



## Thermo- and pH-sensitivity of aqueous poly(*N*-vinylpyrrolidone) solutions in the presence of organic acids

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### ABSTRACT

The phase transition in poly(*N*-vinylpyrrolidone) (PVP) aqueous solutions is shown to occur at heating upon addition of organic acids such as isobutyric, isovaleric, and, especially, trichloroacetic (TCA) ones. The cloud point temperature ( $T_c$ ) of PVP solutions drops from 70 to 6 °C when the TCA concentration rises from 0.2 to 0.3 mol/l. A decrease in  $T_c$  is even more drastic when HCl is also added though HCl addition to the system without TCA does not result in phase separation. These phenomena are explained by the reversible coordination between the non-ionized form of TCA and PVP units via hydrogen bonding. An increase in the medium acidity depresses TCA dissociation, resulting in an increase in PVP–TCA associate concentration. Calculations based on the  $pK_a$  values of TCA confirm this suggestion. The similar behavior is observed with poly(*N*-vinylcaprolactam) systems. The amount of TCA bound to PVP has been determined by means of separation of the precipitate by centrifugation at temperatures above  $T_c$  and subsequent titration of TCA in the polymer with NaOH. It is shown that the precipitate contains one TCA molecule per 3–6 VP units, this value decreasing down to 1.25–2 upon HCl addition to the system.

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### 1. Introduction

In recent years, an interest arose to thermosensitive polymers which have lower critical solution temperatures (LCST). These water-soluble polymers exhibit abrupt coil-to-globule transitions on increase in the solution temperature. At present, this effect is explained by weakening hydrogen bonds in the hydrate shell which results in the destruction of polymer–hydrate complex, stabilizing the polymer in the solution. Due to enhancing the role of hydrophobic interactions inside polymer chains on heating, the collapse of macromolecules occurs. Several reviews are published on the subject [1–5]. The phenomenological model of early stages of the homopolymer collapse, including the fast formation of denser parts of the chain (the necklace structure), is suggested [6].

There are a number of water-soluble thermo-responsive polymers. Poly(*N*-isopropylacrylamide) (PNIPAM) and poly(*N*-vinylcaprolactam) (PVCL) [1–3] which have temperatures of phase separation close to the temperature of the human body and perspective for the application in medicine are among the most studied. Cloud point temperatures ( $T_c$ ) of such polymers change on addition of various organic and inorganic compounds. PVCL, the

closest analogue of poly(*N*-vinylpyrrolidone) (PVP), was studied in detail from this point of view in works by Kirsh [2,4,7,8].  $T_c$  of PVCL aqueous solutions were found to decrease upon addition of some salts, alcohols, and organic acids [2,7–10]. Ionic surfactants, amides, and mineral acids were shown to raise  $T_c$  [2,8,10–12]. The effect of additives seems to be specific, and the nature of this phenomenon is a subject of argument [2–4,8].

Some thermosensitive polymers, for example, poly(dimethylaminoethyl methacrylate) (PDMAEMA) and its copolymer with ethylacrylamide and copolymers of NIPAM with poly(methacryloyl-L-leucine), containing basic groups [13], or polyacids such as poly(propylacrylic), poly(ethylacrylic), poly(methacrylic) (PMAA) acids, and MAA copolymer with VCL [14], copolymers of acrylic acid (AA) with NIPAM, *N,N*-dimethylacrylamide, and 1,3-dioxolane [15] are also pH-responsive. It can be seen from these works that with increasing the medium acidity,  $T_c$  of polymers, containing basic groups, increase and  $T_c$  of those, containing acidic groups, decrease. In the first case, salts form and the electrostatic repulsion of the charged groups prevents from phase separation while in polyacids, the proportion of uncharged COOH groups increases, enhancing coil-to-globule transition.

PVP widely used in medicine and biotechnology [2], is the closest analogue of PVCL. However, being less hydrophobic, this polymer exhibits thermosensitivity only under pressures higher than 1 kbar [16]. Recently, it was shown that in the presence of

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some salts [17] and alcohols [18] phase transition was observed in PVP aqueous solutions under normal conditions, too. Copolymers of VP with more hydrophobic monomers such as VCL [19], NIPAM [20] or DMAEMA [21] also exhibit phase separation, their  $T_c$  values decreasing with increasing the proportion of the second component.

