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Effect of ionic strength of the solution of some hydrogen — bonded interpolymer complexes on the stability and thermodynamic parameters

Summary — The effect of ionic strength of the solution on the complex formation of poly(acrylic acid) (PAA) with poly(vinyl pyrrolidone) (PVP) has been studied in aqueous solutions containing various inorganic salts (NaCl, KCl, NH_4Cl). Stability constant (K_s), degree of linkage (θ) and related thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) have been compared for different complexation systems. The comparative study indicated considerable difference in the values of these parameters, which has been explained on the basis of relative strength of H-bond present in different systems.

Key words: interpolymer complexes, ionic strength, thermodynamic parameters, H-bonding, poly(acrylic acid), poly(vinyl pyrrolidone).

WPŁYW SIŁY JONOWEJ ROZTWORU NIEKTÓRYCH KOMPLEKSÓW INTERPOLIMEROWYCH Z UDZIAŁEM WIĄZAŃ WODOROWYCH NA STABILNOŚĆ I PARAMETRY TERMODYNAMICZNE TAKICH UKŁADÓW

Streszczenie — Scharakteryzowano wpływ siły jonowej roztworu na proces komleksowania w układzie poli(kwas akrylowy)/poli(winylopirolidon); badania prowadzono w roztworach wodnych zawierających różne sole nieorganiczne (NaCl, KCl, NH_4Cl). Określano stałą stabilności (K_s, rys. 1), stopień związania (θ, tabela 2) oraz podstawowe parametry termodynamiczne (ΔG^0, ΔH^0 and ΔS^0, rys. 2 i 3, tabela 3) omawianych układów ulegających skompleksowaniu. Wyniki wskazują na istotne różnice wartości wspomnianych parametrów w zależności od względnej siły wiązań wodorowych występujących w rozpatrywanych roztworach a także od oddziaływań hydrofobowych. Doświadczalną podstawę badań stanowiły pomiary pH (tabela 1).

Słowa kluczowe: kompleksy interpolimerowe, siła jonowa, parametry termodynamiczne, wiązania wodorowe, poli(kwas akrylowy), poli(winylopirolidon).

Interpolymer complexes (IPC) stabilized by hydrogen bonding between polycarboxylic acids and non ionic polymers have been the subjects of intensive fundamental and applied research during the past decades [1—10].

These complexes have attracted much attention not only because they mimic the biological systems, but also because they present interesting solution and solid state properties. They are good candidates for different technological applications such as carriers for enzymes and drugs, biosensors, biological substrates, light emitting diodes, *etc*. [1—3, 9, 10]. Additionally, the concept of interpolymer complexation by hydrogen bonding has been successfully used in construction of polymeric micelles [9, 11—15].

It is well known that IPC stabilized by hydrogen bonding in aqueous solutions are additionally stabilized by hydrophobic interactions. Hydrophobic interactions are strengthened at higher temperature. However, hydrogen bonds — which are mainly formed at a relatively low temperature — weaken with temperature increase. Hence the stability of IPC greatly depends on a delicate balance between the contributions of hydrogen bonding and hydrophobic interactions [10, 15—17]. Hydrophobic interactions can also be affected by different substances added to the aqueous solutions.

Interpolymer complex formation and its stability also depend on various internal/external parameters. These parameters include: the structure, solvent nature, pH, ionic strength, *etc*. Though considerable research have been carried out on IPC subjects, but the influence of different additives, such as low molecular salts, on hydrogen bonded IPC in aqueous solutions has not been well known.

Turro with coworkers [18] demonstrated the unfavorable action of inorganic salts on the complex formation between poly(acrylamide) and poly(carboxylic acid). Budtova and coworkers reported that increasing ionic

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strength depressed the complexation of poly(acrylic acid) (PAA) with poly(vinyl alcohol) (PVA) and hydroxyethylcellulose [19]. Prevyesh *et al.* studied the effect of added salts on the stability of IPC composed of PAA, poly(vinyl pyrrolidone) (PVP) and hydroxypropylcellulose (HPC) [20].

Chen and Morawetz [21] demonstrated that the addition of NaCl reduced the intensity of interactions between PAA and PVP or poly(oxyethylene) (PEOX). Frenkel with coworkers published several papers on the influence of ionic strength of solution on complexation. They noted that the presence of low molecular salts in aqueous solutions disturbed the complexation of PAA with PVP [19] and poly(oxyethylcellulose) (POEC) [19]. Recently Nurkeeva's group in series of papers have described how an addition of inorganic salts could influence the pH_{crit} significantly [22—27] and clarified the effect of ionic strength on the complex formation. Sivadasan *et al.* [18], Iliopoulos and Audebert [28] and Moharram and coworkers [29] also studied the effect of ionic strength on the complexation of PAA.

