Polymer Vol. 37 No. 12, pp. 2415–2421, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00 + 0.00

Effect of inorganic salts on the main parameters of the dilute aqueous poly(vinylpyrrolidone) solutions

Ulviya U. Salamova* and Zakir M. O. Rzaev
Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

and Şemsettin Altındal
Physics Department, Faculty of Arts and Sciences, Gazi University, 06500 Teknikokullar, Ankara, Turkey

and Aldar A. Masimov
Physics Department, Baku State University, 370145 Baku, Azerbaijan

(Received 22 May 1995)

The effect of inorganic salts (cosolute) on the main parameters of dilute aqueous poly(vinylpyrrolidone) (PVP) solutions, such as cloud points, phase diagram, θ temperature and viscosity was studied experimentally using various concentrations of salts and said polymer at varying temperatures. It is shown that, thermodynamic incompatibility of aqueous PVP-salts solutions strongly depends on the character of effect of salts (water-structure breakers or water-structure makers). Inclusion of salts into aqueous PVP solution leads to decreasing of the θ temperature and intrinsic viscosity which is caused by effect of the cosolute ions in enhancing the segment–segment interactions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(vinylpyrrolidone); water; inorganic salts)

INTRODUCTION

The interest in the behaviour of interaction in aqueous solutions of synthetic and natural polymers is due to several factors, among which the main factor is that the water–polymer interactions play an important role in biological processes. Such interactions are related both to different conformational changes of macromolecules and their different biofunctional role in the body. The problems of consistency of polymers and inorganic salts in saltivated solutions, such as water medium, are changeable or ambiguously explained questions.

The possibilities of investigation of the effect of inorganic salts on the water–polymer systems become widely spread due to the fact, that inorganic electrolytes in water medium put essential effects on water's physical structure and so on the basic parameters of polymer solutions in wide limits of concentrations.

The poly(vinylpyrrolidone) (PVP) is one of the rate synthetic water soluble polymers employed in biological systems and medicine[1–3]. However, the problem of water solutions in the presence of inorganic salts on electrolytes is not widely investigated. For example, in the papers[4,5] there are given ranges of the θ temperature for aqueous PVP solutions with different molecular masses with concentration in limits 3–10%. The Flory temperature is calculated by the method of extrapolation in the present Na_2SO_4 and is 28°C. The thermodynamic basis of the method for determination of θ temperature for polymer solution was described by Sakellariou[6]. In this work the phase diagram of PVP–water–Na_2CO_3 system was also constructed by the same procedure over wider polymer concentrations. Kinetic studies associated with the interaction between sodium dodecyl sulfate and PVP in aqueous solution were described in the work[7].

In this study some results on the effect of inorganic salts have been discussed over basis parameters of the dilute aqueous PVP solutions, such as cloud points phase diagram, θ temperature and viscosity.

EXPERIMENT

Materials

PVP, supplied by BDH, has nominal molecular weight $M_n = 44\,000$ and intrinsic viscosity $[\eta] = 0.21\,\mathrm{dl\,g^{-1}}$ at 25°C in water. Polymer solutions were prepared in bidistilled and deionized water. The following inorganic salts were used as the electrolytes: MX, where M = Na, K, Li, NH_4; X = F, Cl, Br, CO_3, SO_4, HPO_4, PO_4, HS, ClO_4, SCN and S_2O_3. PVP solution concentrations in water 0.4–1.0 g dl^{-1} and salt concentration 0.2–1.2 mol dl^{-1} were used for the construction of the phase diagrams.

---

*To whom correspondence should be addressed. Present address: Physics Department, Faculty of Arts and Sciences, Gazi University, 06500 Teknikokullar, Ankara, Turkey

Measurements

The θ temperature of PVP in water and aqueous salt solutions were measured by studying the variation of the cloud points of the dilute polymer solutions in the presence of the above indicated electrolytes at 25–85°C temperature regions in a custom-made apparatus using a known method[6]. The intrinsic viscosity of aqueous polymer solutions were measured in the Ubbelohde viscometer.

RESULTS AND DISCUSSION

I. The cloud point and phase diagram of PVP–H_2O–salt systems

First of all, dilute aqueous PVP solutions have been compared with inorganic salts in the regimes of increasing dynamic temperature. Concentrations of PVP in water 0.4–1.0 $\mathrm{g\,dl^{-1}}$ and salt concentration 0.2–1.2 $\mathrm{mol\,dl^{-1}}$ have been used.

