Microcalorimetric Study of Thermal Cooperative Transitions in Poly(*N*-vinylcaprolactam) Hydrogels

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ABSTRACT: Structural cooperative transitions in thermosensitive nonionic hydrogels of poly(*N*-vinylcaprolactam) (PVCa) were studied using high-sensitivity differential scanning calorimetry (HS-DSC). The thermoshrinking of the PVCa gel is endothermic, much like first-order phase transitions. According to the HS-DSC data, the gel system undergoes two successive cooperative transitions between 25 and 50 °C. The low-temperature transition (31.5 °C) is proposed to be associated with the microsegregation resulting in formation of hydrophobic domains (micromicelles) in the gel whereas the high-temperature transition (37.6 °C) is due to the gel volume collapse. The transition temperatures decrease in the presence of NaCl and increase with increasing sodium dodecyl sulfate (SDS) concentration. Dependences of the transition enthalpies and entropies on NaCl and SDS concentrations display a more complex character. The influence of sodium chloride and SDS on the transition temperatures is in agreement with the general expectations taking into account their effect on hydrophobic interactions and the ability to form micromicelles.

I. Introduction

Phase transitions in polymer gels and single macromolecules are of considerable interest. Particular attention of both scientists and technologists has been given to the gel collapse phenomenon, i.e. the sharp volume transition of a gel from the swollen state to the shrunken one in response to infinitesimal changes in environmental conditions.

Investigations of the phase transitions in network systems were initiated by Dušek and Patterson,[1] who had predicted theoretically a discontinuous volume change for chemically cross-linked gels. Later Tanaka et al. [2−4] observed the critical behavior of cross-linked ionized polymer networks as a result of temperature or solvent composition variations, as well as the pronounced collapse transition. It was suggested that the volume phase transition in gels is analogous to the coil-to-globule transition in single polymer chains in poor solvents.[5−7]

The volume phase transition of polymer gels is a universal phenomenon; i.e. it has been observed for gels with different chemical composition and can be induced by many factors such as temperature, solvent composition, pH, ionic strength, light, and some others.[8−15] Recently, a new type of the collapsed gel systems was observed as a result of interaction of polyelectrolyte networks with oppositely charged low molecular weight surfactants.[16,17] Theoretical approaches to the description of the collapse of both polyelectrolyte and uncharged networks have been developed.[8,17−23]

As a rule, temperature is one of the most universal parameters affecting the phase behavior of neutral and charged gel systems.[4,10−12,21] The volume phase transition in thermoresponsive nonionic gels, i.e. the gel shrinking with increasing temperature, was first demonstrated by Hirokawa et al.[10,11] for poly(*N*-isopropylacrylamide) (NIPA) gels. This phase transition is typical of gels based on polymers with a lower critical solution temperature (LCST). Recently, a new type of nonionic hydrogel, namely, chemically cross-linked poly(*N*-vinylcaprolactam) (PVCa), was synthesized that undergoes the collapse transition under heating.[24]

Critical phenomena associated with the volume phase transition in acrylamide and NIPA gels were studied by friction measurements,[25] dynamic light scattering,[26] and small-angle neutron scattering.[27] The last method is highly informative as it allows one to detect in detail spatial inhomogeneity of polymer chains in the gels. The gel collapse can also be studied by measurements of linear dimensions or weights of macrosamples of gels prepared in appropriate molds.

The majority of the experimental methods mentioned above give no way to characterize the phase transitions in the gels by the free energy, enthalpy, and entropy of the transition. That is the main reason why thermodynamics of the phase transitions in polymer gels until recently remained, in the main, a subject of theoretical considerations. Considerable progress toward this goal may be achieved by using high-sensitivity differential scanning calorimetry (HS-DSC).