Though, some amount of work have been reported in the literature regarding the fundamental studies on the effect of inorganic salts on H-bonded interpolymer complexes, but detailed thermodynamic studies of these systems are particularly missing. For this we have studied the role of ionic strength of the solution on IPC stabilized by H-bonding, through calculations of stability constant (K_s), degree of linkage (θ) and related thermodynamic parameters (*e.g.* ΔG^0, ΔH^0, ΔS^0) of these complexes, depending on the type of various inorganic salts present in the solution. In this work an attempt has been made to correlate the relative enthalpy and entropy changes of the complexes at various temperatures with respect to ionic strength of the complexing medium.

EXPERIMENTAL

Materials

— **Poly(acrylic acid) (PAA)**: Purified acrylic acid (distilled twice in vacuum, boiling point 63 °C, 12 mm Hg) was polymerized in the presence of benzoyl peroxide as an initiator in a moist dioxane/methanol mixture [17, 30]. The polymerization time was 2.5 h in nitrogen at 50 °C. The reaction mixture was dissolved in methanol and reprecipitated twice with ethyl acetate. The polymer was dried to constant weight in vacuum at 110 °C. The viscosity average molecular weight ($\overline{M}_\eta$) of the polymer was calculated from intrinsic viscosity (η) of polymer in 2 M NaOH aqueous solution at a constant temperature of 25 °C, using the Mark-Houwink equation $\eta = KM_\eta^{\alpha}$ [31, 32]. The constant K and α in the above equation were equal to $42.2 \cdot 10^{-3}$ ml g^{-1} and 0.64, respectively; $\overline{M}_\eta = 4.0 \cdot 10^5$.

— **Poly(vinyl pyrrolidone) (PVP)**: PVP was supplied by Fluka, Switzerland, in the form of white crystalline powder. The viscosity average molecular weight ($\overline{M}_\eta$) of the polymer was calculated from viscosity measurements using the following equation: $[\eta] = 6.76 \cdot 10^{-2}$ $M_\eta^{0.55}$ (in aqueous medium at 25 °C), $[\eta]$ is intrinsic viscosity and $\overline{M}_\eta = 2.4 \cdot 10^4$ (g/mol) [31, 33].

— The inorganic salts (NaCl, KCl, NH_4Cl), of analytical grade, were used as received.

— Double distilled water was used as the solvent for all the measurements.

Measurement of pH

The pH measurements of aqueous solutions of the polymer or complex were carried out in a water jacketed cell by ATI ORION pH meter (model 525A), using a combination electrode (ORION pH Triode 91-57) with autocalibration for buffers 1.68, 4.01, 7.00, 10.01 and 12.46 within a range of ±0.001 pH units. Two points standard calibration was performed at the beginning of each day measurements and also with one standard every 2 h to compensate the possible electrode drift. In all experiments the temperature was thermostatically controlled within ±0.05 °C by water circulating through a jacket of glass cell, and the sample solution was continuously stirred using a magnetic stirrer. The pH was measured at a polymer concentration of $1 \cdot 10^{-3}$ mol · L^{-1} in the absence and presence of stoichiometric concentration of PVP. Complexes did not precipitate at this concentration.

The data obtained from pH measurements for systems of different compositions at various temperatures are given in Table 1.

RESULTS AND DISCUSSION

It is well known that poly(acrylic acid) forms interpolymer complexes of stoichiometric composition with

Table 1. pH data for complexes at various temperatures

System	Composition of complex (unit mole)	pH at various temperatures								
		20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C
	1.0 PAA	4.320	4.337	4.355	4.377	4.400	4.425	4.435	4.470	4.470
I	1.0 PAA + 1.0 PVP	4.520	4.549	4.577	4.620	4.665	4.698	4.737	4.779	4.776
II	1.0 PAA + 1.0 PVP + NaCl	4.341	4.350	4.368	4.392	4.416	4.440	4.446	4.475	4.473
III	1.0 PAA + 1.0 PVP + KCl	4.368	4.358	4.379	4.406	4.431	4.461	4.474	4.504	4.498
IV	1.0 PAA + 1.0 PVP + NH_4Cl	4.399	4.361	4.403	4.434	4.463	4.494	4.510	4.536	4.523