Phase cosolutes have not been observed in the aqueous mixture of PVP with $NaNO_3$, KBr, $NaClO_4$, NaSCN, NaHS, $NaHSO_4$, $Na_2S_2O_3$, NaCl and NaF by the increasing of temperature (25–85°C). As a result of the investigation it has been found out that aqueous solutions with the following salts are thermodynamically incompatible: Na_2SO_4, Na_2CO_3, Na_3PO_4, Na_2HPO_4, NaH_2PO_4, K_3PO_4, K_2HPO_4, KH_2PO_4, K_2CO_3, KF, Li_2SO_4 and $(NH_4)_2HPO_4$. Under normal atmosphere pressure by the increasing of temperature aqueous mixture of these salts with aqueous of PVP solutions become consolute and layered into two phases up to the boiling temperature of water. For the aqueous PVP–salt mixtures experiments have been done in five fixed volume fractions of polymer at the different concentrations of salts. The obtained results show that values of the temperature at which the phase consolutes are different from each other, are dependent on the type of the salts. *Table 1* shows the temperature of phase consolute t_p which is thought to be valid for all investigated systems at the fixed volume fraction of PVP ($\phi_2 = 0.7 \times 10^{-2}$). It can be seen that with increasing salt concentration, the values of θ temperature at which the consolute begin to take place decrease. The similar results have been obtained for five fixed volume fractions of polymer in the investigation system. *Figures 1* and *2* show phase diagrams of aqueous PVP–K_3PO_4, PVP–KH_2PO_4, and PVP–Li_2SO_4, PVP–Na_2CO_3, respectively.

As the curves demonstrate, the essential changes in the system occur with limits up to 1.5×10^{-3} of volume fraction of polymer, moreover, the character of change of all curves is almost the same, i.e. mechanism of consolute does not depend on the concentration of the used salts. All of the investigated aqueous PVP–salt solutions show a similar character of change of phase diagrams. The plots show that the increasing of the concentration of polymer cannot lead to an unlimited decrease in temperature of phase consolutes, i.e., the concentration has a limit.

The comparison of the determined values of the temperature of phase consolute t_p in aqueous PVP–salt solutions for Na (Na_2CO_3, Na_2PO_4 and $NaHPO_4$) and K (K_2CO_3, K_3PO_4, $KHPO_4$ and H_2PO_4) salts, shows that Na salts have lower values of the temperature of consolute and difference Δt_p between values t_p the investigated salt is the following: $\Delta t_p = t_p(KX) - t_p(NaX)$, where X is anions of salts, the changes on

Table 1 The temperature of phase consolute (t_p) which are thought to be valid for all studied systems at the fixed volume fraction of polymer ($\phi_2 = 0.7 \times 10^{-2}$)

Salts	C ($\mathrm{mol\,l^{-1}}$)	t_p (°C)	Salts	C ($\mathrm{mol\,l^{-1}}$)	t_p (°C)
KH_2PO_4	0.80	80	KF	0.90	75
	0.90	70		1.00	67
	1.00	50		1.00	59
	1.10	50		1.20	52
K_3PO_4	0.30	73	K_2HPO_4	0.40	63
	0.35	57		0.45	49
	0.40	47		0.50	40
K_2CO_3	0.45	72	Na_3PO_4	0.25	73
	0.50	64		0.30	53
	0.55	55		0.35	35
	0.60	44			
Na_2CO_3	0.40	82	Na_2HPO_4	0.30	68
	0.45	70		0.35	52
	0.50	58		0.40	42
	0.60	38			
Li_2SO_4	0.70	72	NaH_2PO_4	0.80	85
	0.80	60		1.00	66
	0.90	44		1.20	43
	1.00	34			
Na_2SO_4	0.35	89	$(NH_4)_2HPO_4$	0.80	85
	0.40	75		0.65	52
	0.45	65		0.70	42
	0.50	53			

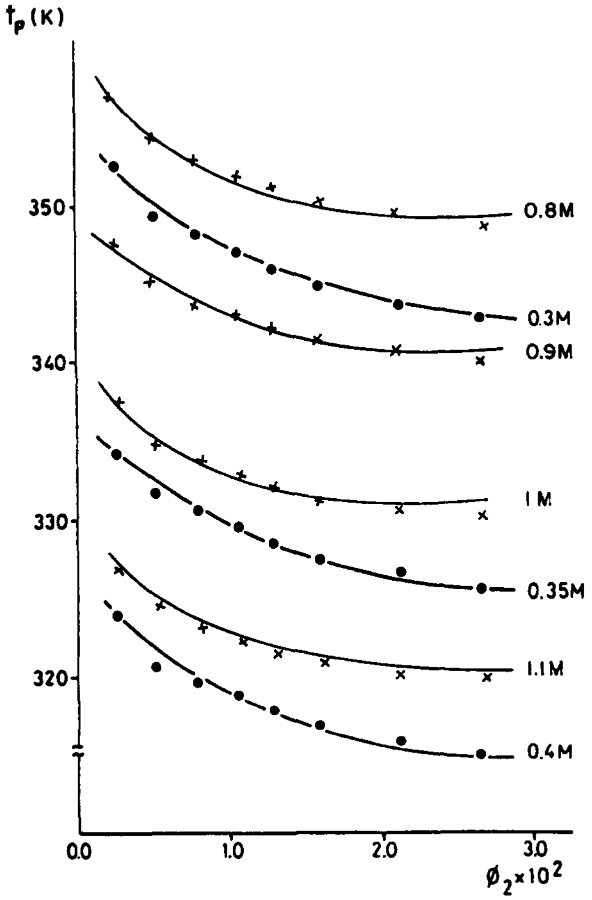

Figure 1 The phase diagrams of aqueous PVP–K_3PO_4 and PVP–KH_2PO_4 solutions. (●) Aqueous PVP–K_3PO_4, (×) aqueous PVP–KH_2PO_4