Ionic surfactants [22], phenols and other aromatic compounds [2,23,24], and also some organic acids [2,14,24] form complexes with PVP, apparently, changing the hydrophobicity of the polymer. pH-responsive intermacromolecular complexes between PVP and PAA, PMAA or polyvinyl alcohol are also known [25].

If organic acids are included in copolymer chains, the degree of acid ionization, depending on pH of the solutions, is shown to be very important for phase separation [14,15]. When complex formation between polymers and organic acids takes place, the acid dissociation is also expected to be important. In this connection, the effect of acids on the phase separation behavior of PVP aqueous solutions has been studied in comparison with that of PVCL.

## 2. Experimental

PVP from Loba-Chemie, Wein-Fischamend, Australan Präparate, Austria ( $M_w = 4.2 \times 10^4$ ) was used without purification.

PVCL was synthesized by free-radical polymerization of *N*-vinylcaprolactam in isopropanol [26], precipitated into ethyl ether, reprecipitated from isopropanol, filtered off and dried in vacuum for 3 days at heating. Polymer of  $M_w = 2 \times 10^4$ ,  $M_w/M_n = 3.2$  (GPC, Waters,  $\text{CHCl}_3$  with 1% LiCl) was taken into experiments.

Isovaleric (*i*-VA), isobutyric (*i*-BA), and trichloroacetic (TCA) acids purchased from Aldrich were used without further purification.

TCA solution (1.33 M) in distilled water was added dropwise to the PVP aqueous solutions at constant stirring with the magnetic bar. If some polymer precipitated because the temperature was higher than  $T_c$  of the polymer, the solution was cooled in the refrigerator for the polymer to dissolve. The subsequent HCl (11.5 M) addition was carried out in the same way. The flask, containing the solution, was put into the thermostat where it was heated with the rate of  $1^\circ\text{C}/\text{min}$ . Values of  $T_c$  were determined visually.  $T_c$  was registered in 0.5 min after the weak opalescence appeared. According to the random control of some points by UV-vis spectrophotometry performed in our preceding paper [17], the measurement accuracy is within  $0.5^\circ\text{C}$ .

To determine the TCA/PVP ratio in the PVP-TCA interaction product, TCA and HCl were added to the prechilled polymer solution at constant stirring. Concentrations of the system components were chosen so that  $T_c$  of the solution was lower than  $20^\circ\text{C}$ . Then,  $T_c$  was measured, and the polymer precipitated at the ambient temperature was separated by centrifugation for 1 h at 5000 R.P.M. The supernatant liquid was decanted, and the polymer was redissolved in water. The concentration of TCA bound to the polymer was determined by titration of this solution with NaOH. To control whether the whole polymer was separated, extra TCA was added to the supernatant liquid, and the slightly cloudy solution was centrifuged. The amount of the dried polymer was found to be not more than 5% of that taken in the experiment. To be sure that no HCl is left in the polymer,  $\text{Cl}^-$  concentration was determined by the Volhard method [27].

## 3. Results and discussion

### 3.1. Carboxylic acids

It is known that the addition of low-molecular mass organic acids such as formic, acetic, and oxalic ones to aqueous PVCL solutions causes a decrease in  $T_c$  [8]. In the case of PVP, the addition

of these acids does not result in phase separation up to  $100^\circ\text{C}$ . However, if water-soluble carboxylic acids with longer hydrocarbon chains are introduced, phase separation occurs.  $T_c$  plotted against concentrations of *i*-VA and *i*-BA added are presented in Fig. 1. As can be seen from the picture, the concentration ranges where phase separation occurs are very narrow, the longer the acid hydrocarbon radical the lower its concentration being necessary to cause polymer precipitation on heating. It is interesting to note that, according to our data [18], in the presence of *i*- $\text{C}_5\text{H}_{11}\text{OH}$  and *i*- $\text{C}_4\text{H}_9\text{OH}$  which have the same number of carbon atoms as *i*-VA and *i*-BA, phase separation is observed in the same, very narrow, concentration ranges as in the case of corresponding acids, indicating an important role of hydrophobic interactions in these systems.