poly(vinyl pyrrolidone) in aqueous solution. The stabilization of such complexes is due to the cooperative interaction through the formation of hydrogen bonds between acid (as hydrogen bond donors) and base (as hydrogen bond acceptors) groups in the polymer chain and also by hydrophobic interactions [1—3, 32—34]. The complex formation in such systems is controlled by several critical factors such as minimal molecular weight, critical pH of complexation, minimal amount of active group sequence, solvent nature, temperature *etc.* [17, 32, 34]. Given all this, to study the effect of ionic strength on stability constant K_s and related thermodynamic parameters of PAA/PVP complexes in aqueous solutions, several two-component interpolymer complexes were prepared by mixing of PAA with stoichiometric quantities of PVP (1:1 molar ratio) in pure aqueous medium and in the mediums containing inorganic salts such as NaCl, KCl or NH_4Cl (systems I—IV, see Table 1).

The procedure chosen for calculations of the stability constant K_s and degree of linkage θ of interpolymer complexes was the same as in earlier communications [17, 32, 34—36]. The degree of linkage θ is defined as the ratio of the binding groups to the total number of potentially interacting groups [equation (1)] and it is related to the stability constant K_s of the interpolymer complex by the equation (2) [2, 35—37]:

$$\theta = 1 - \left(\frac{[H^+]}{[H^+]_0} \right)^2 \tag{1}$$

$$K_s = \frac{\theta}{C_0 (1-\theta)^2} \tag{2}$$

where: C_0 — *initial concentration of poly(carboxylic acid)* [*mol* · L^{-1}], [H^+] *and* [H^+]$_0$ — *proton concentrations in the polymer solution in the presence or absence of complementary polymer.*

T a b l e 2. Degree of linkage (θ) of complexes at various temperatures

System	Degree of linkage (θ) at various temperature								
	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C
I	0.603	0.622	0.641	0.673	0.706	0.716	0.752	0.760	0.755
II	0.091	0.057	0.058	0.068	0.072	0.068	0.052	0.023	0.013
III	0.200	0.092	0.107	0.125	0.133	0.152	0.164	0.146	0.122
IV	0.304	0.106	0.199	0.231	0.251	0.272	0.292	0.262	0.216

The stability of these complexes in different media at higher temperature is likely to be influenced by the relative strength of H-bonds present in them. The values of θ and K_s have been determined at several temperature for the complex system in salt free solution and also in solutions containing inorganic salts (Table 2). It should be noted that the effect of addition of inorganic salts on hydrogen-bonding complexation is determined by two opposite factors. On one hand an increase in the ionic strength of a solution leads to a partial dissociation of poly(carboxylic acid) which is unfavorable for complexation. On the other hand, however, the addition of inorganic salts leads to the strengthening of hydrophobic interactions which are favorable for complexation. The balance between these two opposite factors will determine how a system will respond to the presence of low molecular weight ions in solution [15]. Prevysh *et al.* [20], Frenkel [19], Turro [18], Staikos [38] and Iliopoulos with coworkers and — in a series of papers during recent years — Nurkeeva *et al.* [22—27] have described how an addition of inorganic salts could influence the pH_{crit}, and stability of interpolymer complex significantly, and that this effect was greatly dependent on the nature of the non-ionic polymer. They found that for complexes of PAA with PVP, HPC, poly(vinyl methyl ether) (PVME), poly(acrylamide) (PAAm) the decrease in pH_{crit} was observed in the following order: NaCl > KCl > NH_4Cl. The corresponding plots of ln K_s *versus* reciprocal of temperature for systems I to IV are shown in Figure 1.

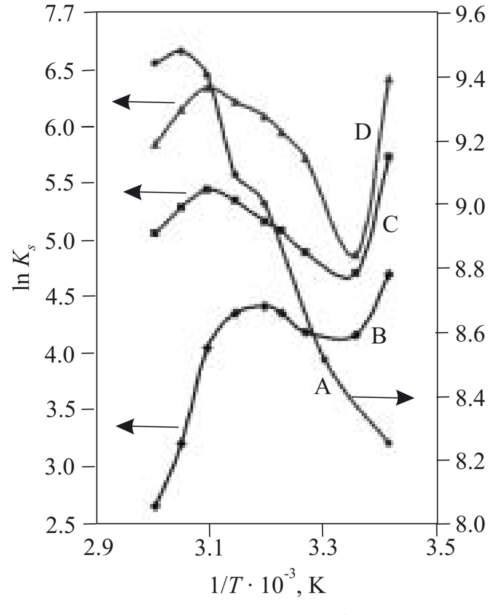

Fig. 1. Relationship of ln K_s *versus 1/T for complexation systems: I (A), II (B), III (C), IV (D) (see Table 1)*