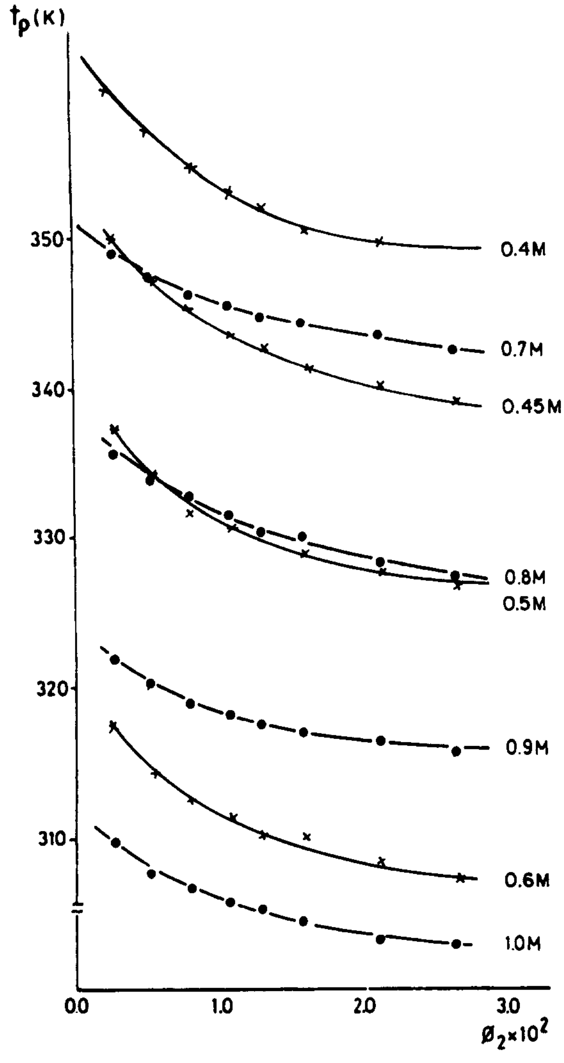

Figure 2 The phase diagrams of aqueous PVP–Li_2SO_4 and PVP–Na_2CO_3 solutions. (●) Aqueous PVP–Li_2SO_4, (×) aqueous PVP–Na_2CO_3

Table 2 The values of the temperature of consolute (t_p) and difference (Δt_p) for any PVP–salt system

Salts	*C* (mol l^{-1})	t_{p1} (°C)	Salts	*C* (mol l^{-1})	t_{p2} (°C)	$(\Delta t_p) = t_{p2} - t_{p1}$ (°C)
K_3PO_4	(0.35)	57	Na_3PO_4	(0.35)	35	22
K_2HPO_4	(0.40)	63	Na_2HPO_4	(0.40)	42	21
KH_2PO_4	(1.00)	60	NaH_2PO_4	(1.00)	66	−6
K_2CO_3	(0.50)	64	Na_2CO_3	(0.50)	58	6

the nature of anions. The results of Δt_p are presented in *Table 2*.

It is commonly known, that ions of Na and K have a similar structure of exterior electronic shells and equal charge with a difference in radius (Na = 0.98 Å, K = 1.33 Å)[8]. Then, since the smaller the radius of anion and accordingly larger the number of hydration (Na = 7–9, K = 4–6)[9], there is higher probability of interactions of ions with the water molecules. Such behaviour of the above mentioned ions in the investigated systems can also be explained by the essential difference in the energy of interaction of cations Na and K with the water molecules ($-E_{Na^+} = 101.2\,kJ\,mol^{-1}$; $-E_{K^+} = 75.7\,kJ\,mol^{-1}$)[9].