The HS-DSC technique has been developed to study cooperative conformational transitions of biopolymers in extremely dilute solutions, but until recently, this method has rarely been employed in more traditional polymer physics.[28−31] The method is mostly based on the use of the so-called Privalov highly sensitive and precise, adiabatic differential scanning microcalorimeters DASM-1M, DASM-4, and DASM-4A (NPO BIOPRIBOR, Russian Academy of Sciences, Pushchino, Russia), which outperform by at least 2 orders of magnitude conventional scanning calorimeters commonly used in polymer research. HS-DSC allows determination of the partial heat capacity of a polymer as a function of temperature with high precision at very low polymer concentrations (down to about 0.1−0.3%). These data can be easily converted into temperature

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dependences of Gibbs free energy, entropy, and enthalpy by the standard thermodynamic relations. A further benefit of HS-DSC is the rather small time and sample consumption. Normally, it is possible to perform a calorimetric experiment for a time shorter than 2 h with a sample of about of 0.1−0.5 mg.[32,33]

The aim of this work is to demonstrate the application of HS-DSC to study the thermodynamics of the cooperative conformational and phase transitions in thermosensitive polymer hydrogels. The results of an investigation on the phase behavior of neutral PVCa hydrogel with no additives and in the presence of an anionic surfactant (SDS) and inorganic salt (NaCl) studied by HS-DSC are presented.

II. Experimental section

1. Preparation of Samples. Synthesis and characterization of the PVCa network as well as the procedure for preparing its hydrogel samples were described elsewhere.[24] In this study, the PVCa network prepared with 0.5 mol % of bisacrylamide as a cross-linking agent was used. The equilibrium weight fraction of polymer in the network swollen in water was 0.04 at 21 °C.

Sodium dodecyl sulfate (SDS) and NaCl, both of analytical reagent grade (REACHIM, Russia), were used without further purification. Bidistilled deionized water was used to prepare all solutions and gel suspensions.

To prepare gel samples for calorimetric and turbidimetric measurements, a weiged sample of the swollen gel with some additional amount of water was first mechanically crushed using a hand-operated glass homogenizer with a Teflon plunger. This coarse gel suspension was additionally sonicated with a UZDN-1 ultrasonic homogenizer at 22 kHz for 10 min under cooling to reduce the size of the gel particles. The resulting suspension was centrifuged at 2200*g* for 10 min to separate coarse gel particles. This procedure provides a way for preparation of fine-grained gel suspensions.

According to optical microscopy, most of the gel particles in the suspension were irregular in shape and had linear dimensions of the order of tens of micrometers. The suspension was transparent and remained stable at room temperature for a long time without any visible precipitation of aggregated gel particles. The suspension was used in both microcalorimetric and turbidimetric experiments. The concentration of gel particles in the aqueous stock suspension was varied from 25 to 40 mg/mL. This corresponds to 1.0−1.6 mg of dry network/mL of the suspension. To prepare samples with a desirable amount of the gel, the stock suspension was diluted by water or by the aqueous stock solution of an additive as required.

2. Calorimetric Measurements. These were carried out using the DASM-4 and DASM-1M differential adiabatic scanning microcalorimeters (NPO BIOPRIBOR, Pushchino, Russia) with cell volumes of 0.47 and 1.0 mL, respectively. The measurements were taken in the temperature range of 5−125 or 5−100 °C at a constant heating rate which was varied from 0.25 to 2.0 K/min and at a constant excess pressure of 2.5 atm. Calorimetric tracings were digitized and input into a computer by a Genitizer GT-01212B digitizer. Primary data processing was performed with the Nairta software developed in the authors' laboratory. For each experiment, two heating scans were normally carried out. The first scan was done with both calorimetric cells filled with a solvent (water or an aqueous solution of an additive). This gave an instrumental base line. In the second scan, one of the cells contained the solvent and the other cell contained a gel sample in the same solvent. During this scan the difference in heat capacities of the sample and the solvent was measured as a function of temperature. After subtraction of the instrumental base line, these data were converted to the apparent partial heat capacity of the polymer, assuming the polymer to have a specific partial volume of 1 mL/g. Figure 1 presents an example of such a thermogram. To calculate the excess heat capacity associated with a cooperative transition of the polymer, a base line of the transition was determined taking into account heat capacity contributions of the pre- and post-transition states as shown by the dashed line in Figure 1.

The observed cooperative transitions were characterized by the transition temperature and enthalpy. The transition temperature was taken as the temperature of a maximum or a shoulder of the thermogram. The transition enthalpy was determined as the area under the excess heat capacity peak and expressed per mole of repeating vinylcaprolactam units with molecular mass of 139 Da. Deconvolution of the excess heat capacity functions of the gel into constituent peaks was performed with the PeakFit 4 software using four-parameter Pearson distributions as peak functions.