As it has been mentioned above, PVP forms complexes with many organic compounds, including a number of organic acids such as benzoic, salicylic, aminobenzoic ones, and aromatic compounds, for example, naphthalene, biphenyl, and phenols [23,24] where hydrophobic interactions are also supposed to take place. The fact that stability constants of PVP complexes with phenols and organic acids are much greater than those in the case of unsubstituted aromatic compounds [2,23,24] and increase with increasing acidity of OH groups in phenol derivatives indicates the contribution of hydrogen bonds between these groups and C=O groups of the polymer. Apparently, these two types of interactions take place also between carboxylic acids studied and PVP, violating the polymer-hydrate complex and resulting in phase separation on heating.

### 3.2. TCA

Even stronger effect on the behavior of PVP aqueous solutions is observed if TCA is used as an additive, which, according to nuclear quadrupole resonance data [24], forms complexes with PVP via

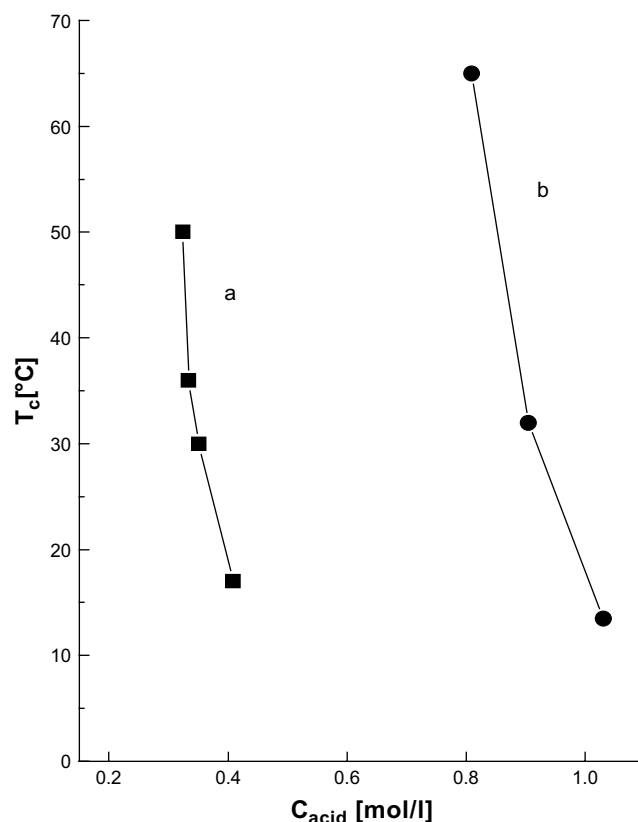
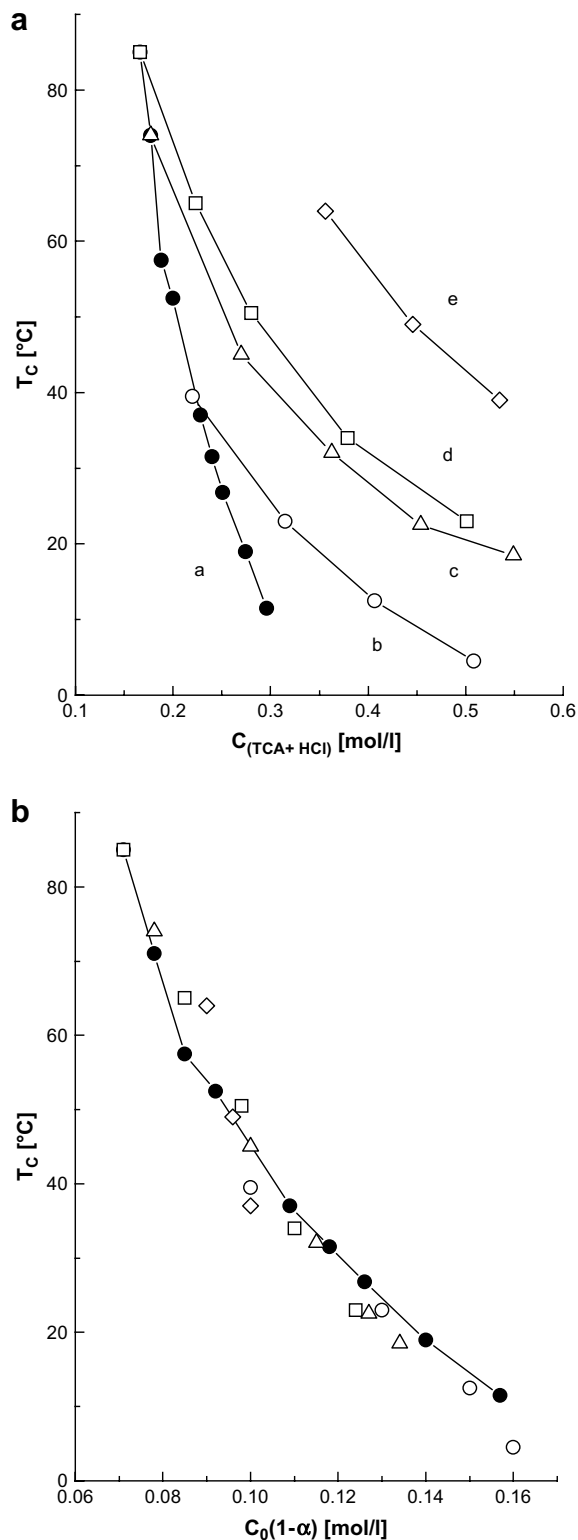


