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Stability constants and thermodynamic parameters of some intermacromolecular complexes in relation to their specific interaction forces

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Summary

Intermacromolecular complexes of poly (acrylic acid) (PAA) with poly (ethylene oxide) (PEO), poly (ethylene imine) (PEI) and poly (vinyl pyrrolidon) (PVP) were prepared. The stability constants and thermodynamic parameters (e.g. ΔH^0 and ΔS^0) of these complexes were determined at several temperatures. The enthalpy and entropy changes of the systems with temperature have been interpreted in terms of various mode of interaction between the components and compared with each other.

Introduction

The phenomena of the interpolymer interaction have been the focus of intensive fundamental and applied research [1-3]. Formation of interpolymer complexes can be achieved through the specific interactions such as electrostatic interactions, hydrogen bonding and hydrophobic interactions etc. [1,2].The interpolymer complexes resulting from these interactions possess distinguished characteristics that are different from those of the individual components [4-9]. On the basis of the dominating interaction forces, interpolymer complexes can be divided into several classes: polyelectrolyte complexes, which are formed by mixing oppositely charged polyelectrolytes, i.e. polyanions and polycations, due to coulombic forces; hydrogen-bonding complexes, which are stabilized through hydrogen bonds between a poly acid and a poly base; charge-transfer complexes, which are formed between polymers with electron-doner and electron-acceptor groups; stereo complexes which are typically formed through vander waals forces by two polymers with identical chemical structure and complementary stereoisomerism.

In additional, interpolymer complexes may be stabilized by other interactions such as hydrophobic interaction in aqueous solution [1,10]. Hydrophobic force is different from the others because hydrophobic interaction is caused by rearrangement of water molecules rater than direct cohesive force between the molecules. Hydrophobic interaction forces the particles to coil up into compact globules, playing an essential role in the stabilization of the polymer complex particles in water.

Polyelectrolyte complexes and hydrogen-bonding complexes have received the most attention [10]. Though a considerable amount of work have been reported in the literature regarding the fundamental studies on these types of polymer complexes and their applications, but detailed thermodynamic studies are particularly lacking. Keeping this object in mind some intermacromolecular complexes have been prepared by selecting and interacting poly (acrylic acid) (PAA) with poly (ethylene imine) (PEI), poly (vinyl pyrrolidone) (PVP) and poly (ethylene oxide) (PEO). These systems are interesting in view of the fact that nature of interacting forces between the two reacting polymer is different; one could expect them to influence the stabilization of these complexes. The stability constants K and related thermodynamic parameters [e.g. the change in standard free entropy (ΔS^0) and change in standard free enthalpy (ΔH^0)], of these complexes, will depend on various reacting unit present in the complexes. In this report, an attempt has been made to estimate the degree of linkage (θ), the stability constant (K) and related thermodynamic parameters of interpolymer complexes of homopolymers.

Experimental

Poly (acrylic acid) (PAA)

Purified acrylic acid (distilled twice in vacuo, b. p. 63°C, 12mm Hg) was polymerized with benzoyl peroxide as an initiator in a moist dioxane-methanol mixture [11]. The polymerization time was 2.5h 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 vacuo at 110°C. The viscosity average molecular weight of the polymer was calculated from intrinsic viscosity of polymer in 2 M NaOH aqueous solution at a constant temperature of 25°C using the Mark-Houwink equation $[\eta] = KM_\eta^\alpha$. The constant K and α in the above equation were equal to 42.2×10^{-3} ml g^{-1} and 0.64, respectively [12-14].

The viscosity average molecular weight $\overline{M_\eta} = 4.0 \times 10^5$.