3. Cloud Point Determination. The cloud point of the gel suspensions was estimated visually. A sample of the gel suspension (about 1 mL) was placed into a thermostated glass cell fitted with a thermometer, and the temperature was gradually increased at a constant rate of 1 K/min. The cloud point was determined as the temperature at which a sharp appearance of turbidity in the bulk volume of the suspension was observed. This coincided within 1 deg with the temperature at which the system became transparent under cooling. PVCa gel samples used for turbidimetric measurements had the same composition as those used in the microcalorimetric experiments.

III. Results

1. Thermal Behavior of PVCa Gels in Water. The special procedure to prepare gel samples for microcalorimetric measurements was motivated by several reasons. First, the preparation of a gel sample in the form of a fine suspension was dictated by some design features of the calorimetric cells. A sample under study must be in a fluid state to be placed into the cell, and it must be possible to vary its concentration in the cell with rather high accuracy. Second, the microparticle form of the gel sample seems to be most favorable for its fastest response to changes in external conditions, in particular, in temperature. The efficiency of the proposed procedure for gel sample preparation is demonstrated below.

The thermogram obtained during heating of the PVCa gel suspension in pure water is presented in Figure 1. The single but markedly broad and asymmetric peak of the heat capacity is observed within the temperature range of 5−100 °C. These results show that the PVCa gel undergoes a complex cooperative transition within a 30 deg interval beginning at 27 °C, which is accompanied by a considerable endothermic heat effect. The temperature interval of the transition is in agreement with macroscopic volumetric measurements.[24] The complete reproducibility of the thermograms was demonstrated during the second and subsequent heatings at the same heating rate. This means that the observed transition in the PVCa gel appears to be completely reversible, in agreement with swelling equilibrium data.[24]

The data presented in Figure 1 show that the heat capacity peak has a remarkable shoulder on its left side. This peak asymmetry suggests that the cooperative transition in the PVCa gel is rather complex. This may be the result of overlapping of either two close successive transitions within one cooperative domain or independent transitions within two different domains. However, the first interpretation is much more likely in the case of homopolymer networks in a one-component solvent.

The thermal behavior of PVCa gel could not be explained by the colloid character of the system. Hirotsu,[34] who studied the shape- and size-dependent swelling of polymer gels, has demonstrated that in the case of nonionic gels showing the continuous volume

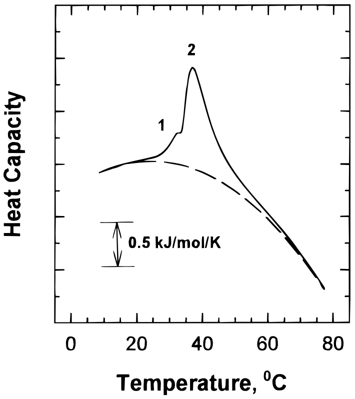

Figure 1. Typical thermogram of the PVCa hydrogel without any additives: 1, low-temperature transition; 2, high-temperature transition. The heating rate is 1 K/min. The transition base line is approximated by a dashed line.

phase transition the transition temperature does not depend on the size of the gel particles between 0.2 and 3.5 mm. Most likely, this is the case for gel particles of somewhat smaller size as well.

To characterize the phase behavior of the PVCa gel, two transition temperatures, $T_{t,1}$ and $T_{t,2}$, as well as the total transition enthalpy, $\Delta_t H$, were used. $T_{t,1}$ corresponds to the shoulder on the left side of the thermogram and $T_{t,2}$ is the temperature of its maximum.

The design of the DASM microcalorimeters does not allow one to perform precise measurements under cooling. Therefore, calorimetric experiments at different heating rates were carried out to elucidate possible effects of kinetic factors on the observed transitions. Such experiments should demonstrate whether the sample has time to achieve its equilibrium state at each temperature in the course of the scan. It was found that a change in the heating rate from 0.25 to 2.0 K/min does not bring any systematic effects on shape and position of the thermograms. Variations of the transition temperatures and enthalpy determined at the different heating rates were rather comparable with experimental errors of their determination at a fixed heating rate (±0.5 °C for the transition temperature and ±0.1 kJ mol^{-1} for the transition enthalpy) (Figure 2). Therefore, characteristic times of the transitions are apparently shorter than those of the thermal equilibration of the cells. Possibly, this is a consequence of the micrometer dimensions of gel particles used in our experiments.