Fig. 1.  $T_c$  of 1% PVP aqueous solutions in the presence of (a) *i*-VA and (b) *i*-BA.



**Fig. 2.** (a)  $T_c$  of 0.83% PVP aqueous solutions plotted against concentrations of (a) TCA and (b–e) sums of TCA and HCl concentrations.  $C_0 = 0.220$  (open circle), 0.177 (open triangle), 0.166 (open square), 0.132 mol/l (open diamond). (b) Data from a are replotted on the coordinates  $T_c$  vs.  $C_0(1-\alpha)$ . The symbols are the same as in a.

hydrogen bonding. In Fig. 2a (curve a)  $T_c$  of 0.8% PVP solutions is plotted against the TCA concentrations ( $C$ ). It is seen that in the TCA concentration range 0.17–0.30 mol/l,  $T_c$  drops from 80 to 10 °C. Whether the TCA concentration is increased by gradual addition of it or it is decreased back by addition of the polymer solution, in both

cases experimental points lie on the same curve which evidences the reversible coordination between TCA and VP units similarly to PVP complexes with many other organic compounds mentioned above [2,23,24]. It is obvious that only a small part of TCA added takes part in this interaction. Apparently, hydrogen bonding, being weak as it is, in the case of PVP–TCA interaction, plays a greater role in comparison with that between PVP and hydrocarbon acids.

In Fig. 3, the plot of  $T_c$  versus TCA/PVP molar ratio at the constant TCA concentration is presented. It is seen that in the region of high PVP concentrations, a much sharper dependence is observed than in the field of lower concentrations which indicates that in this system, there exist some minimal ratios where phase separation takes place.

### 3.3. TCA and HCl

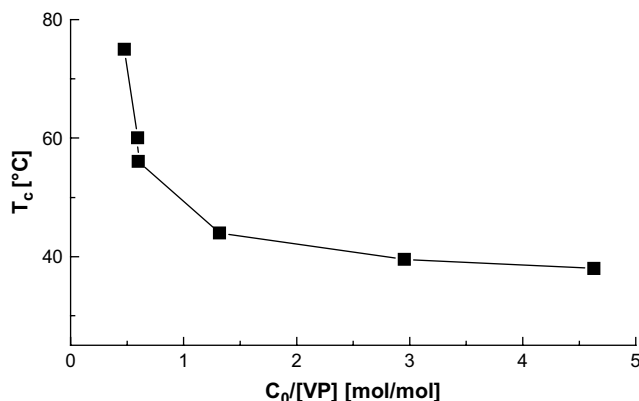
It is known that the addition of strong mineral acids to PVCL solutions causes a slight increase in  $T_c$  [2,4,8]. Quantitative data on the  $H_2SO_4$  effect are presented in Kirsh works [4,8]. This phenomenon was explained by protonization of the oxygen atom in the C=O group of the polymer that increases the PVCL– $H_2O$  complex stability.

