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Behaviour of poly(*N*-vinylcaprolactam) macromolecules in the presence of organic compounds in aqueous solution

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Abstract

Dynamic light scattering measurements have been performed for aqueous solutions of thermosensitive linear poly(*N*-vinylcaprolactam) (PVCa) macromolecules in the presence of NaCl and different water soluble amphiphilic organic compounds: pyrogallol (neutral amphiphilic compound), cetylpyridinium chloride (cationic surfactant) and sodium dodecylsulfate (anionic surfactant). A decrease in the macromolecular hydrodynamic diameter is observed upon addition of ionic surfactants (SDS, CPC) at low surfactant concentrations. This trend changes to an increase in the macromolecular hydrodynamic diameter at high surfactant concentration at temperatures below the temperature of polymer aggregation. This effect is in contrast with the behaviour of the systems of PVCa–non-ionic organic compounds (pyrogallol) and NaCl where we always observed the weak monotonic decrease of the hydrodynamic diameter with the increase in the concentration of organic compound, NaCl.

The behaviour of ternary systems PVCa macromolecules–ionic surfactant–pyrogallol and PVCa macromolecules–ionic surfactant–NaCl was studied. The addition of pyrogallol leads to the suppression of the intermacromolecular aggregation induced by temperature increase that is still observed at low surfactant concentrations and to the decrease of macromolecular hydrodynamic diameter. Also, the addition of NaCl to the PVCa/ionic surfactant systems results in the increase of the macromolecular hydrodynamic diameter. It is speculated that these results are due to the suppression of the cross-linking role of surfactant aggregates upon the addition of NaCl and pyrogallol.

Keywords: Thermosensitive polymer; Poly(*N*-vinylcaprolactam); Dynamic light scattering

1. Introduction

An increasing interest is attracted today towards polymer–surfactant systems, due to both the technological applications in chemical industry and the relevance of polymer–surfactant interactions in biological systems. The complexes of non-ionic thermosensitive polymers and ionic surfactants were shown to be particularly suitable for the design of novel systems with non-trivial rheological properties, since (physical) cross-linking effects can be influenced both by ionic surfactants and by temperature. Thus, as these polymers become less polar with the increase of temperature, they offer better nuclei for surfactant self-assembly at higher temperatures. Solvation of the polymer may involve the hydrophobic interaction in which the local structure of water in the neighbourhood of the hydrophobic portion of the segment is thought to play a role. Addition of other solution components such as salt, co-solvents, or surfactants, or changing the molecular weight of the polymer, can affect the solubility strongly [1].

One of the interesting phenomena occurring in polymer systems is the coil–globule transition, which has been extensively studied for the last three decades [2,3]. 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 increase of attraction between the 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 [4–7]. This system has been studied extensively in the last years [8–13]. The shrinking of polymer coils above the critical temperature is explained

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by the increase in the hydrophobic interactions of the non-polar PNIPA groups with increase in temperature. An important and useful feature of thermosensitive polymers is the possibility of controlling their LCST by various means either by varying the monomer composition [8,9] or by using different additives.

In the present paper following Ref. [14], we continue to study the ternary systems containing PVCa, which is a thermosensitive polymer. The properties of PVCa are not so well studied as those of PNIPA, although recently a number of papers dedicated to this polymer were published [15–21]. The interest in PVCa is connected with the combination of very interesting features of this polymer: it is thermosensitive, water and organic soluble, biocompatible and possesses a high absorption ability. Therefore, PVCa finds applications in medicine and biochemistry.

Earlier we have shown that the main difference in the macromolecular behaviour for PVCa and PNIPA is the effect of ionic surfactant on the swelling at the temperatures below T_{cr} [14]. We have seen that in the case of PVCa the particle size is decreased with increase in surfactant concentration up to 3 mM. At the same time, in the case of PNIPA the monotonous increase of particle size upon the addition of ionic surfactants was observed [22,23]. This swelling of PNIPA can be interpreted as the indicator for enhanced osmotic pressure of surfactant counter ions, which are brought to the interior of PNIPA coil together with the surfactant molecules themselves. The observed essential difference in the behaviour of ternary systems based on PVCa and PNIPA was explained as follows [14]. The optimum structure of the 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 in 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 allowed an explanation of all the experimental data, however, the molecular origin of the fact that surfactants cannot effectively cross-link PNIPA chains still remains to be understood.