The results shown in Figure 2 do not change for PVCa gel samples with different contents of gel particles in the gel suspension (from 2×10^{-6} to 1×10^{-5} mol of repeating units/mL). The average values of these transition parameters are $T_{t,1} = 31.5 \pm 0.3$ °C, $T_{t,2} = 37.6 \pm 0.8$ °C, and $\Delta_t H = 1.9 \pm 0.1$ kJ mol^{-1}.

It should be emphasized that this complex character of the collapse transition cannot be discovered by macroscopic volumetric measurements where a continuous gel shrinking is observed within the interval 30–40 °C.[24] The two consecutive transitions can only be resolved by the use of the HS-DSC method.

2. Effects of Additives on the Cooperative Transitions in PVCa Gel. The excess heat capacity functions of the PVCa hydrogel at different SDS concentrations are presented in Figure 3. The second and subsequent heating scans of each of the gel samples reproduced the first ones, indicating complete reversibility of the transitions. The data show that even a minor content of the surfactant added to the gel suspension has a pronounced effect on the processes occurring in the PVCa network on heating. Upon the addition of SDS, the heat capacity peak is noticeably shifted toward higher temperatures. With increasing SDS concentration, the bimodal shape of the thermogram is displayed more and more clearly, since the temperature of the second transition increases with SDS concentration much more markedly than that of the first one.

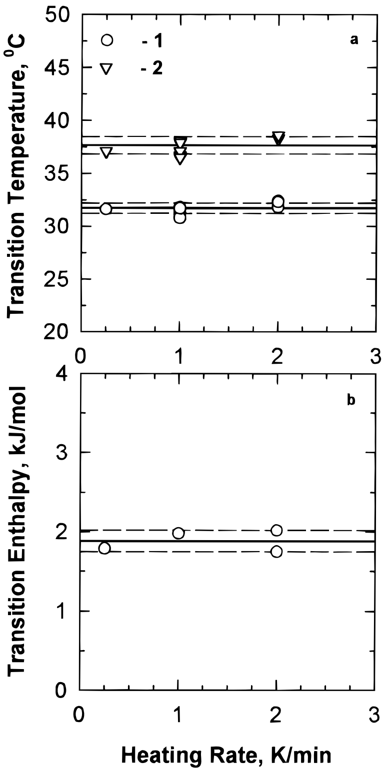

Figure 2. Transition temperatures (a) and the total transition enthalpy (b) of the PVCa hydrogel without any additives against the heating rate: 1, low-temperature transition; 2, high-temperature transition. Confidence intervals are presented by dashed lines.

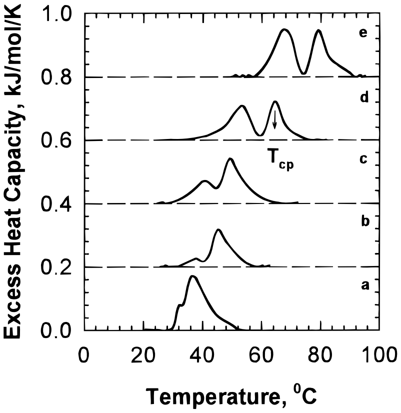

Figure 3. Excess heat capacity functions of the PVCa hydrogel at different SDS concentrations: 0.00 (a), 0.64 (b), 1.00 (c), 2.80 (d), and 5.20 (e) mM. The arrow indicates the cloud point of the gel suspension. The curves are shifted relative to each other by 0.2 kJ mol^{-1} K^{-1} along the ordinate scale.

The excess heat capacity functions of the PVCa hydrogel at different NaCl concentrations are given in Figure 4. The salt affects the thermal behavior of the PVCa gel oppositely to SDS: both peaks are displaced to lower temperatures with increased salt concentration. This process does not seem to be accompanied by any change in the resolution of the peaks.

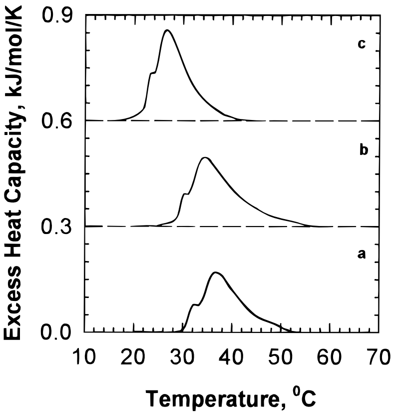

Figure 4. Excess heat capacity functions of the PVCa hydrogel at different NaCl concentrations: 0.0 (a), 0.2 (b), and 1.0 (c) M. The curves are shifted relative to each other by 0.3 kJ mol^{-1} K^{-1} along the ordinate scale.