As for PVP, HCl addition to the polymer solutions does not change their behavior. However, HCl addition to PVP solutions containing TCA causes even more drastic decrease in  $T_c$  than it does with increasing TCA concentration only. In Fig. 2a (curves b–e)  $T_c$  of PVP solutions are plotted against the sum of TCA and HCl concentrations at various initial TCA concentrations ( $C_0$ ). At the TCA concentration of 0.17 mol/l,  $T_c = 75$  °C, but if twice as much HCl is added,  $T_c$  drops to 20 °C.

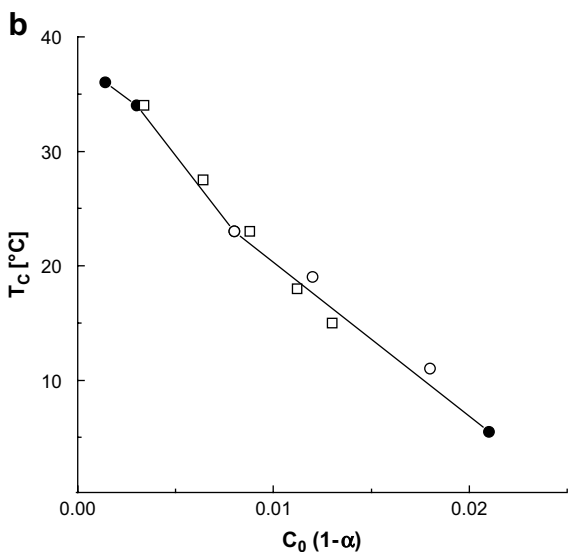
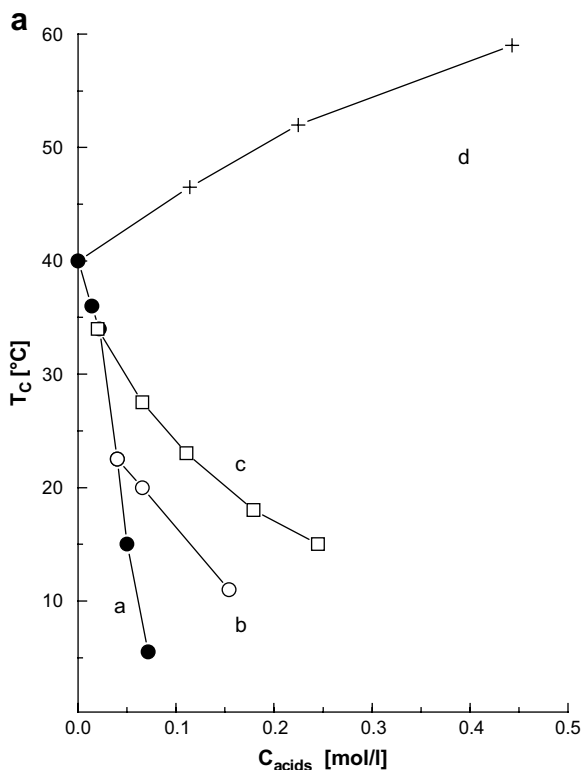
Moreover, PVCL solutions exhibit the similar behavior. TCA addition to PVCL solutions is known to decrease  $T_c$  [8]. According to our observations, HCl addition to this mixture results in a further decrease in  $T_c$  (Fig. 4a, curves a–c), though HCl addition to PVCL solutions in the absence of TCA slightly increases  $T_c$  (Fig. 4a, curve d).

From the data obtained, it is obvious that  $T_c$  depends on the concentration of monomer units bound with TCA. However, TCA is a rather strong acid ( $K_a = 0.13$  mol/l at 25 °C) [28], and it is known that ionized carboxyl groups interact weakly with PVP. For example, complex formation between PVP and aromatic compounds, containing COOH groups, depends on pH and does not proceed in alkaline media [23] when the carboxylic group is ionized. As it is already mentioned, the behavior of polyacids and a number of copolymers, containing acidic groups, for example, the VCL–MAA copolymer [14,15], depends on pH. The presence of  $COO^-$  groups in the polymer resulted in their repulsion from each other, but at low pH they were not dissociated, and phase separation occurred.