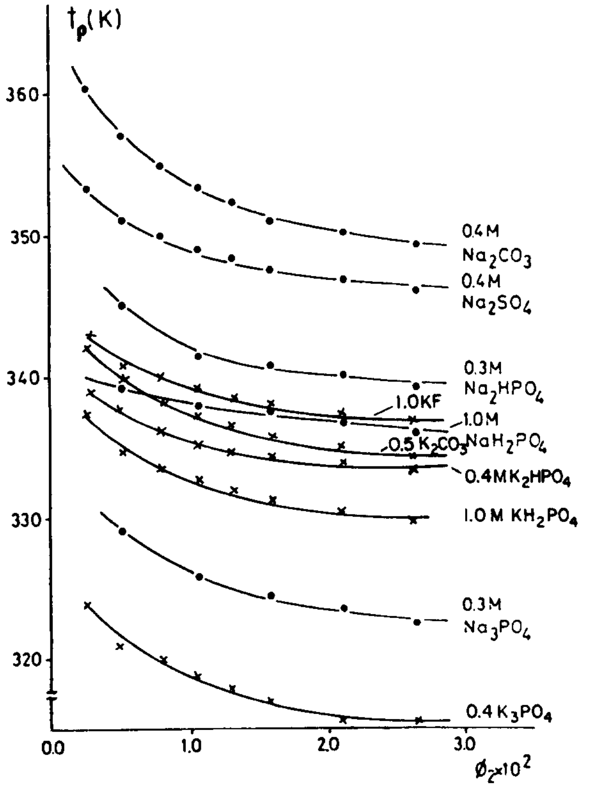

Figure 3 The dependence of the temperature of consolute on the volume fraction of PVP for different Na and K anions. (×) Aqueous PVP–salts of K, (●) aqueous PVP–salts of Na

It is also known that, for the same structure of electronic shells and equal charge, polarization and diffusion actions of an ion increases following decreasing of its radius. These statements confirm the experimental results obtained by us for Na and K, that salts of Na correspond to lower temperature of phase consolutions with the exception of the NaH_2PO_4 salts. The latter fact we explain by the acid character of salts of NaH_2PO_4 and KH_2PO_4, especially for the salt of KH_2PO_4.

The comparison of the values of the consolute temperature for aqueous PVP–Na_2HPO_4, PVP–K_2HPO_4 and PVP–$(NH_4)_2HPO_4$ systems correspond to the theoretical aspects mentioned above. For PVP–$(NH_4)_2HPO_4$ systems the value of the temperature of consolute is the highest in comparison with PVP–Na_2HPO_4 and PVP–K_2HPO_4, that are explained by higher values for the radius of the NH_4^+ ion (1.43 Å). Similar conditions can be made from the values of the consolute temperature for aqueous PVP–Na_2SO_4 and PVP–Li_2SO_4 systems. Since the Li ion has the radius 0.78 Å, the consolute in the PVP–Li_2SO_4 system emerges at a temperature lower than Na_2SO_4.

It is known[10], that the effect of inorganic salt on the structure of water essentially depends on the nature of the anions. To compute the role of anions in the structure changes of aqueous PVP–salts solutions, we measured the dependence of the temperature of consolute on the volume fraction of PVP (*Figure 3*) at the below Na salt concentrations: Na_2SO_4 (0.4 mol l^{-1}), Na_2CO_3 (0.4 mol l^{-1}), Na_2HPO_4 (0.3 mol l^{-1}), NaH_2PO_4 (1.0 mol l^{-1}) and Na_3PO_4 (0.3 mol l^{-1}); and K salts: KF (1.0 mol l^{-1}), K_2CO_3 (0.5 mol l^{-1}), K_2HPO_4 (0.4 mol l^{-1}), KH_2PO_4 (1.0 mol l^{-1}) and K_3PO_4 (0.4 mol l^{-1}).

From this graph it follows that:

$$PO_4^{3-} > HPO_4^{2-} > SO_4^{2-} > CO_3^{2-} > H_2PO_4^{-} \text{ (for Na)}$$

$$PO_4^{3-} > HPO_4^{2-} > CO_3^{2-} > H_2PO_4^{-} > F^{-} \text{ (for K)}$$

Taking into consideration that structure changes of water essentially depend on the anions, one may conclude, that for the PVP–salts systems, where the anion of the salts is a water-structure breaker (PO_4^{3-} and HPO_4^{2-}) the phase consolute is observed at low temperatures, but if water-structure makers ($H_2PO_4^{-}$ and F^{-}) are present in the system, then thermodynamic incompatibility is reached at the higher temperature. Soluability of PVP in water is due to the presence of polar fragments in the lotaval chain of the polymer, i.e. the carbon group. Being in water PVP obtains strong hydrogen connections with the molecules of the water, i.e. =C=O...H–O–H or ⩾N...H–O–H.

It is known that for the water system with LCST, increasing temperature or inclusion of inorganic salts yields the collapse (breaker) of hydrogen connections[11,12]. If in aqueous PVP solution one puts a salt of strong water-structure breakers (basically, because of anions), then the breakdown of hydrogen connections leads the structure of the solution to one where thermodynamic incompatibility is reached with a small increase of temperature. Indeed, phase consolute of aqueous PVP solutions with salts (Na_3PO_4, Na_2HPO_4) can be observed in the limit 25–35°C.

But if in the aqueous PVP–salts systems there exists water-structure maker anions, the effects of salts in collapsing hydrogen connections (because of cations) will be negligible. The thermodynamic incompatibility of PVP with the salt in the water can be reached only by increasing temperature, that leads to the breakdown of strong hydrogen connections between the carbonyl group of the polymer and the molecules of water. All the mentioned are observed in the system PVP–KF–water and PVP–KH_2PO_4–water, where the phase consolute starts at 60–70°C.

Thus, thermodynamic incompatibility of aqueous PVP–salts solutions strongly depends on the character the salts (water-structure breakers or water-structure makers) on the structure or the thermodynamic state of water.