Poly (ethylene oxide) (PEO)

PEO was supplied by Iwai Kagaru Co Ltd., Japan. Its weight average molecular weight ($\overline{M_\eta}$) was 1.9×10^4 as calculated from viscosity equation. The viscosity average molecular weight of the PEO was calculated from intrinsic viscosity of polymer in water at a constant temperature of 25°C using the Mark-Houwink equation $[\eta] = KM_\eta^\alpha$. The constant K and α in the above equation were equal to 49.9×10^{-3} ml g^{-1} and 0.67, respectively [12-14].

Poly (vinyl pyrrolidone) (PVP)

PVP was supplied by Fluka Switzerland in the form of a white powder. The weight average molecular weight ($\overline{M_\eta}$) of the polymer was calculated from viscosity measurement using the following equation:

$$[\eta] = 6.76 \times 10^{-2}\, M^{0.55} \text{ (in aqueous medium at 25°C)} \qquad (\mathbf{1})$$

Where [η] is intrinsic viscosity and $\overline{M_\eta} = 2.4 \times 10^4$ (g/mol) [12-14].

Poly (ethylene imines) (PEI)

PEI was supplied by BDH chemical Ltd (Poole. UK) in the form of a 50% viscous aqueous solution, with number average molecular weight $\overline{M_\eta} = 1.5 \times 10^5$.

Solvent

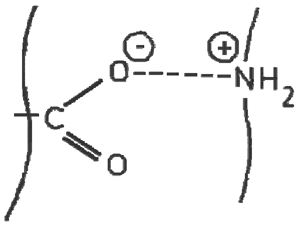
Double distilled water was used as the solvent for all the measurements.

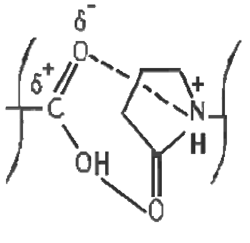
Measurement of pH

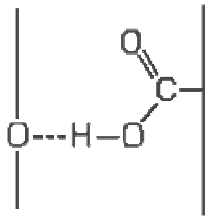
The pH measurement of aqueous solution of the polymer or complex was carried out in a water jacketed cell an Ec digital pH meter using a combination electrode. The temperature of the sample solution was thermostically controlled within ± 0.05°C by circulating water. The pH was measured at a polymer concentration of 1×10^{-3} mol^{-1} L^{-1} in the absence and presence of stoichiometric concentration of PEI, PEO and PVP. complexes did not precipitate at this concentration.

Results and Discussion

Poly (acrylic acid) (PAA) homopolymer is known to interact with PEI, PVP and PEO respectively to form interpolymer complexes [2,5,10]. In these complexes, the nature of interacting forces involved in the various pairs of reacting polymer (e. g. PAA-PEI, PAA-PVP, PAA-PEO) are different [15-18]. For instance in PAA-PEI, strong electrostatic interactions. In PAA-PVP strong hydrogen bonding and ion-dipole interaction of different magnitude and in PAA-PEO hydrogen bonding interactions, are involved respectively. Keeping this in mind several two component interpolymer complexes have been prepared by mixing PAA with stoichiometric quantities of PEI, PVP and PEO (1:1 unit molar ratio) in aqueous solution:


PAA+ PEI


PAAA+ PVP


PAA+PEO

Since the nature of the interacting forces between reacting monomers are different, one could expect them to influence the stability of these complexes at higher temperature.

Osada, s procedure has been chosen for calculating the stability constant (***K***) and degree of linkage (***θ***) [19-21].

The degree of linkage, which is defined as the ratio of the binding groups to the total of potentially interacting groups. The stability constant (K) of the interpolymer complex is related to θ by the following equation:

$$\theta = 1 - ([H^+]/[H^+]_0)^2 \quad (2)$$

$$K = \frac{\theta}{C_0(1-\theta)^2} \quad (3)$$

Where C_0 is the initial concentration of poly carboxylic acid (unit mol/L) and $[H^+]_0$ are proton concentration of the poly carboxylic acid solutions in the presence and absence of the complementary proton-accepting polymer. Osada studied the effect of molecular weight of PVP and poly ethylene glycol (PEG) on stability and thermodynamic parameters for a system containing poly (methacrylic acid) PMAA-PEG, PMAA-PVP and PAA-PEG and found out that when comparing the complexing systems PMAA-PEG and PAA-PEG, the value of $\boldsymbol{\theta}$ was higher for PMAA than ***PAA.*** The higher complexation power of PMAA was explained in terms of hydrophobic interactions between the $\boldsymbol{\alpha}$ methyl groups of PMAA and the two $-CH_2$ units in PEG.He also found the higher value of $\boldsymbol{\theta}$ and ***K*** with PEG of higher molecular weight. Perez Gramatges [22] also used the same methods to study the thermodynamics of complex formation through hydrogen bonding for poly acrylic acid with poly (N-vinyl-2-pyrrolidone) and Chitosan. They also observed the stronger hydrophobic interactions in the PMAA-PVP complex as compared with the PAA-PVP system is manifested by the lower stability of the later in organic solvent the values they obtained are in good agreement with those reported with Osada, which indicate that for high enough molecular weight the coperativity of the reaction between PAA and PVP provides the necessary stabilization to bring complexing in water. Effect of copolymer structure on stability and Degree of Linkage have also been reported by Chatterjee [23] for interpolymer complex of Acrylamid-vinyl alcohol (AAm-VA) graft copolymer, methacrylic acid-acrylamid (MAA-AAm) random copolymer and PEI. In the present work the aim is to investigate the temperature dependence of stability constant and thermodynamic parameters for different complex of PAA with complementary polymers due to different types of interacting forces involved in them not the molecular weight and structural effect. They earlier workers also have not considered the effect of ion-dipole interactions in PAA-PVP complexes [1,2]The values of $\boldsymbol{\theta}$ and ***K*** have been determined at several temperatures for the complex system ***I-III*** is given in Table 1. The corresponding plots of Ln ***K*** versus reciprocal temperature are shown in figure 1. The complexation system ***I*** and ***II*** showed an increase in Ln ***K*** with increase in temperature (cf. curves A, B in Figure 1). However in the case of system ***III***, there is fall in Ln ***K*** with increase in temperature (cf. curve C in Figure 1).It is shown that the relative stability of system ***I*** is much greater compared to other system.

Table 1: Degree of the linkage of complexes at various temperature

System	Composition of complex (unit mole)	Degree of linkage (θ)						
		20 ˚C	30 ˚C	40 ˚C	45 ˚C	50 ˚C	55 ˚C	60 ˚C
(I)	1.0 PAA+1.0PEI	0.593	0.716	0.876	0.889	0.912	0.926	0.923
(II)	1.0PAA+1.0PVP	0.604	0.642	0.706	0.717	0.752	0.760	0.761
(III)	1.0PAA+1.0PEO	0.999	0.998	0.996	0.995	.0994	0.993	0.993