It is naturally to suggest that the decrease in  $T_c$  observed is caused by the formation of hydrogen bonds between PVP monomer



**Fig. 3.** The dependence of  $T_c$  on the [TCA]/[VP] molar ratio for [TCA] = 0.22 mol/l.



**Fig. 4.** (a) The effect of addition of various acids on  $T_c$  of 0.3% PVCL aqueous solutions: (a) TCA; (b, c) TCA + HCl; (d) HCl.  $C_0 = 0.040$  (open circle),  $0.020$  (open square). (b) Data from a are replotted on the coordinates  $T_c$  vs.  $C_0(1 - \alpha)$ . The symbols are the same as in a.

units and non-ionized TCA molecules. To check this supposition, it is interesting to elucidate the dependence between  $T_c$  and the concentration of non-ionized TCA in the PVP–TCA solutions.

TCA dissociation degree  $\alpha$  can be determined from the known equation:

$$K_a = \frac{[TCA^-][H^+]}{[TCA]} = \frac{(C_0\alpha)^2}{C_0(1 - \alpha)} \quad (1)$$

where  $TCA^-$  represents the dissociated form of TCA,  $C_0$  is an initial TCA concentration, and  $K_a$  a dissociation constant of TCA.  $K_a$  and

$\alpha$  values are proved not to change considerably with temperature (see Appendix, (a)). So,  $K_a = 0.13 \text{ mol/l}$  [28] is used for all calculations.

From Eq. (1), it follows that in the range of TCA concentrations 0.13–0.30 mol/l where PVP phase separation takes place (see Fig. 2a, curve a)  $\alpha$  changes from 0.62 to 0.47. So, in this region, about a half of TCA is present in the solution in the ionized form.

At the presence of HCl which can be considered entirely dissociated, the content of  $H^+$  in the system increases up to the value of  $C_0\alpha + C_1 = C_0(\gamma + \alpha)$  where  $C_1$  is the HCl concentration, and  $\gamma = C_1/C_0$ . In this case

$$K_a = \frac{C_0\alpha(\gamma + \alpha)}{1 - \alpha} \quad (2)$$

According to Eq. (2), in the region of TCA and HCl concentrations used in the experiment,  $\alpha$  decreases drastically with increasing  $\gamma$  (see Appendix, (b)). So, TCA dissociation is strongly suppressed on HCl addition.

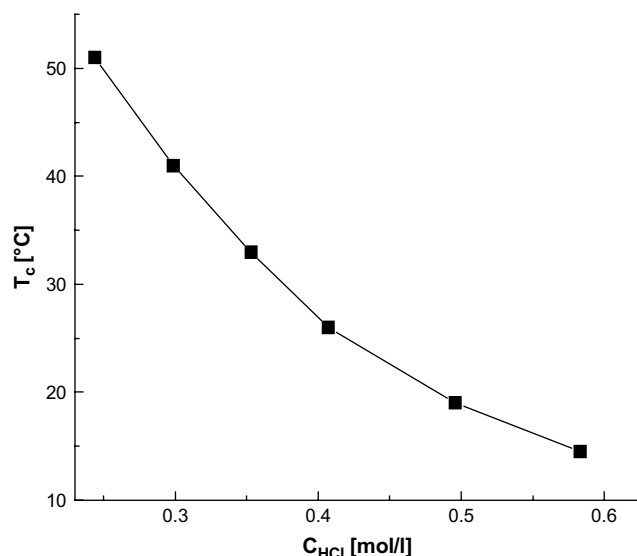
$T_c$  vs.  $(C_0 + C_1)$  plot presented in Fig. 2a for PVP has been replotted on the coordinates  $T_c$  vs. the concentration of non-ionized form of TCA  $C_0(1 - \alpha)$  (Fig. 2b), using  $\alpha$  values obtained from Eq. (2). It is seen that all the points lie on the same curve, including those that relate to the case of HCl absence. The same phenomenon is observed for PVCL solutions (see Fig. 4a and b).

Thus, the anticipation that  $T_c$  of PVP aqueous solutions in the presence of TCA depends on the concentration of the non-dissociated form of the latter is confirmed. The same turned out to be true for PVCL solutions.