It can be seen from this Figure that the complexation system I (*i.e.* PAA/PVP in salt free solution) showed an increase in ln K_s with increase in temperature (*cf.* curve A in Fig. 1). However, in the case of systems II, III and IV there is an initial fall in ln K_s with increase in temperature up to 25 °C and then there is an increase beyond this temperature. This could be due to the fact that in system I the interaction of reacting units (*e.g.* AA/VP) involved strong hydrogen bonding. In addition, hydrophobic interactions also play a significant role in the stability of this interpolymer complex [2, 15, 34—36, 39]. It is also known that hydrophobic interactions are reinforced with increasing temperature in an aqueous medium. In the systems II—IV, however, all the curves indicated distinct minima at a specific temperature. This could be anticipated that the addition of salts increased the ionic strength of the solution and caused partial dissociation of PAA. This results in some preliminary interactions between carboxylic groups of the acid and positive ions of the salts. With an increase in the temperature these interactions become less significant. It is shown that the fall in K_s for system IV is more pronounced (curve D). This is due to binding ability of the salts with PAA, which can be arranged for PAA/PVP complex system, diminished in the following order: NaCl > KCl > NH_4Cl [15]. It can be seen from the Fig. 1 that for all these systems (*i.e.* II—IV) beyond 25 °C, as a result of strong H-bonding, K_s will increase with increase in temperature up to 50 °C for the systems III, IV (curve C, D) and 45 °C for system II (curve B). It should be noted that for polyelectrolytes like PAA, addition of salts led to the charge screening effects, which also favored compaction of macromolecules. Hence, the enhancement in complexation ability of these polymeric pairs can be explained by additional stabilization of IPC by hydrophobic interactions caused by deterioration of thermodynamic quality of the solvent in the presence of salt which is more visible in case of NH_4Cl. At 50 °C K_s decreases for systems III and IV because of the slow disintegration of the complexes while system II disintegrates at lower temperature, *i.e.* 45 °C, because of weaker H-bonding.

The thermodynamic parameters [*e.g.* change in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0)] can be calculated from the temperature dependence of the stability constant (K_s) using the thermodynamic equations [2, 32, 34—37]:

$$\Delta G^0 = -RT \ln K_s \tag{3}$$

$$\frac{d(\ln K_s)}{d(1/T)} = \frac{-\Delta H^0}{R} \tag{4}$$

$$\Delta S^0 = \frac{-(\Delta G^0 - \Delta H^0)}{T} \tag{5}$$

where: R — *molar gas constant.*

The standard enthalpy and entropy changes for the complexation systems I—IV have been calculated on the basis of the above equations at several temperatures and the corresponding plots have been shown in Fig. 2, 3.

T a b l e 3. Maximum values of ΔH^0 and ΔS^0 for complexes

System	Maxima of ΔH^0, kcal·mol^{-1}			Maxima of ΔS^0, cal·deg^{-1}·mol^{-1}		
	(max)1	(max)2	(max)3	(max)1	(max)2	(max)3
I	9.415	12.971	3.176	48.373	59.092	28.647
II	-0.487	-1.100	-12.547	9.935	4.500	-30.774
III	3.978	4.153	-6.851	22.730	23.711	-10.357
IV	15.8	6.000	-8.108	68.200	32.300	-12.449

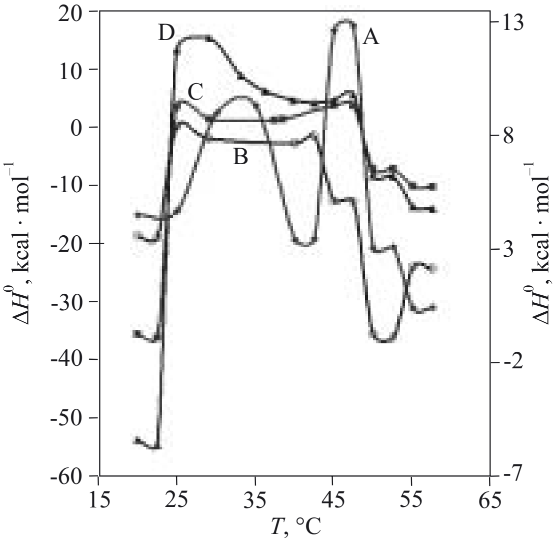

Fig. 2.: Temperature dependence of standard enthalpy changes ΔH^0 for complexation systems: I (A), II (B), III (C), IV (D)

