed. In this case the hydrodynamic diameter of particles weakly depends on temperature up to some critical temperature (T_{cr}). This means that at these surfactant concentrations the solubilization of charged surfactants by polymer prevents coil–globule transition and macromolecular aggregation. This effect is caused by the change of the hydrophilic–hydrophobic balance of the PVCa macromolecule due to the adsorption of ionic surfactant by polymer and the transformation of neutral polymer to polyelectrolyte. The other factor to prevent the macromolecular aggregation is the repulsion between similarly charged particles formed by the PVCa macromolecule and ionic surfactants.

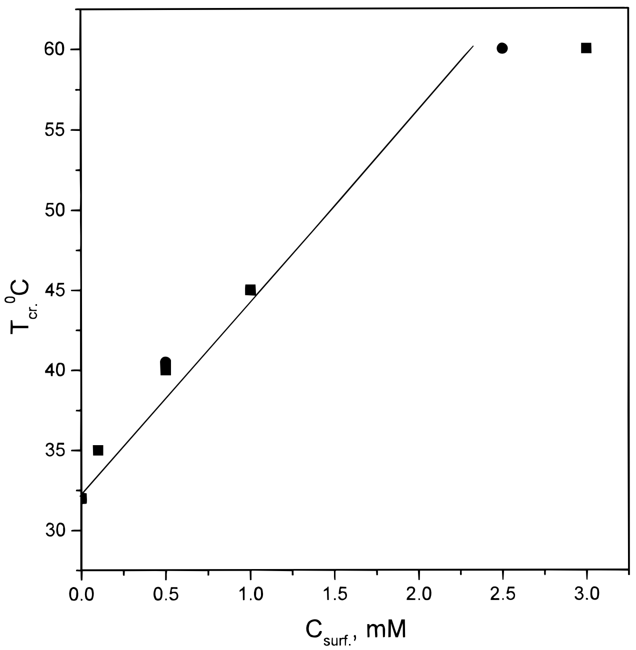

Figure 7. Dependence of characteristic collapse temperature on SDS (closed square) and CPC (closed circle) concentration.

In the dependence of the diameter of nonaggregated polymer species as a function of temperature in the presence of ionic surfactants, it is possible to distinguish three temperature regions (Figure 5, curves 2–4 and Figure 6 curves 3 and 4). At the temperature below some characteristic temperature only the slight temperature effect on the particle size is observed. Then a much sharper decrease of D_h takes place around some temperature, which is apparently connected with the coil–globule (collapse) transition of a single macromolecule. At the further temperature increase (above the collapse transition temperature) the value of D_h is practically constant. The particle size in the globular state conditions is nearly independent of temperature. The addition of ionic surfactant leads to the shift of collapse transition temperature to the higher temperature region.

Figure 7 shows the dependence of the temperature of sharp decrease of D_h as a function of the surfactant concentration in the presence of SDS and CPC. The increase of ionic surfactant concentration leads to the increase of the collapse transition temperature. The elevation of the transition temperature apparently results from repulsive osmotic pressure of counterions of ionic surfactants adsorbed by PVCa macromolecules.

It is worthwhile also to mention the special effect observed at the low CPC concentrations of 0.25 mM. In this case the temperature increase up to 35 °C results in a sharp growth of the hydrodynamic diameter (Figure 6, curve 2), which is most probably connected with

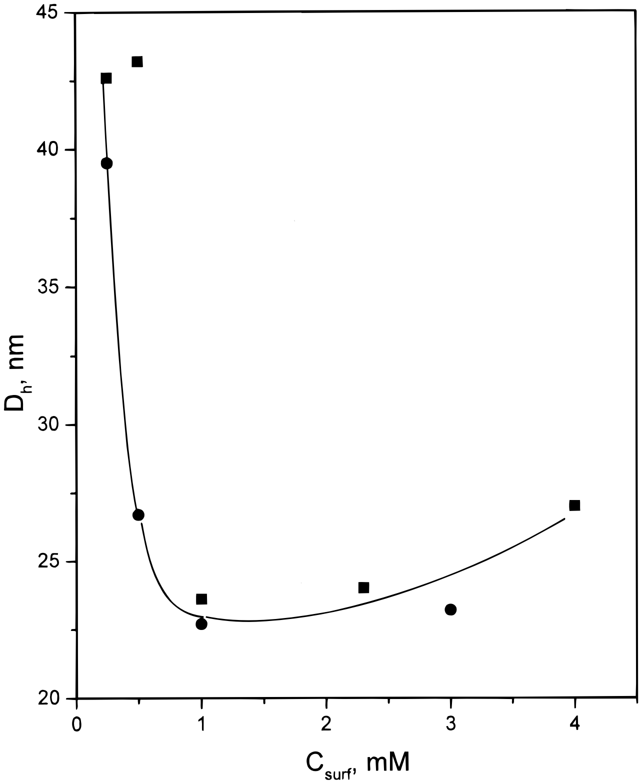

Figure 8. Dependence of the hydrodynamic diameter of PVCa macromolecules (D_h) on SDS (closed circle) and CPC (closed square) concentration in the collapsed state at 60 °C.