This idea is also corroborated by the fact that HCl addition to the PVP–*i*-BA system ( $[HCl]/[i-BA] = 0.5-2$ ) does not result in  $T_c$  change.  $K_a$  of *i*-BA is four orders of magnitude lower than that of TCA. So, it is practically non-dissociated in water, and an increase in the solution acidity cannot affect the concentration of its non-ionized form.

### 3.4. Sodium trichloroacetate

Contrary to TCA, sodium trichloroacetate (TCA-Na) addition does not lead to the PVP solutions thermosensitivity, but if HCl is also added, phase separation is observed. The effect of HCl addition on the  $T_c$  of 0.8% PVP aqueous solution in the presence of TCA-Na (0.2 M) is shown in Fig. 5. It is seen that phase separation takes



**Fig. 5.** The effect of HCl concentration on  $T_c$  of 0.83% PVP aqueous solutions in the presence of TCA-Na (0.22 mol/l).

**Table 1**  
The analysis of the TCA content in the dense PVP–TCA interaction product.

Run	Composition of initial solution			$T_c$ (°C)	Interaction product	
	[TCA] (mmol/l)	[VP] <sup>a</sup> (mmol/l)	[HCl] (mmol/l)		[TCA] <sup>b</sup> (mmol/l)	[VP]/[TCA] <sup>c</sup>
1	336	322	0	7	87.8	3.67
2	306	332	0	18	54.1	6.14
3	286	67.9	0	14.5	22.3	3.04
4	269	87.6	0	15	31.6	2.77
5	230	54.7	115	12.5	31.3	1.75
6	268	86.5	142	14.5	55.3	1.56
7	266	86.0	212	14.5	68.2	1.26

<sup>a</sup> The concentration of PVP monomer units.

<sup>b</sup> The concentration of TCA bound with PVP.

<sup>c</sup> The number of PVP monomer units per one TCA molecule.

place in the same concentration range as in the case of TCA–HCl system (Figs. 2a and 5). In the absence of HCl, pH of the TCA–Na solution is about 7. At the HCl concentration of 0.24 mol/l when the acidity of the solution is only a little bit lower (pH = 6.5), phase separation is observed at  $T_c = 51$  °C. If twice as much HCl is added and pH drops to 2,  $T_c$  of the solution is 19 °C. Thus, the system turns out to be thermo- and pH-responsive.

Apparently, TCA<sup>-</sup> anion, being present in the solution due to dissociation of the salt, is protonized in the acidic medium, and non-dissociated TCA formed affects the system in the same way as it is described above.

### 3.5. The analysis of the PVP–TCA interaction product

The composition analysis of the TCA–PVP interaction product has been carried out. The TCA or TCA and HCl solutions were added to the PVP solution so that the amount of acids was enough to cause phase separation at ambient and even at lower temperatures. Polymer precipitated was separated by centrifugation and the content of the TCA in the polymer was determined by titration with NaOH. Cl<sup>-</sup> was not found in the polymer.