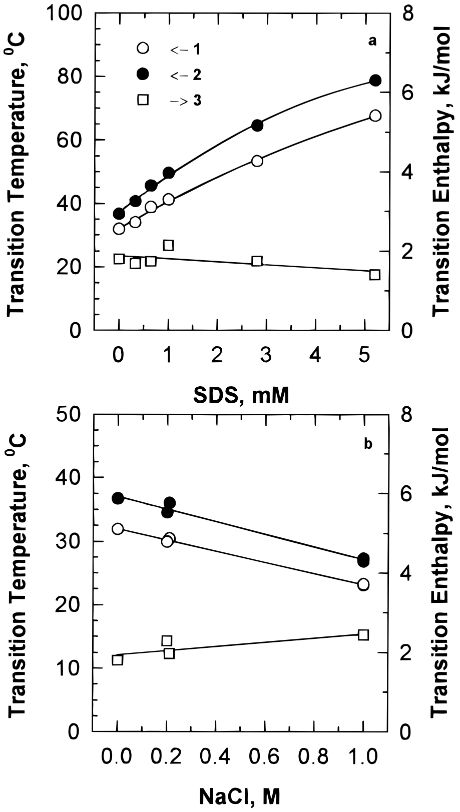

Figure 5. Transition temperatures (1, 2) and the total transition enthalpy (3) of the PVCa hydrogel against SDS (a) and NaCl (b) concentrations: 1, low-temperature transition; 2, high-temperature transition.

Figure 5 shows plots of the transition temperatures and the total transition enthalpy against SDS and NaCl concentrations. It is of special interest that on addition of SDS both transition temperatures increase by 30–40 deg, although the SDS concentration remains considerably below its cmc in water[35] and the surfactant/network ratio does not exceed 1 mol of SDS/mol of repeating units (Figure 5a). This trend is in agreement with the results of ref 24. On the other hand, the salt effect on the PVCa gel phase behavior is somewhat weaker in comparison with the SDS effect. Nevertheless, at a high salt concentration, the transitions can be observed even at room temperature (Figure 5b). The total transition enthalpy slightly decreases when SDS concentration increases and increases with an increase in the NaCl concentration.

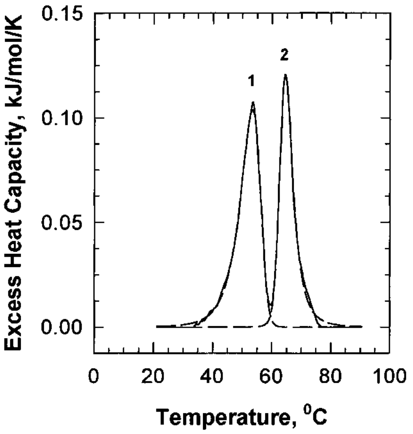

Figure 6. Excess heat capacity function of the PVCa hydrogel at SDS concentration 2.8 mM shown by the solid line and its constituent peaks presented by the dashed lines which are obtained as the result of deconvolution of the function with four-parameter Pearson distributions (standard fitting error is 0.0016).

It is interesting to estimate separately the thermodynamic functions of both transitions. This requires the deconvolution of the experimental excess capacity functions into constituent peaks. Normally, such a procedure is based on the appropriate thermodynamic model for the transition.[33] However, in our case it is rather difficult to propose a microscopic model for the observed PVCa gel transitions. Therefore, an empirical deconvolution of the excess heat capacity functions of the PVCa hydrogel was performed assuming that each of the constituent peaks can be fitted with a four-parameter Pearson distribution, which normally gives a very high fitting flexibility. Figure 6 gives an example of such a deconvolution. As a rule, the standard fitting error was rather small in comparison with experimental errors. Each peak was characterized by the midpoint temperature ($T_{t,i}$, $i = 1,2$) and the transition enthalpy ($\Delta_t H_i$, $i = 1, 2$). From this the transition entropy, $\Delta_t S_i = \Delta_t H_i / T_{t,i}$, is obtained.