In the present work, we study the behaviour of PVCa in water using the dynamic light scattering (DLS) technique with the main emphasis on the effect of the association of PVCa with the ionic surfactant in the presence of NaCl and water-soluble non-ionic organic compounds. The aim of the present work is the study of PVCa solution properties in the presence of different organic compounds as a function of temperature. The variation of the different types of additives (both of ionic surfactant and compounds with specific interactions, which can play a role of reversible junctions between monomer units of polymer chains) allows to study the interplay between the attraction of polymer segments and the electrostatic repulsion created by the charged species. DLS measurements have been performed for aqueous solutions of linear PVCa at several polymer concentrations and over a wide range of concentrations of organic compounds.

2. Experimental section

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

The polymer was prepared by free-radical polymerisation of VCa in benzene solutions. The polymerisation at 30°C was carried out in ampoules for 96 h. Monomer solutions were prepared shortly before use by the addition of specified amounts of VCa, initiator and benzene. The initial content for VCa 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 ampoules 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/non-solvent techniques involving the addition of diethyl ether to a benzene solution of the polymer. In the present work, fraction of the polymer 1.5×10^6 g/mol was used.

Cetylpyridinium chloride (CPC) (Aldrich), sodium dodecyl sulfate (SDS) (Aldrich), pyrogallol (Aldrich) and sodium chloride (Aldrich) were used without further purification.

The solvent for PVCa was de-ionised water, which was purified by an Elgastat UHQ-PS purification system. The polymer–surfactant solutions were prepared at least 1 day before the DSL measurements.

2.1. Dynamic light scattering

DLS measurements were performed with a Brookhaven Instruments BI-200SM Goniometer and a BI-9000 digital correlator. The light source was Spectra Physics Model 127 helium/neon laser (633 nm, 35 mW). Time correlation functions were analysed using a second-order cumulant fit.[1]

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 60°C. At each temperature the sample was allowed to equilibrate ca. 30 min before the measurement. The equilibrium state was controlled by following the intensity of scattered light as a function of time (stability test).

All DLS measurements reported below have been performed in dilute solutions. This is confirmed by unimodality of the correlation functions.

[1] Owing to fairly low scattering intensity in some cases, cumulant fit was shown to give results with better reproducibility than, e.g. CONTIN.

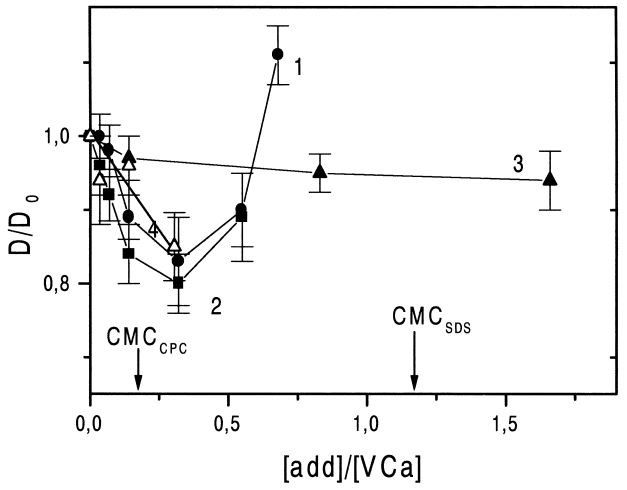

Fig. 1. Dependence of hydrodynamic diameter of PVCa macromolecules D/D_0 on surfactant concentration at 20°C. Additive concentration is molar ratio between additive molecule and monomer unit of PVCa [add]/[VCa]: (1) CPC; (2) SDS; (3) NaCl; and (4) pyrogalol.

Before use, the solutions were filtered through Millipore membranes with 0.22 μm pore size.

Static light scattering measurements (Zimm method) were used for the determination of M_w. M_w of the polymer studied in the present work was shown to be equal to 1.5×10^6 g/mol. Gyration radius was equal to 83 nm. The second virial coefficient is 2.2×10^{-4} cm^3 mol/g^2 at 20°C.

Assuming that the PVCa coils behave like hard spheres in dilute water solutions [15], 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 $M_w = 1.5 \times 10^6$ g/mol, $R_g = 83$ nm therefore, $C^* = 1.1$ mg/ml. We will perform further analysis at the concentrations below C^*.

To check the stability of pyrogallol solution under laser irradiation and daylight effect on the PVCa–pyrogallol system, two consecutive DLS measurements for the same system were done. After the first measurement every other day the second DLS measurement was repeated. It was shown that correlation function for these measurements is similar, which indicates that the system is stable.