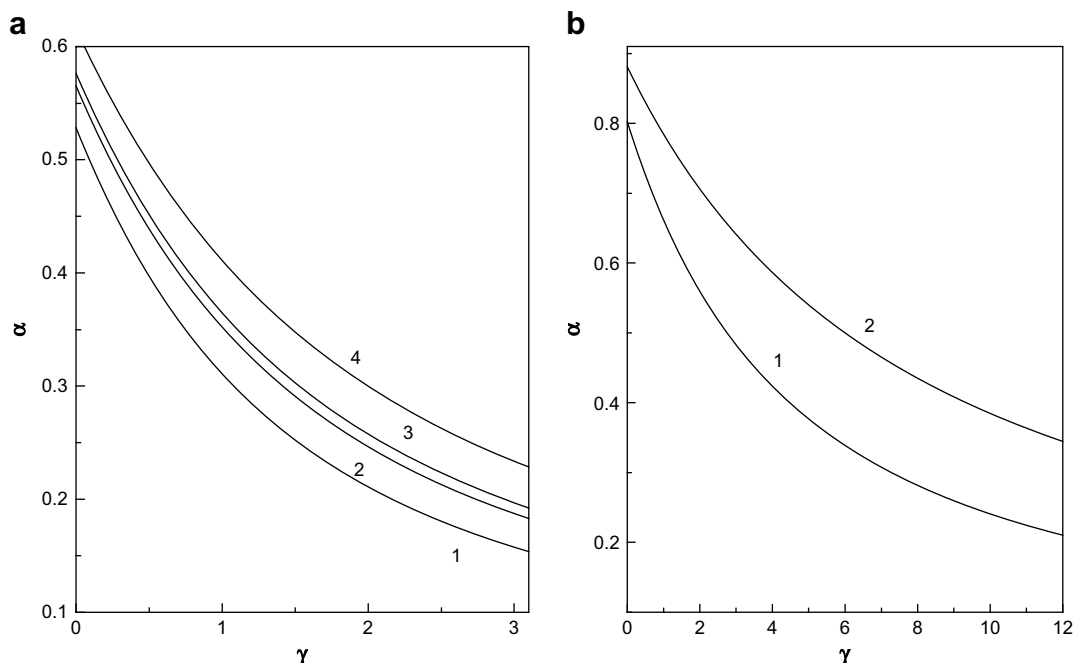
Compositions of initial solutions and products obtained are presented in Table 1. As it is calculated from these data, in the TCA concentration range used which is limited by the condition  $T_c < 20$  °C, the product contains one TCA molecule per 3–6 VP units, depending on the initial compound concentrations. On HCl addition, and at the [HCl]/[TCA] ratio close to 1, the most part of VP units is bound to the TCA molecules. It is obvious that at lower TCA/PVP ratios where  $T_c$  is higher, segments of PVP chains free of TCA are longer. An increase in the TCA content in the precipitate with increasing the HCl concentration in the initial solution confirms the supposition that non-ionized form of TCA takes part in its coordination with PVP.

## 4. Conclusions

It has been shown that though PVP is not a thermosensitive polymer under usual conditions, carboxylic acids addition to PVP aqueous solutions results in phase separation. Reversible interaction between acids and PVP is shown to take place which raises the hydrophobicity of the polymer and decreases its  $T_c$ . The most pronounced effect is observed when TCA is used. HCl addition to the PVP–TCA system results in even more drastic decrease in  $T_c$ . This phenomenon is supposed to be connected with the fact that the non-ionized form of TCA takes part in the complex formation via hydrogen bonds between COOH groups of TCA and C=O groups of PVP. The same is shown to be true for PVCL. This supposition is confirmed by calculations performed. HCl addition to the PVP–TCA–Na system also results in phase separation. Thus, PVP aqueous solutions are proved to become thermo- and pH-sensitive upon addition of TCA or its sodium salt in acidic media.

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**Fig. 6.**  $\alpha$  vs.  $\gamma$  (Eq. (2)) (a) for data of Fig. 2,  $C_0 =$  (1) 0.220, (2) 0.177, (3) 0.166, (4) 0.132 mol/l, and (b) for data of Fig. 4,  $C_0 =$  (1) 0.040, (2) 0.020 mol/l.

## Appendix

- (a)  $K_a$  values for temperatures from 10 to 80 °C were calculated using Eq. (1) from the work by Schüürmans et al. [29] and the Gibbs equation:

$$pK_a = 0.175\Delta G - 1.74 \quad (A1)$$

$$\Delta G = T\Delta S - \Delta E$$

where  $\Delta E = 18.4$  kJ/mol, and  $\Delta G = 15$  kJ/mol for  $T = 298$  K. From these data  $\Delta S = 0.0114$  kJ/mol·grad.  $\Delta E$  and  $\Delta S$  values are considered to be independent of temperature. The  $K_a$  values obtained turned out to be in the range between 0.122 mol/l for 10 °C, and 0.167 mol/l for 80 °C. Since  $K_a$  values do not change much with temperature, and it does not result in considerable changes in  $\alpha$ , for calculations of the latter, the  $K_a$  value equal to 0.13 mol/l for 25 °C [27] was used for all temperatures.

- (b) Values of  $\alpha$  for all experimental points shown in Fig. 2 (curves b–e) for PVP and Fig. 4 (curves b, c) for PVCL related to the cases of various TCA and HCl concentrations, were calculated from Eq. (2), represented graphically in Fig. 6.

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