II. θ temperature of PVP in aqueous salt solutions

The θ temperature of polymers is a very important parameter for both free and attached chains. At the θ point, the chains assume their unperturbed dimensions and the intermolecular interactions vanish[13,14]. At the same time segmental interactions become attractive[13]. Determination of the θ temperature is usually implemented by light scattering and osmotic pressure measurements. Both measurements are based on the fact that the second virial coefficient vanishes at the θ point[14]. In this paper we shall report on the θ point of PVP aqueous salt solutions.

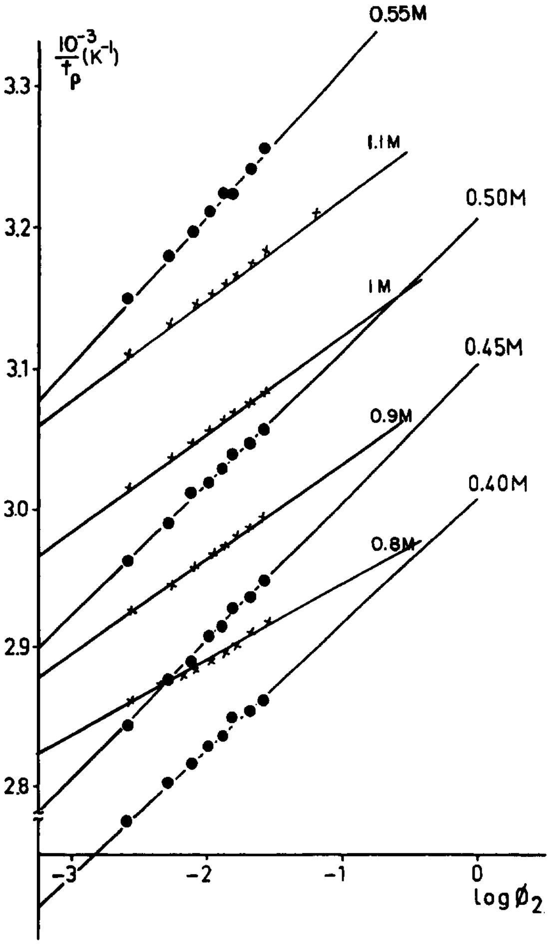

Figure 4 Sakellariou plots of aqueous PVP–salts solutions: PVP–KH_2PO_4 and PVP–Na_2CO_3. (×) Aqueous PVP–KH_2PO_4, (●) aqueous PVP–Na_2CO_3

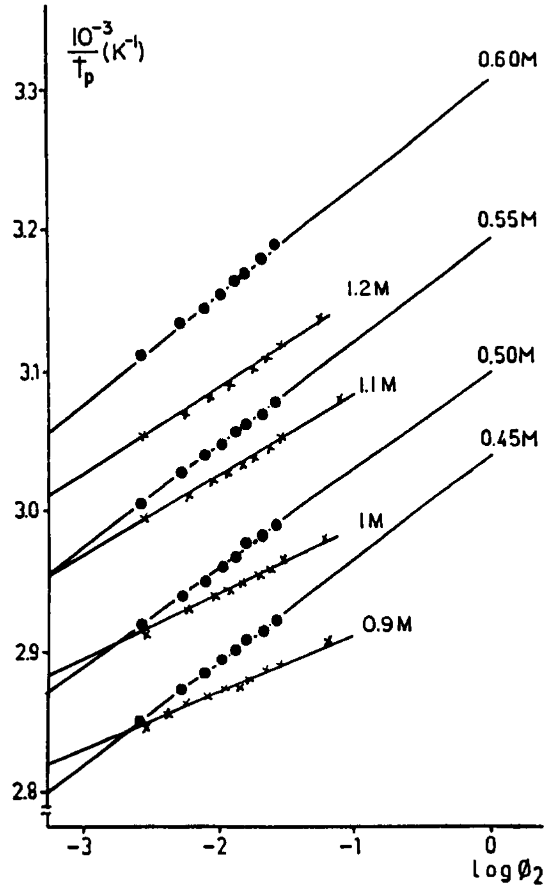

Figure 5 Sakellariou plots of aqueous PVP–salts solutions. (×) Aqueous PVP–KF, (●) aqueous PVP–K_2CO_3