3. Results and discussion

Fig. 1 demonstrates the dependence of the hydrodynamic diameter (D/D_0) for the polymer particles of PVCa in the presence of different additives: ionic surfactants (cationic CPC and anionic SDS); non-ionic organic compound (pyrogallol); and NaCl on the additives concentration at 20°C. Polymer concentration is 1 mg/ml in terms of polymer repeat units. The change in the hydrodynamic diameter is expressed as a ratio between the hydrodynamic diameter D of particles in the presence of additives and the initial hydrodynamic diameter D_0 of PVCa macromolecules in pure water. The additive concentration ([add]/[VCa]) is expressed as a molar ratio between the added compound and the monomer unit of PVCa. The straight lines connecting experimental points should be regarded just as a guide for eyes (here and below). In the presence of surfactant (CPC as well as SDS), the non-monotonic changes of hydrodynamic diameter are observed with increase in the surfactant concentration. The concentration dependencies of the hydrodynamic diameter exhibit a minimum. This transition could be caused by the enhancement of the intramacromolecular hydrophobic attractions resulting from the complexation of surfactants and PVCa macromolecules [14].

Here, it should be noted that the critical temperature of the polymer collapse for PVCa in water is 34°C [14,16]. So, even at temperatures below this critical value the addition of ionic surfactant (anionic as well as cationic) induces some shrinking of PVCa macromolecules (Fig. 1, curves 1 and 2).

Taking into account that the complexation of surfactants and PVCa macromolecules leads to the formation of the surfactant micelles, the experimental data obtained should be considered in terms of critical micelle concentration (CMC) and critical aggregation concentration (CAC) at which the surfactants form micelles in the presence of polymer. It is known that the CMC for SDS is equal to 8.1 mM [24–26] while for CPC the value of CMC is 0.9 mM in polymer-free surfactant solutions [26]. The CAC in the presence of the polymer is below CMC; for example, for PNIPAM–SDS system the CAC is only 0.79 mM; which is ten times less than the CMC for SDS in polymer-free solutions [22,25]. The comparison of the experimental data shown in Fig. 1 and CMC values allows to conclude that a minimum in the hydrodynamic diameter as a function of concentration is observed at a surfactant concentration more than four times less than the CMC in the case of SDS. For CPC, this minimum of the hydrodynamic diameter is observed slightly above CMC.

The theoretical results indicate that two dominant driving forces leading to the complexation of non-ionic polymers and surfactants are: (i) the tendency of the polymer to adsorb at the micellar core–water interface; and (ii) the existence of specific attractions between the polymer segments and the surfactant hydrophilic moities [27]. The difference in the relation between CMC and the concentration corresponding to minimum of hydrodynamic diameter for SDS and CPC can be connected with the sign of surfactant charge taking into account the slightly positive and negative charges of dipoles of amide groups. Partial negative charge of the dipoles (oxygen atoms) promotes the formation of hydrogen bonds with water molecules, while partial positive charges (nitrogen atoms) occur in close proximity to the chain and create a field of positive charges within the area with low dielectric permeability. This field apparently inhibits cationic-amine interactions. In the case of anionic surfactant

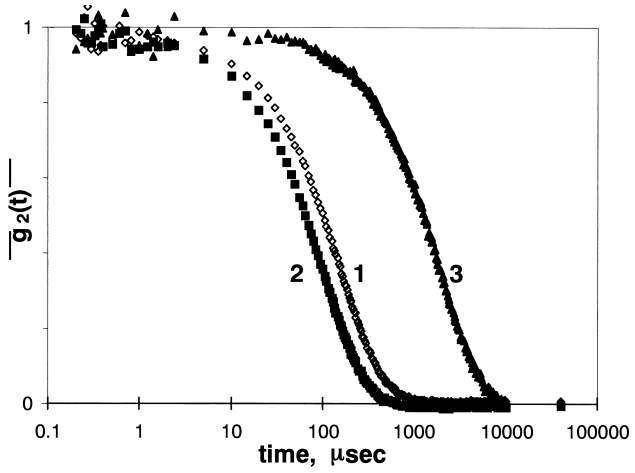

Fig. 2. Normalised correlation functions $g(t)$ of PVCa against logarithmic time, measured at: (1) 20; (2) 30; and (3) 33°C.