polymer aggregation. Upon a further temperature increase (above 35 °C), the value of D_h sharply drops. This behavior of the PVCa macromolecules at low ionic surfactant concentrations can be explained as follows. At low surfactant concentration the amount of the surfactant molecules absorbed by the macromolecule is not enough to protect the polymer coils against intermolecular precipitation and to stabilize the system. As result the macromolecules are collapsed and aggregated, but the number of macromolecules forming aggregate is limited. This limit depends on the surfactant concentration.

Taking into account the geometrical considerations, we can calculate the reduction of surface area due to the intermacromolecular aggregation. The value of D_h for the initial macromolecule is 68 nm, and the value of D_h for the maximum aggregates at 0.25 mM of CPC molecules added is 122 nm. Consequently, the ratio between the total surfaces of the individual macromolecules (not forming the aggregate) and the aggregate surface is 2. In other words, the aggregate formation leads to an approximately 2-fold decrease of the particle surface, which allows, at the present surfactant concentration, coverage of the polymer aggregates by the skin of the surfactant. It is similar to the stabilization of polymer latex particles by ionic surfactants. With a 2-fold increase of the CPC concentration (0.5 mM CPC) the aggregation should not be observed because the amount of the surfactant molecules is enough to protect all individual polymer particles. This is in agreement with our experimental results (Figure 6, curve 3).

Figure 8 demonstrates the dependence of the hydrodynamic diameter of the globular particles as a function of surfactant concentration at 60 °C. One can see that in the presence of ionic surfactants the particle size in the globular state is a function of the surfactant concentration. The increase of the surfactant concentration up to 1 mM leads to a sharp decrease of the globular diameter. Upon a further increase of the surfactant concentration, the globular size changes only slightly.

Comparison with the Results for PNIPA. Now let us to consider the known results concerning the swelling behavior of PNIPA in the presence of ionic surfactants and compare them with the data obtained in the present paper for the effect of ionic surfactants on the swelling behavior of PVCa. Earlier it was shown[21−23] that for PNIPA solutions the addition of the anionic SDS in the concentration range 0.001−0.008 M causes the increase of the collapse transition temperature. In aqueous SDS solution above the critical temperature the PNIPA macromolecules do not aggregate but remain in the solution because they are stabilized by surfactant ions adsorbed through hydrophobic interactions.[20] As one can see from the above results we observed a similar situation for the ternary systems PVCa−ionic surfactants−water.

However, in our present work there are data concerning the effect of ionic surfactant on the behavior of neutral thermosensitive PVCa that are in contradiction with known results for a similar ternary system, PNIPA−surfactant−water. The main difference in the macromolecular behavior is the effect of ionic surfactant on the swelling at the temperatures below T_{cr}. We have seen that in the case of PVCa the particle size is decreased upon the increase of surfactant concentration up to 3 mM. However, in the case of PNIPA the monotonic increase of particle size upon the addition of ionic surfactants was observed.[13−15] This swelling was interpreted as the indicator for cooperative binding of surfactants to polymer chain, resulting in an expansion of chains due to the repulsive interactions between the adsorbed amphiphiles.[13]

An analogous behavior for microgel particles of PNIPA was observed by Chi Wu and co-workers.[15] It was shown that microgel particles swell as the SDS concentration increases in the whole studied range of concentration from 1.42 to 9.5 mM. The effect of the surfactant type and concentration on the particle size and electrophoretic mobility of cross-linked PNIPA microgel latexes was studied also in ref 21. It was shown that in the presence of anionic SDS in the concentration range 0.001−0.008 M the particle diameter always increases.[22]

These results for PNIPA were explained by the fact that increasing surfactant concentration results in intramolecular solubilization of PNIPA by surfactants, which effectively increases the swelling degree of PNIPA coils. This intramolecular solubilization is consistent with the elevation of the collapse transition temperature of the SDS−PNIPA solutions as compared to the surfactant-free system.[13] The structure of aqueous solutions of PNIPA and SDS is presented as the solution of “necklaces”, where each independent NIPA macromolecule has collected a set of SDS micelles.[24]