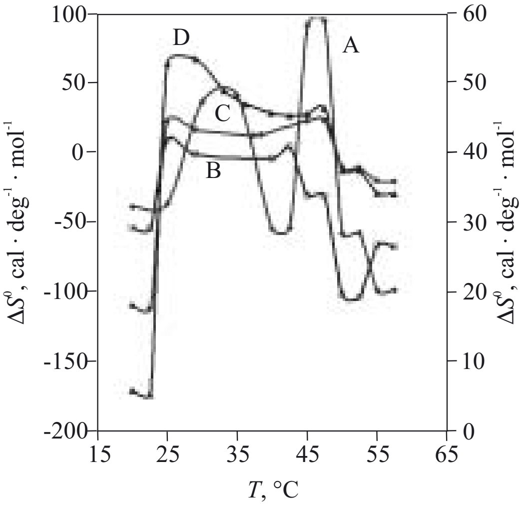

Fig. 3. Temperature dependence of standard entropy changes ΔS^0 for complexation systems: I (A), II (B), III (C), IV (D)

Table 3 gives the maximum values of ΔH^0 and ΔS^0 for systems I—IV at the temperature at which they were observed. The net enthalpy change (ΔH^0) and overall change in entropy (ΔS^0) during interpolymer complex formation consist of three basic steps, namely desolvation, complex formation as a result of H-bonding and conformational changes involving complex formation. Therefore, the overall changes in ΔH^0 and ΔS^0 are the sums of these contributions [2, 32, 34]. Since the contribution to each step will be different for the various systems, different values for ΔH^0 and ΔS^0 are understandable, when comparing ΔH^0 *vs. T* and ΔS^0 *vs. T* curves for all complex systems in different media (*i.e.* in solution free of salt and in solutions with salts). The first peak observed at 25 °C for the systems II—IV (*cf.* curves B, C, D in Fig. 2, 3) indicates the release of more ions due to the presence of salt in the medium, which get more solvated and results in higher ΔH^0 and ΔS^0 of solutions. However the first peak for the system I (*i.e.* curve A, in Fig. 2) may be attributed to strong H-bonding and possibly the release of more solvated molecule during complexation [17]. The second peak is observed at 45 $^{\circ}$C for the systems I, III and IV and at 40 $^{\circ}$C for the system II. As can be seen, this peak is highest for the system I (*i.e.* PAA/PVP in salt free solution) due to the maximum H-bonding between PAA and PVP. A relatively higher peak for the system IV as compared to the system III at this temperature is due to the stronger H-bonding as a result of greater reinforcement of hydrophobic interactions in NH_4Cl medium. The second peak for system II is observed at earlier temperature due to weaker H-bonding as compared to the other systems.

The third peak for the systems I, III and IV is observed at ~52 $^{\circ}$C and for the system II at ~45 $^{\circ}$C. Also here can be seen that the decrease in ΔH^0 and ΔS^0 *vs.* T curves in the case of system I is higher (*cf.* curve A in Fig. 2, 3). This may be assigned to the weaker reinforcement of hydrophobic interactions in this case as compared to the other systems. As explained above, the addition of inorganic salts and increase in temperature both lead to the strengthening of hydrophobic interactions.

CONCLUSION

It may be concluded that intermacromolecular complex formed as a result of H-bonding between PAA and PVP is influenced by the presence of specific types of inorganic salts. The effect of inorganic salts on H-bonding complexation is determined by the action of two opposite factors. On one hand, an increase in the ionic strength of a solution leads to a partial dissociation of PAA which is unfavorable for complexation. On the other hand, however, the addition of inorganic salts deteriorates the thermodynamic quality of the solvent with respect to polymers, *i.e.* their presence leads to the strengthening of hydrophobic interactions which are favorable for complexation.

The contribution of each of these factors is reflected in the temperature dependence of K_s and other related thermodynamic parameters. The information obtained in this research can be used for the prediction of the solubility behavior of polymeric materials based on IPC in the media of different ionic strength.

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