(SDS), a field of positive charges within the area with low dielectric permeability promotes the formation of mixed polymer–surfactant micelles. So, for SDS–PVCa and CPC–PVCa systems we could have different binding constants.

The strong effect of the chemical structure of the hydrophilic part of the surfactant on the behaviour of the polymer–surfactant complexes for the case of PNIPAM was shown in Refs. [23,28]. For this case, the addition of SDS leads to the swelling of the particles and the increase in the phase transition temperature, while dodecylpyridine bromide (DPB) has much smaller effect. This difference cannot be due to the association between the surfactant hydrophobic tail and PNIPAM because DPB and SDS have an identical hydrophobic tail. Authors connect this fact with the slightly protonised amide groups in PNIPAM in de-ionised water (pH close to 5.5) that promotes the formation of mixed polymer–anionic surfactant micelles in contrast to the surfactants of the same charge.

The effect of the proximate partial positive charge on the amine-proton, reactivity of amide groups is a function of both amine-to-dipole distance and local dielectric permeability [20]. In a complex manner these depend on the configurational state of the residue and the configurational isomerism of the chain. This fact can be one of the main points in the different behaviours of PVCA and PNIPA in the presence of small amount of ionic surfactants demonstrated in Fig. 1 and in Ref. [14].

With a further increase of the surfactant concentration the shrunken polymer molecules expand again and the hydrodynamic diameter eventually reaches the same value as for 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 counter ions, which penetrate inside the polymer–surfactant aggregates. The influence of this osmotic pressure should be pronounced especially 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 in the excluded volume due to the binding of surfactants to the polymer chains.

The shrinking of the PVCa macromolecule upon addition of pyrogallol (Fig. 1, curve 4), which is a neutral amphiphilic molecule, is similar to the corresponding effect for charged surfactants, but is not accompanied by the re-swelling at higher concentrations. This fact can be explained by the complex formation between pyrogallol molecules and PVCa due to specific interactions (hydrogen bonds) between amide group of PVCa and the hydroxy-groups of pyrogallol. Earlier it was shown that the shrinking of polyvinylpyrrolidone macromolecules in the presence of different phenols in aqueous solution is proportional to the amount of hydroxy-groups of phenols due to the formation of labile hydrogen cross-linking between the hydroxy-groups and different parts of the macromolecule [29,30]. In this case, pyrogallol molecules form intramolecular cross-linking between different parts of the macromolecule due to three functional hydroxy-groups that results in the macromolecular shrinking. The fraction of intramolecular cross-linking formed as a result of macromolecule shrinking is proportional to the added pyrogallol. However, the re-swelling of macromolecules that is observed at high surfactant concentration in the case of pyrogallol does not take place. The absence of re-swelling in the case of neutral compounds is in agreement with the explanation presented above that the swelling of polymer macromolecules at high concentrations of ionic surfactant is induced by the osmotic pressure of the surfactant counter ions, which penetrate inside the polymer–surfactant aggregates.

In the presence of NaCl, a slight monotonic decrease of macromolecular hydrodynamic diameter takes place (Fig. 1, curve 3). This can be explained by the fact that addition of NaCl leads to a slight increase of hydrophobic interactions.

3.1. Temperature effect

Fig. 2 shows the normalised correlation functions $g(t)$ of PVCa vs logarithmic time, measured at 20, 30 and 33°C. The correlation functions are mono-modal. The relaxation time decreases with increasing temperature from 20 to 30°C that indicates a decrease in the particle size. The temperature increase up to 33°C leads to polymer aggregation that is accompanied by an increase in relaxation time. At 33°C the aggregation of PVCa macromolecules is observed, as there is a sharp increase of the scattered light intensity. In this case, it is difficult to characterise the particle sizes. Above 33°, PVCa is water-insoluble and tends to form large aggregates due to the hydrophobic association of globules (Fig. 2, curve 1). The temperature of 33°C is 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