The difference of the swelling behavior of PVCa and PNIPA macromolecules in the presence of the ionic surfactants can be connected with stronger hydrophobic interactions in the case of PVCa. One of the confirmations for this is that PVCa is soluble in organic solvents. Also, we have shown that there is no principal difference in the PVCa behavior in the presence of cationic and anionic surfactant. Normally, this is regarded as the indication of stronger hydrophobicity of polymer.[25−30]

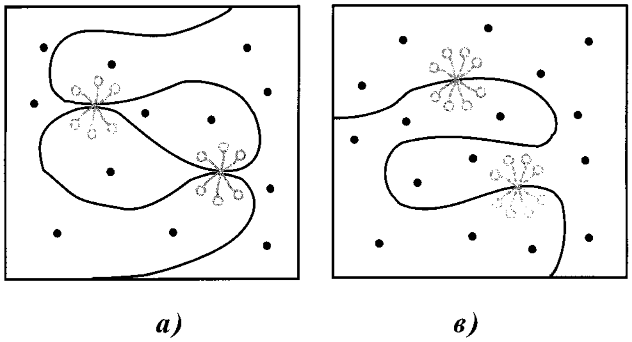

Figure 9. Schematic presentation PVCa−ionic surfactant complexes (a) and PNIPA−ionic surfactant complexes (b). Counterions are shown by black circles.

The explanation of the observed essential difference in the behaviors of ternary systems based on PVCa and PNIPA can be the following (Figure 9). The optimum structure of polymer/surfactant complex in the case of PNIPA may include only one piece of chain per micelle forming “necklaces”, while for PVCa the incorporation of two different pieces of chain in the same micelle is possible. Therefore, the surfactant micelles for the case of PVCa play the role of cross-links (these cross-links can be either intra- or intermolecular, depending on concentration) while for PNIPA chains, the formation of such cross-links is for some reasons significantly suppressed. This hypothesis allows us to explain all the experimental data, however the molecular origin of the fact that surfactants cannot effectively cross-link PNIPA chains has still to be understood. The bare fact that PNIPA is less hydrophobic that PVCa cannot explain this important difference.

Conclusions

To summarize, the behavior of a thermosensitive PVCa in the presence of ionic surfactants has a number of differences in comparison with the surfactant effect on the swelling behavior of PNIPA. The temperature dependence of swelling of PVCa in the presence of ionic surfactants depends considerably on the initial composition of the system.

(1) At polymer concentrations below c*. Below c^* in a pure aqueous solution the individual PVCa polymer coils form intermolecular aggregates upon heating. The addition of the ionic surfactant results in the slight decrease of the particle size at the temperatures below the collapse transition temperature. Therefore, for this case the temperature increase does not lead to the intermacromolecular aggregation, apparently due to the formation of the charged macromolecule−surfactant complexes. The collapse transition temperature for these complexes is increased. Below the collapse transition temperature the mixed chain−surfactant aggregates lead to the effective cross-linking between the different parts of the PVCa macromolecule, resulting in the decrease of the particle size. Note that a similar assumption was previously used to interpret the viscosimetry data for poly(vinylpyrrolidone).[31,32]

The suppression of the aggregation of PVCa macromolecules above the collapse transition in the presence of ionic surfactant is valid only if the surfactant concentration is more than 0.25 mM. At lower surfactant concentrations (0.25 mM CPC) the aggregation of few particles was observed. In this case the formation of intermacromolecular cross-links takes place in addition to the intramolecular ones. But the temperature increase leads to the enhancement of hydrophobic interactions and to the polymer collapse that is accompanied with destruction of intermacromolecular aggregates. The latter point follows from the fact that the particle size in the collapsed state is equal to the single polymer size in this state for the system at higher surfactant concentrations (Figure 6).

The further surfactant concentration increase results in the restructuring of the polymer−surfactant aggregates. At the concentration above 3 mM the swelling of the polymer particle is observed, which is connected with the increase of the amount of the surfactant molecules penetrating the polymer coil. Surfactants bring with them inside the polymer macromolecule the mobile counterions (Na^+ or Cl^-), which leads to osmotic pressure, inducing a significant swelling of the complexes.

(2) At polymer concentrations above c* (5 mg/mL). In this case, the addition of the ionic surfactant to the polymer solution leads to the increase of the particle size at all studied surfactant concentrations. At the high polymer concentration the mixed polymer/surfactant micelles are formed from both the different pieces of an individual macromolecule and the polymer units of the neighboring macromolecules. Apparently, this is due to the intermacromolecular aggregation and the size of the aggregates is increased proportionally to the amount of added surfactant, because of the formation of the intermacromolecular cross-links by surfactant−polymer mixed micelles. In the semidilute regime the polymer concentration is such that polymer chains form a transient physical network and the cooperative diffusion coefficient depends on the mesh size of this network.

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