Table 3 The θ temperature values for PVP in all studied aqueous salt solutions

Salts	C (mol l^{-1})	R	θ (°C)	Salts	C (mol l^{-1})	R	θ (°C)
KH_2PO_4	0.80	0.999	64	KF	0.90	0.992	65
	0.90	0.998	55		1.00	0.998	55
	1.00	0.999	46		1.11	0.991	45
	1.10	0.998	35		1.20	0.995	38
K_3PO_4	0.30	0.779	61	K_2HPO_4	0.40	0.998	55
	0.35	0.991	40		0.45	0.999	40
	0.40	0.992	29		0.50	0.976	33
K_2CO_3	0.45	0.999	56	Na_3PO_4	0.25	0.993	57
	0.50	0.998	50		0.30	0.997	36
	0.55	0.998	40		0.35	0.995	16
	0.60	0.998	29				
Na_2CO_3	0.40	0.995	59	Na_2HPO_4	0.30	0.983	54
	0.45	0.979	49		0.35	0.985	35
	0.50	0.997	39		0.40	0.991	22
	0.60	0.975	19				
Li_2SO_4	0.70	0.993	59	NaH_2PO_4	0.80	0.983	77
	0.80	0.976	42		1.00	0.985	57
	0.90	0.998	33		1.20	0.991	35
	1.00	0.995	19				
Na_2SO_4	0.35	0.983	73	$(NH_4)_2HPO_4$	0.60	0.998	49
	0.40	0.999	62		0.65	0.995	38
	0.45	0.965	48		0.70	0.996	30
	0.50	0.980	36				

For the PVP aqueous salt solutions PVP–KH_2PO_4, PVP–Na_2CO_3, PVP–KF and PVP–K_2CO_3 Sakellariou plots are demonstrated in *Figures 4* and *5*, where the θ temperature was found using extrapolation. *Table 3* shows the values of θ temperature for PVP in all investigated aqueous salt solutions.

The dependence of Flory temperature for aqueous PVP–salt solution on the concentration of the used salts is shown in *Figure 6*; for extrapolation of this dependence and use of the least squares method gives the θ temperature for PVP in water as $\theta = 149 \pm 7$°C, which corresponds to the literature data ($\theta = 140 \pm 7$°C)[4].

As the experimental results show, the temperature of PVP in water is about 149°C, but with different inorganic salt changes the temperature value is dependent on the type of salt (*Table 3*). This phenomena can be explained by the fact that the presence of an inorganic salt in water breaks down the hydrogen connections of the water and hence yields the decreasing value of temperature, under which the behaviour of PVP in such a solution becomes ideal. The salts of the type Na_2CO_3, Na_3PO_4, Na_2HPO_4, K_3PO_4, KH_2PO_4, K_2CO_3 and $(NH_4)_2HPO_4$(*) decrease the Flory temperature for PVP in water to the minimal values (16–30°C). But in salts of the type NaH_2PO_4, KH_2PO_4, Na_2SO_4 and KF(**) this decrease is not very great (45–77°C). The mentioned negligible effect of salts of the type (**) on the Flory temperature aqueous PVP solutions we explain by the water structure-maker properties of anions, the presence of which in water leads to the strengthening of hydrogen connections. But in the case of salts (**) of the ions of Na and K, which yield a small destruction of the water structure, the inclusion of the salts into aqueous PVP solution yields small changes of Flory temperature.

Thus, on the basis of this one can assert that inclusion of inorganic salts into aqueous PVP solution leads to a decrease of the Flory temperature of the system. Moreover, the effect of the salts strongly depends on the water-structure breakers or water-structure makers effects of anions of the salts on the structure or thermodynamic state of water.

III. Viscosity of PVP–salt–water systems

It is known that the viscosity of polymer solutions is determined not only by volume fraction of polymer but also by thermodynamic compatibility of solvent to polymer[15]. As it has been shown presence of inorganic salts on aqueous dilute PVP solution causes the breakdown of strong connections between the carbonyl group of the polymer and the molecules of water occurs, in the result of which the 'first' structure of water in solutions changes, i.e. the thermodynamic incompatibility between water and PVP changes.

In order to estimate the qualitative character of the structure changes in the investigated PVP–salt systems, we have carried out measurements. The results of intrinsic viscosity of aqueous PVP and PVP–salt solutions are given in the *Table 4*. The data of *Table 4* indicate that the presence of different inorganic salts in water changes the value of intrinsic viscosity of PVP. This phenomenon can be explained by the fact that the presence of inorganic salts in aqueous PVP solutions changes the 'first' physics structure solutions in the direction of untwining of the macromolecules in the globules. That is why movement of molecules of the polymer in solutions becomes eased, decreasing the viscosity of the PVP–salt system. On the other hand, the observed reductions of $[\eta]$ in the presence of the cosolutes represent the effect of the cosolute ions in enhancing the segment–segment interactions. This should parallel their effect on the θ temperature, where the cosolute increases the tendency of the polymer molecule to go into the more concentrated phase of the precipitate associated with more segment–segment interactions.