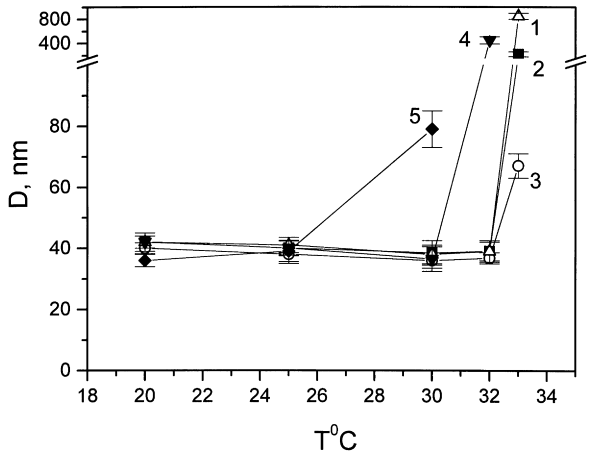

Fig. 3. Dependencies of the hydrodynamic diameter of PVCa on temperature in: (1) pure water; (2, 3) in the presence of NaCl; and (4, 5) pyrogallol. NaCl concentrations are 1 mM (2); 6 mM (3). Pyrogallol concentrations are: 1 mM (4); 2.2 mM (5).

[16]. Earlier it was shown [24] that in the vicinity of the LCST of the system, PVCa macromolecules can adopt a specific more or less dense conformation involving hydrophobic (micellar) cores. The phase separation of this system observed at temperatures higher than LCST can be considered as a result of aggregation of these compact hydrophobic micelles.

Fig. 3 demonstrates the temperature dependencies of the hydrodymanic diameter for the macromolecular size in the presence of NaCl (curves 2 and 3) and pyrogallol (curves 4 and 5). The addition of NaCl (up to 6 mM) does not lead to significant changes in the temperature dependence of PVCa. However, it should be noted that the addition of NaCl leads to a decrease in the transition temperature of PVCa at much higher salt concentrations (0.2–1 M) [17], in this case the transition can be observed even at room temperature. On the other hand, the addition of pyrogallol at the same concentrations (below 6 mM) results in the decrease of the temperature at which the aggregation begins (Fig. 3, curves 4 and 5). Therefore, the effect of pyrogallol on the behaviour of PVCa can be explained by the intensification of hydrophobic interactions within the macromolecular coil.

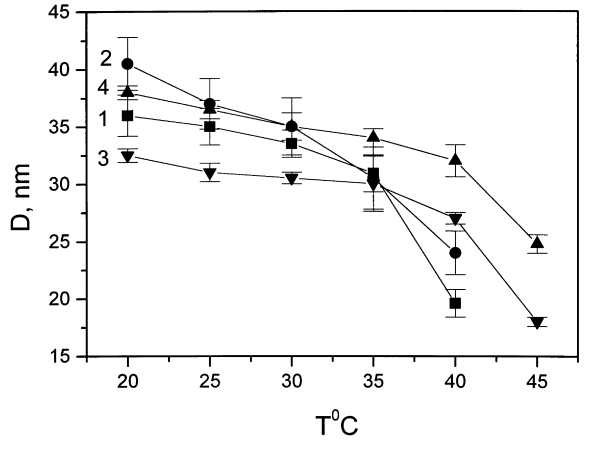

Fig. 4. Dependencies of the hydrodynamic diameter of PVCa on temperature in the presence of SDS and NaCl. SDS concentarations are 0.5 mM (1, 2) and 1.0 mM (3, 4). NaCl concentration is 6 mM (2, 4). PVCa solution concentration is 0.5 mg/ml in terms of polymer repeat units.

Figs. 4 (curves1 and 3) and 5 (curve 1) show the dependencies of the hydrodynamic diameter of PVCa on temperature in the presence of SDS (Fig. 4) and CPC (Fig. 5). At temperatures below the characteristic temperature, only a slight temperature effect on the particle size is observed. Then, much more sharp decrease of D_h takes place around some temperature, which is apparently connected with the coil–globule (collapse) transition of single macromolecule. In this case the intramolecular aggregation rather than intermolecular aggregation can be explained by the solubilisation of charged surfactants by polymer and transformation of neutral polymer to charged polymer–surfactant complex, which is stabilised by surfactants surrounding the hydrophobic PVCa globule. The increase of the concentration of ionic surfactant leads to the shift of collapse transition temperature to the higher temperature region (see Fig. 4, curves 1 and 3).

Now let us consider the conformational behaviour of PVCa macromolecules in ternary systems of PVCa–surfactant–NaCl and PVCa–surfactant–pyrogallol.