The estimated thermodynamic parameters of the PVCa gel transitions are listed in Table 1.

It is convenient to express the effect of some physicochemical factor (X) on a phase or conformational transition by excess thermodynamic functions of the transition, i.e., by increments of the transition functions relative to the reference state with $X = 0$

$$\Delta_t H^E(X) = \Delta_t H(X) - \Delta_t H(0) \tag{1a}$$

$$\Delta_t S^E(X) = \Delta_t S(X) - \Delta_t S(0) \tag{1b}$$

Figure 7 displays excess transition enthalpies and entropies for both transitions of the PVCa hydrogel as a function of SDS and NaCl concentrations. Note that dependences of the excess transition enthalpies and entropies on SDS concentration resemble partly curves of binding of low molecular weight ligands to a polymer matrix.[36] They seem to level off at rather high SDS concentrations. On the other hand, these parameters change approximately linearly with increasing salt concentration, as is typical of the “salting-out” phenomenon.[37] It is also interesting that in the SDS case both excess transition functions are positive for the first transition and negative for the second one. Also, they are positive for both transitions in the NaCl case,

Table 1. Thermodynamic Parameters of the Thermal PVCa Gel Transitions

		transition 1			transition 2			
no.	conditions	$T_{t,1}$, °C	$\Delta_t H_1$, kJ mol^{-1}	$\Delta_t S_1$, J mol^{-1} K^{-1}	$T_{t,2}$, °C	$\Delta_t H_2$, kJ mol^{-1}	$\Delta_t S_2$, J mol^{-1} K^{-1}	$\Delta_t H$, kJ mol^{-1}
1	no additives	31.9	0.19	0.62	36.7	1.62	5.23	1.80
2	0.33 mM SDS	34.0	0.27	0.88	40.7	1.42	4.53	1.69
3	0.65 mM SDS	38.8	0.76	2.44	45.6	0.97	3.04	1.74
4	1.00 mM SDS	41.2	0.98	3.12	49.6	1.16	3.60	2.14
5	2.80 mM SDS	53.4	0.98	3.00	64.5	0.77	2.28	1.75
6	5.20 mM SDS	67.6	1.41	4.14	78.8	1.01	2.87	2.42
7	0.21 M NaCl	30.4	0.27	0.89	36.0	1.70	5.50	1.97
8	0.20 M NaCl	29.9	0.21	0.69	34.5	2.08	6.76	2.29
9	1.0 M NaCl	23.1	0.22	0.74	27.3	2.22	7.39	2.44
10	1.0 M NaCl	23.2	0.29	0.98	26.8	2.15	7.17	2.44

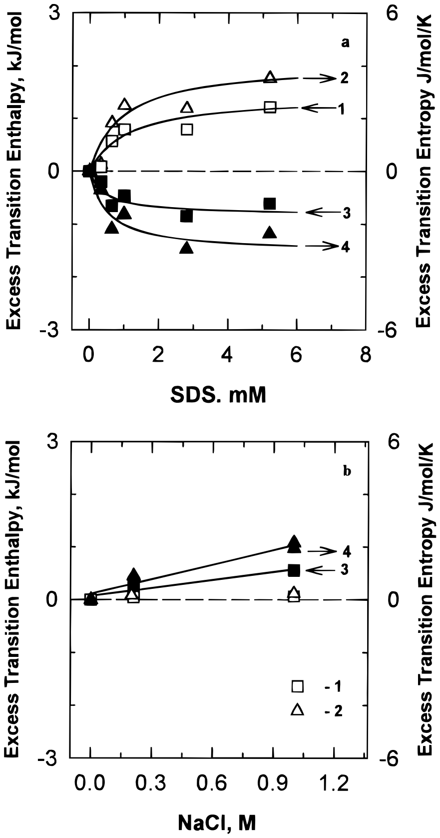

Figure 7. Excess thermodynamic transition functions of the PVCa hydrogel versus SDS (a) and NaCl (b) concentrations. Curves 1 and 2 are the functions for the low-temperature transition and curves 3 and 4 are the functions for the high-temperature transition. The excess transition enthalpy is displayed by the left ordinate scale and the excess transition entropy is exhibited with the right one.

although the salt effect on the second transition is much more pronounced.