As it is known the values of the Huggins constant K_H depend on the nature of the solvent and on the solvent–polymer interactions. Values of the Huggins constant for the aqueous PVP and PVP–salt solutions are shown in *Table 5*. The data of *Table 5* indicate that the values of the Huggins constant for all investigated systems are higher than 1, with the exception of the PVP–Na_2SO_4 and PVP–K_3PO_4 aqueous solutions. Similar results have been obtained in other works[13,14], where aqueous salts solutions of PEO have been investigated. The authors explained this by the presence of salts in the polymer

Table 4 The results of intrinsic viscosity of aqueous PVP and PVP–salt solutions

Salts	C (mol l^{-1})	$[\eta]_H$ (dl g^{-1})	$[\eta]_K$ (dl g^{-1})	$[\eta]_{M-R}$ (dl g^{-1})
PVP–(Pure)	0.00	0.2135	0.217	0.2135
Na_2SO_4	0.50	0.169	0.170	0.170
Li_2SO_4	0.90	0.170	0.171	0.171
Na_2CO_3	0.50	0.162	0.163	0.162
K_2CO_3	0.55	0.170	0.171	0.170
KF	1.20	0.167	0.166	0.167
K_3PO_4	0.35	0.176	0.175	0.175
KH_2PO_4	1.10	0.160	0.162	0.161
K_2HPO_4	0.45	0.161	0.162	0.162
Na_3PO_4	0.30	0.162	0.163	0.162
NaH_1PO_4	1.20	0.155	0.154	0.153
Na_2HPO_4	0.35	0.145	0.144	0.145
$(NH_4)_2HPO_4$	0.65	0.150	0.151	0.151

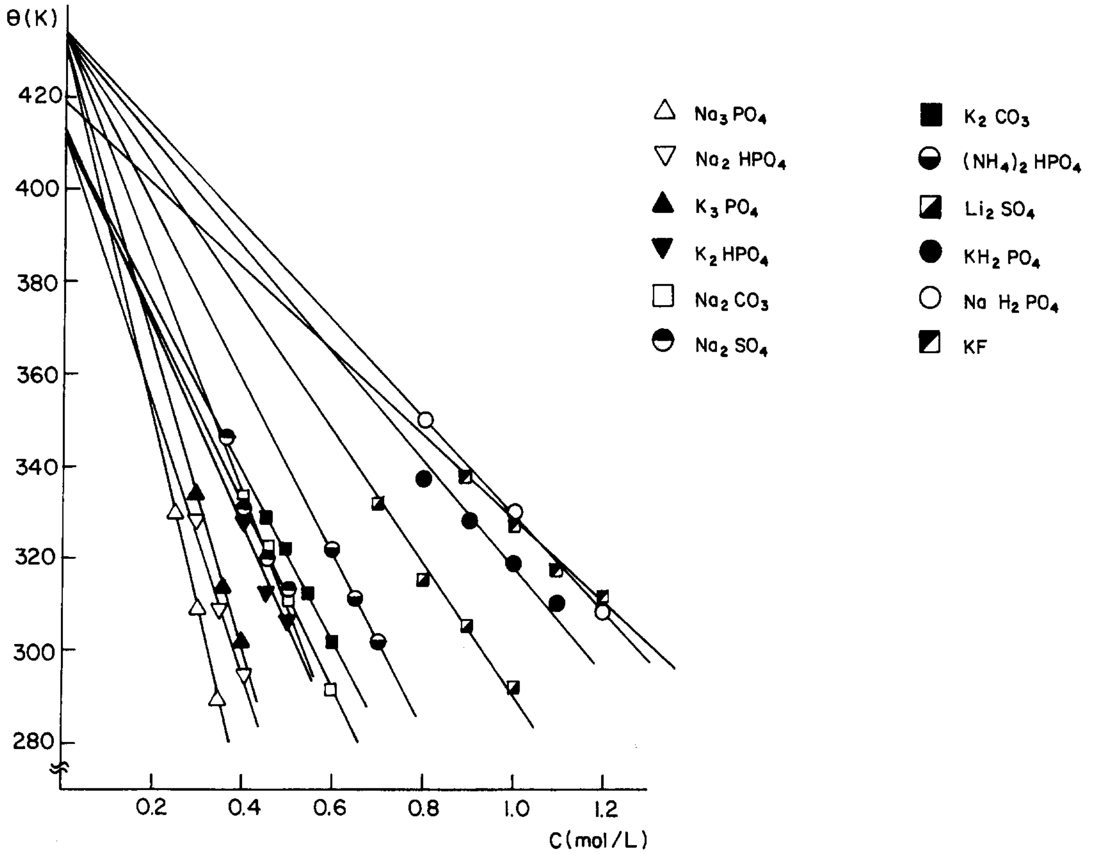

Figure 6 The dependence of Flory temperature for aqueous PVP–salt solution on the concentration of the salts used

Table 5 The values of the Huggins constant for the aqueous PVP and PVP–salt solutions

Salts	*C* (mol l^{-1})	$K_{H,25°C}$	$K_{K,25°C}$	K_H–$K_{K,25°C}$
PVP	0.0	1.317	0.536	0.781
K_3PO_4	0.4	0.802	0.194	0.608
K_2HPO_4	0.5	1.031	0.425	0.606
KH_2PO_4	1.1	0.019	0.412	0.607
Na_3PO_4	0.3	1.163	0.557	0.606
Na_2HPO_4	0.35	1.286	0.681	0.605
Na_2SO_4	0.5	0.854	0.245	0.609
Na_2CO_3	0.5	1.074	0.471	0.603

solutions. But the difference of values K_H–K_K at 25°C for investigation systems lays in the framework of the theory of the viscosity of polymer solutions (*Table 5*).