The addition of NaCl to the aqueous PVCa/surfactant systems does not lead to qualitative changes in the swelling behaviour of the systems under study. However, one may notice the systematic increase of hydrodynamic diameter of the particles (in many cases up to the initial size of PVCa macromolecules in the surfactant-free system) upon the addition of NaCl (cf. Fig. 4, curves 1–4; Fig. 5 curves 1 and 2). The observed effect does not depend on the type of surfactant (CPC or SDS). The increase of size for polymer–surfactant particles in the presence of NaCl is rather counter-intuitive. Indeed, the addition of NaCl leads to: (i) the enhancement of hydrophobic interactions [24]; and (ii) the screening of electrostatic interactions of the charged surfactant molecules. These facts would lead to the decrease in particle size; however in reality, the opposite effect is observed. One of the possible explanations for the observed effect can be that NaCl addition results in the destruction of the intramacromolecular cross-links arising in the presence of ionic surfactant due to polymer segment–surfactant specific interaction [14]. In the presence of salt, the attraction between PVCa segments and surfactant ions is significantly weak, as long as the main contribution to the specific interaction parameter is electrostatic in nature. Inorganic salt may have some effect on amine basicity via their effect on solvation and conformational state of the chains (to deviation in basicity of the group due to variations in their local environment). Therefore, in the presence of salt the binding constants for SDS–PVCa and CPC–PVCa systems are changed. However, since the nature of these cross-links for the case of PVCa is not well explained, this assumption requires additional investigation.

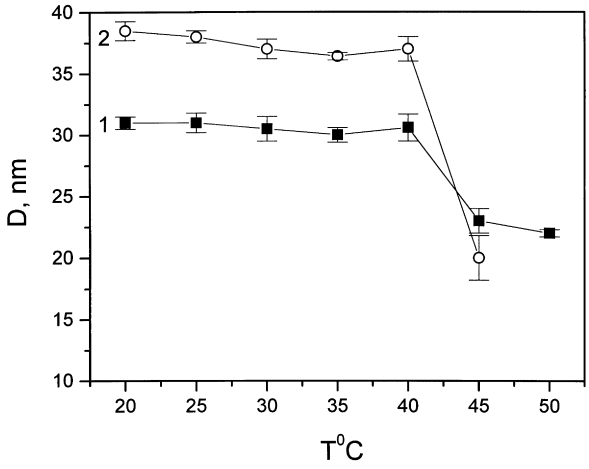

Fig. 5. Dependencies of the hydrodynamic diameter of PVCa on temperature in the presence of CPC (1 mM) (1, 2) and NaCl (6 mM) (2). PVCa solution concentration is 0.5 mg/ml in terms of polymer repeat units.

The stabilisation of polymeric globules by surfactant (as in Figs. 4 and 5) takes place only if the surfactant concentration is high enough. At lower surfactant concentrations aggregation takes place with increase in temperature (see Fig. 6, curve 2). Similar effects are observed for PVCa–pyrogallol complexes (Fig. 3, curves 4 and 5; Fig. 6, curve 1). However, quite unexpected result was observed for ternary systems of PVCa–surfactant–pyrogallol (Figs. 6–8).

For example, Fig. 6, curve 3 shows that if both SDS and pyrogallol are added (at the same concentrations as for curves 1 and 2) the intermolecular aggregation is practically completely suppressed. Fig. 7 illustrates similar results for higher concentrations of all the components. Moreover, it is possible to see that the addition of pyrogallol always results in a decrease of the size of the complex. Fig. 8 shows the results analogous to those in Fig. 6 for the case when cationic surfactant is added.

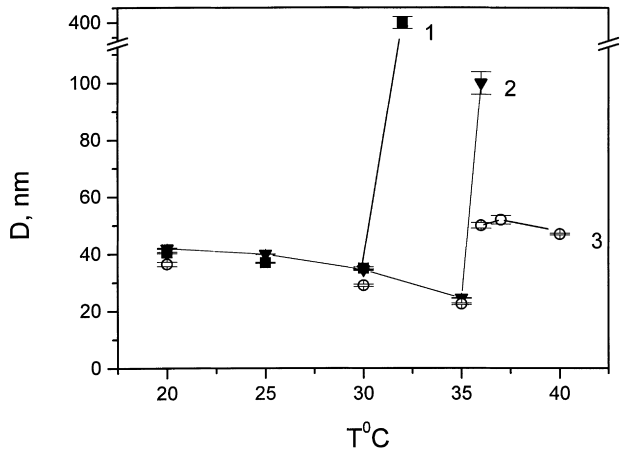

Fig. 6. Dependencies of the hydrodynamic diameter of PVCa on temperature in the presence of: (1, 3) pyrogallol (0.2 mM); and (2, 3) SDS. [SDS]/[VCa] = 0.035.