IV. Discussion

PVCa hydrogels display two successive cooperative transitions. As mentioned above, in this they differ from other nonionic thermosensitive polymer gels (such as NIPA gel) for which only one phase transition was commonly detected.[27−30] However, multiple phase transitions have also recently been revealed for gels of synthetic polyampholytes[38] as well as for some cross-linked proteins.[39] All these gels are ionic in nature. Hence, the PVCa gel is probably the first example of a nonionic homopolymer gel capable of undergoing multiple conformational transitions.

In order to clarify the nature of the transitions observed in PVCa gels, additional experiments on determination of their cloud points were carried out. Cloud points are closely related to phase separations in polymer systems.[1,7,18,27,40,41] Earlier Otake et al.[30] demonstrated that the volume transition temperatures of NIPA gels are very close to the cloud points of aqueous solutions of linear NIPA polymers. In our case, it was possible to determine the cloud point of the PVCa gel using directly its fine suspension. Results of these experiments showed that the temperature at which the turbidity of the suspension appears and disappears (indicated by the arrow in Figure 3d as an example) is very close to the transition temperature of the high-temperature transition. Therefore, the second heat capacity peak can be associated with a volume collapse phase transition for the PVCa gel. The macroscopic volumetric measurements[24] do not invalidate this assumption, although such measurements do not have enough resolution.

The nature of the first cooperative transition in PVCa gels at the temperature $T_{t,1}$ is of great interest. First, it should be stressed that during heating the PVCa gel suspensions were transparent at temperatures of about $T_{t,1}$. Thus the first transition is presumably realized on a nanoscale (1−100 nm). It may be assumed that this transition reflects the phenomenon which is apparently typical of some amphiphilic polyelectrolyte polymers, including networks in water.[42] It is generally believed that hydrophobic domains or micromicelles located periodically can arise as a result of this segregation. Up to now the microphase separation transition for hydrogel was discussed mainly for polyelectrolytes.[27,42,48] However, in principle the microsegregation can be realized for neutral hydrogels as well if the polymer chains have a pronounced amphiphilic character: then micromicelle formation can be thermodynamically more favorable than an overall collapse of the gel. The amphiphilic character of PVCa is due to the simultaneous presence of hydrophobic and polar atomic groups in their structure.

It is possible to find some analogy between the behavior of PVCa hydrogels and aqueous solutions of the linear PVCa polymer. For the last system, Kirsh et al.[41] have found from viscosimetric and fluorescence data 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 the LCST can be considered as a result of aggregation of these compact hydrophobic micelles.

The phase state of a swollen gel network or a polymer solution is determined by competition of interactions between different chemical groups of the polymer and the solvent. Changes in properties of the solvent and of the chemical structure of the polymer can change this interplay. It was suggested[10,21,29] that the phase behavior of hydrogels involving amphiphilic chains with large hydrophobic side groups is presumably governed by the hydrophobic effect.

Let us consider how temperature and the additives used can affect interactions in the PVCa hydrogel. At temperatures lower than the first transition temperature ($T_{t,1} \cong 30$ °C in the absence of any additives), the PVCa chains are solvated to the greatest extent; i.e., there is a large number of contacts between polymer groups and water molecules. In this case, PVCa network chains are likely to be in the conformation typical of flexible macromolecules in good solvents. It is known[43−45] that in this temperature range a decrease in temperature favors the strengthening of the hydration of the hydrophobic groups. When temperature increases, contacts of hydrophobic groups of the polymer with water molecules become thermodynamically less favorable than contacts between these groups. As a result, the polymer chain tends to take a conformation in which hydrophobic groups are mostly shielded by hydrophilic polar groups of the polymer exposed to the solvent (the monomer unit of PVCa consists of both hydrophobic and polar atomic groups). Apparently, this type of conformational transition is partly similar to a first-order phase transition.[7,46] This trend explains formation of PVCa micromicelles in the course of the first transition. However, due to some topological constraints, such a folding of the network chains cannot provide complete burying of all hydrophobic groups in the micromicelle core. Hence, a solvent-accessible surface of the micromicelles should be partly hydrophobic. This must provide a tendency of the micromicelles to further aggregation that results in formation of the collapsed gel phase at higher temperatures.