As it has been shown, including inorganic salts in the PVP–salts system changes the structure of this solution. These changes seem to be caused by interaction between ions of salts and the hydrogen group of PVP, which occur because of direct dipole–dipole interaction between ions of salts and polar groups in chains of PVP, as we suggest.

Thus, if in the aqueous PVP solutions the Huggins constant evaluates interaction only between water and PVP (H_2O...PVP), then in PVP–salt–water systems this constant evaluates three interactions (H_2O... PVP...salt). It is seen from *Table 5* the constant Huggins has the maximum value ($K_H = 1.317$) in the aqueous PVP solutions. The relatively higher value of K_H in aqueous PVP solutions can be explained by the strong interaction between the carbonyl group of the polymer and the molecules of water leading to the hydration of the polar group of PVP by molecules of water. The presence of an inorganic salt in aqueous PVP solutions changes the structure of water by breaking down hydrogen connections between PVP and the molecules of water while changing the hydration balance established around the carbonyl group. In this case ions of salts rivalling with molecules of water interact with unconnected fractions of the polar group in the polymer chain. Thus, including salts in aqueous PVP solutions between PVP and molecules of water, that is the Huggins constant evaluating interaction between PVP and aqueous salt solutions must be smaller than the same constant in the PVP aqueous solution. Then, $\Delta K_H = (K_{H1} - K_{H2})$, where K_{H1} is the Huggins constant of PVP–salt–water system, K_{H2} is the Huggins constant of PVP–water system and ΔK_H is the value which characterizes the qualitative impact of salt on the summary interaction in the PVP–salt–water system, i.e. this parameter estimated the changes of interaction between PVP and the molecules of water, under the effect of salts. The value of ΔK_H is negative, showing that the

Table 6 The values of $\Delta K^*_{H,25}$ for PVP–salt solutions

Salts	*C* (mol l^{-1})	$-\Delta K^*_{H,25}$	$\Delta K^*_{H,25}$ (%)
K_3PO_4	0.4	0.5848	42.16
Na_2SO_4	0.5	0.4628	35.14
KH_2PO_4	1.1	0.2978	22.61
K_2HPO_4	0.5	0.2858	21.7
Na_2CO_3	0.5	0.2428	18.43
Na_3PO_4	0.3	0.1538	11.67
Na_2HPO_4	0.35	0.0308	2.33

decreasing hydrogen connections between PVP and the molecules of water is caused by inorganic salts. The values of ΔK_H are presented in *Table 6*. It can be seen that Na salts have lower values of $\Delta K_{H,25}$ compared with K salts. Therefore, the aqueous PVP–Na–salt solutions have lower values of the temperature of consolute, i.e., they are thermodynamically more incompatible systems.

REFERENCES

1 Zaslavsky, B. Y. and Masimov, A. A. *Topics Current Chem.* 1987, **135**, 275

2 Yamokoshi, Y. N., Yagami, T., Fukuhava, K., Syesoshi, S. and Miyata, N. *J. Chem. Soc. Comm.* 1994, **4**, 517

3 Yomoto, M., Ool, M. and Kawagushi, M. *Sherigeonology* 1994, 41, **53**, 747

4 Molyneux, P. in 'Water Soluble Synthetic Polymers: Properties and Behaviour', Vol. 1, CRC Press, Florida, 1983

5 Meza, R. and Gargalo, L. *Eur. Polym. J.* 1977, **13**, 235

6 Sakellariou, P. *J. Polymer Commun.* 1992, **33**, 1339

7 Wan, A., Wan, M. Z., Wan-Yunus, D., Denver, M., Hall, G. and Wyn Jones, E. *J. Chem. Soc. Faraday Trans.* 1993, **89**, 2737

8 Nekrasov, B. V. 'The Course General Chemistry', Moscow, 1954, p. 714 (in Russian)

9 Krestov, G. A., Novoselov, N. P. and Pereligin, I. S. 'The Ionic Solvatization', Moscow, 1987, p. 53 (in Russian)

10 Verall, R. E. in 'Water: A Comprehensive Treatise' (Ed. F. Franks), Vol. 3, Plenum, 1975

11 Melander, W. and Horvath, C. *Arch. Biochem. Biophys.* 1977, **183**, 200

12 Ueberreiter, K. *Colloid Polymer Sci.* 1982, **260**, 37

13 Flory, P. J. 'Principles of Polymer Chemistry', Cornell Univ. Press, Ithaca, 1953

14 Napper, D. H. 'Polymeric Stabilisation of Colloidal Dispersions' Academic Press Inc., London, 1983

15 Bohdanecky, M. and Kovar, J. 'Viscosity of Polymer Solutions' Polymer Science Library, England, 1982

16 Boucher, E. A. and Hines, P. M. *J. Polym. Sci.* 1978, **16A(2)**, 501