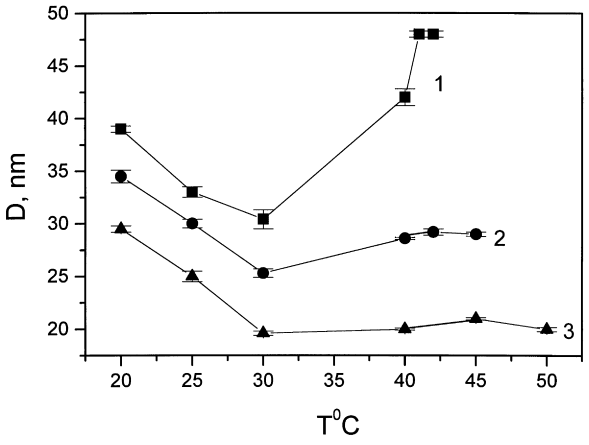

Fig. 7. Dependencies of the hydrodynamic diameter of PVCa on temperature in the presence of SDS (0.5 mM) and pyrogallol. Pyrogallol concentrations are: (1) 0 mM; (2) 1 mM; and (3) 3 mM. [SDS]/[VCa] = 0.07.

Experimental data obtained are a clear signature of the specific interaction between amide groups of PVCa and the hydroxy-groups of pyrogallol leading to the formation of reversible junctions between different polymer chains or different parts of one macromolecule. The mechanism of the inter- or intramacromolecular aggregation is the competition between the attraction of the associating groups, on the one hand, and the repulsion of the chains due to Coulomb interactions of charged groups (charged hydrophilic groups of absorbed surfactants) and translational motion of counter-ions preventing the association for large macromolecular clusters, on the other.

It was found [31] that the formation of macromolecular aggregates is possible only if the attraction energy is much higher than the thermal one, $\gg kT$. In this case, the connection of different chains into intermacromolecular aggregates requires significant gain in the association energy to overcome the Coulombic energy of repulsion of the chain charges as well as translational entropy losses due to the inhomogeneous distribution of counter-ions.

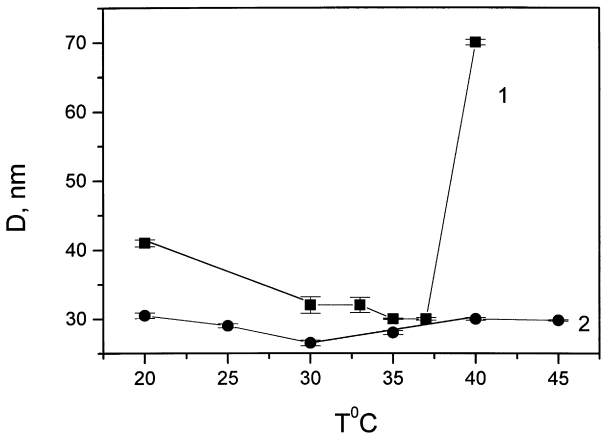

Fig. 8. Dependencies of the hydrodynamic diameter of PVCa on temperature in the presence of CPC (1,2) and pyrogallol (2). Pyrogallol concentrations is 3 mM. [CPC]/[VCa] = 0.07.

The increase in the amount of the associating groups induced by the addition of pyrogallol leads to: (1) the increase of the gain in energy connected with the aggregation of the associating groups; and (2) to the decrease of the gel volume. However, the volume decrease results in the decrease of the translational entropy of counter-ions that could be the strong factor counteracting the intermacromolecule aggregation. Therefore, we see here that the addition of pyrogallol, which can form reversible cross-links between monomer units of PVCa leads to the inhibition of the intermacromolecular aggregation and plays a stabilising role in the case of the PVCa–ionic surfactant complex.

4. Conclusions

The behaviour of PVCa in the presence of ionic surfactant as a function of temperature depends on the formation of mixed aggregates of PVCa and ionic surfactants. The different low-molecular weight water-soluble additives (NaCl and pyrogallol) affect the formation of these mixed aggregates that results in the change of the behaviour of the studied systems. An important finding of this work is that addition of small amount of pyrogallol precludes aggregation of PVCa in the presence of low concentration of ionic surfactant upon the temperature increase. So, the variation of the composition of system is an easy and effective way to influence the temperature behaviour of PVCa and the state of a macromolecule.

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