The NaCl and SDS effects on the transition temperatures of the PVCa gel are in qualitative agreement with the effects of these additives on the Gibbs energy of transfer of hydrophobic groups from their hydrophobic environment to water.[44−46] This energy is increased by salts such as NaCl and decreased by amphiphilic compounds like SDS. Also addition of NaCl leads to the homogeneous increase of hydrophobic interactions; therefore both transitions are shifted to lower temperatures simultaneously (Figure 4), while addition of SDS favors micelle formation, thus making the distinction between two transitions more pronounced.

These relations will become clear if we consider that the work of creating a cavity in the aqueous medium where a molecule of the given hydrophobic compound could be located makes the main contribution to the transfer Gibbs energy.[47,49] This work can be estimated as $A_{cav} \sim \sigma S$, where S is the internal surface of the cavity and σ is the surface tension of the aqueous medium. It is known[45,47] that salts like NaCl increase the surface tension but surfactants of SDS type decrease it. Therefore, the work of cavity creation and thus the transfer Gibbs energy will be increased in the first and decreased in the second case.

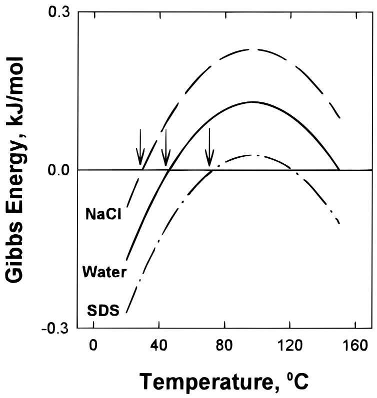

Figure 8. Schematic representation of the temperature dependences of the Gibbs energy of transfer of a PVCa residue from its hydrophobic environment to water in the absence and in the presence of the additives. The transition midpoints at different conditions are shown by arrows.

Since the transfer entropy is likely to be negative over the temperature range used,[46] the mentioned changes in the Gibbs transfer energy must be associated with a decrease in the transition temperature in the presence of out-salting salts and with its increase if there is an amphiphilic compound in the system. This is apparent from the dependence of the Gibbs energy on temperature typical for the transfer of hydrophobic groups from their hydrophobic environment to water[50] (Figure 8). It is common knowledge that such a transfer leads to a positive and rather large change in the heat capacity.[45,46] This results in the fact that the transfer Gibbs energy function passes through a maximum and becomes equal to zero at two temperatures. The transition in the vicinity of the first of these temperatures leads to the collapse phenomenon accompanied with the pretransitional hydrophobic micromicelles formation whereas the vicinity of the second temperature corresponds to the melting of the core. In the case of the PVCa hydrogel under consideration, it is likely that this second type of phenomenon was not observed because they are apparently located at temperatures above the higher temperature operating limit (125 °C) of the microcalorimeters used.

V. Conclusion

HS-DSC analysis was successfully used to study thermal cooperative transitions in the PVCa gel. In contrast to other neutral polymer gels, two successive cooperative transitions were detected for the PVCa gel. The low-temperature transition ($T_{t,1} = 31.5$ °C in water) seems to be connected with microsegregation phenomena resulting in creation of hydrophobic domains or micelles in the gel. It was shown that the high-temperature phase transition ($T_{t,2} = 37.6$ °C in water), which is close to the cloud point of the gel, is probably connected with a volume collapse transition of the gel. The effects of sodium chloride and SDS on both transition temperatures suggest that both transitions are presumably driven by the hydrophobic effect.

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(50) Illustrative calculations of the Gibbs energy of transfer of a PVCa residue from its hydrophobic environment to water were done by using the general thermodynamic relation[46] $\Delta_t G(T) = \Delta_t H(T_t) + \Delta_t C_p(T - T_t) - T[\Delta_t H(T_t)/T_t + \Delta_t C_p \ln(T/T_t)]$, where T_t, $\Delta_t H$, and $\Delta_t C_p$ are the midpoint, enthalpy, and heat capacity increment of the low-temperature transition, respectively. The curve without any additive was calculated with $T_t = 319$ K (46 °C), $\Delta_t H(T_t) = -1.7$ kJ mol^{-1}, and $\Delta_t C_p = 0.035$ kJ mol^{-1} K^{-1}, which are approximately compatible with the obtained experimental data. It was assumed that effects of the additives on the $\Delta_t G$ (±0.1 kJ mol^{-1}) are independent of temperature.

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