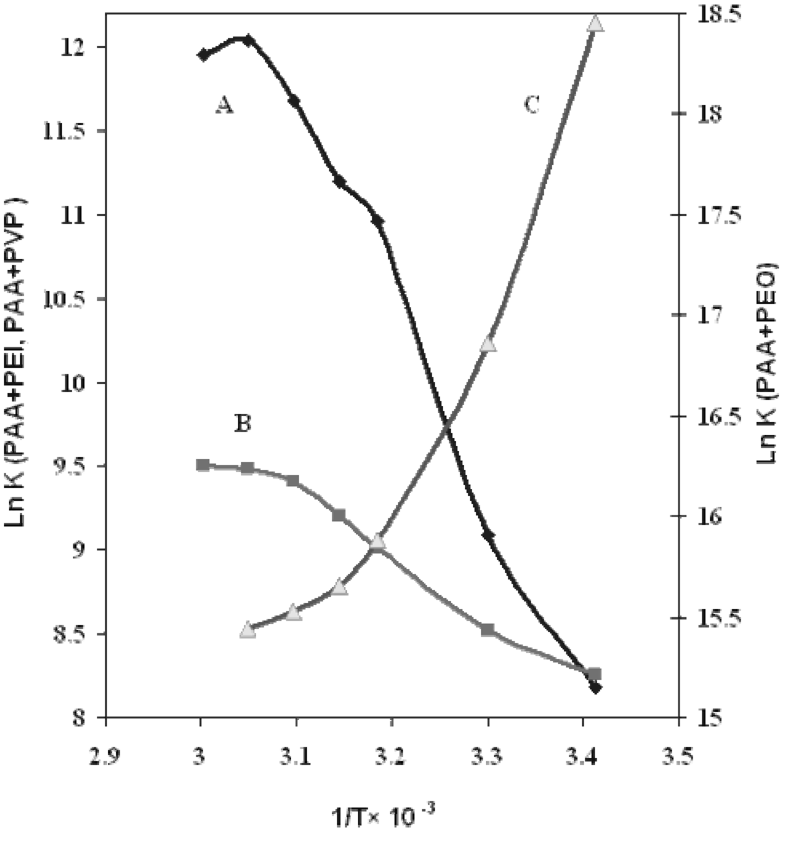


Fig. 1. Relationship of Ln K versus 1/ T for complexation systems: I (A), II (B), III (C)

This trend could be anticipated in view of the fact that in system ***I***, interaction of reacting units (e.g. AA-EI) involves strong electrostatic forces which are only slightly changed at elevated temperature [2,20]. In additional hydrophobic interactions play a significant role in the stability of interpolymer complexes? It is known that hydrophobic interactions are reinforced with increasing temperature in an aqueous medium [2,10,20]. In system ***II*** the two reacting units (e. g AA-VP) form a complex through not only hydrogen bonding but also through ion-dipole interaction. The corresponding plot of Ln ***K*** versus 1/ ***T*** for this complex system indicates an increase with temperature up to ~ 50 ˚C only, and beyond this temperature ***K*** is more or less linear (cf. curve B in Figure 1), which is in good agreement with Osada,s and Gramatages, this is in view of the fact that coulomb forces are only slightly changed at elevated temperature, where as hydrogen bonding breaks up beyond a certain temperature [2,20]. However in system III, PAA forms complexes with PEO only through hydrogen bonding. The decrease of the stability constant K of the complexes with temperature is due to destabilization of the H-bonds with the increase of temperature [1,2,20] (cf. curve C in Figure 1). The thermodynamic parameters (e.g ΔS^0 and ΔH^0) for the interpolymer complexation process can be calculated from ***K*** and its temperature dependence [2,20]:

$$\Delta G^0 = -RTLnK \qquad (4)$$

$$dLn(K)/d(1/T) = -\Delta H^0/R \qquad (5)$$

$$\Delta S^0 = -(\Delta G^0 - \Delta H^0)/T \qquad (6)$$

Where ΔG^0 is the change in standard free energy and R is molar gas constant. The standard enthalpy and entropy changes for the complexation systems I-III have been calculated on the basis of the above equation. The corresponding values have been plotted against temperature in figures 2 and 3.

Table 2: The maximum values of ΔH^0 and ΔS^0 observed for various systems

System	Composition of complex (unit mole)	Maxima observed in ΔH^0 (k cal. mol $^{-1}$)		Maxima observed in ΔS^0 (cal. deg $^{-1}$ mol $^{-1}$)	
		$\Delta H^0_{(max)1}$	$\Delta H^0_{(max)2}$	$\Delta S^0_{(max)1}$	$\Delta S^0_{(max)2}$
(I)	1.0PAA+1.0PEI	35.817	19.985	137.303	85.409
(II)	1.0PAA+1.0PVP	9.415	12.971	48.373	59.09
(III)	1.0PAA+1.0PEO	-15.04	-5.238	-16.275	14.68

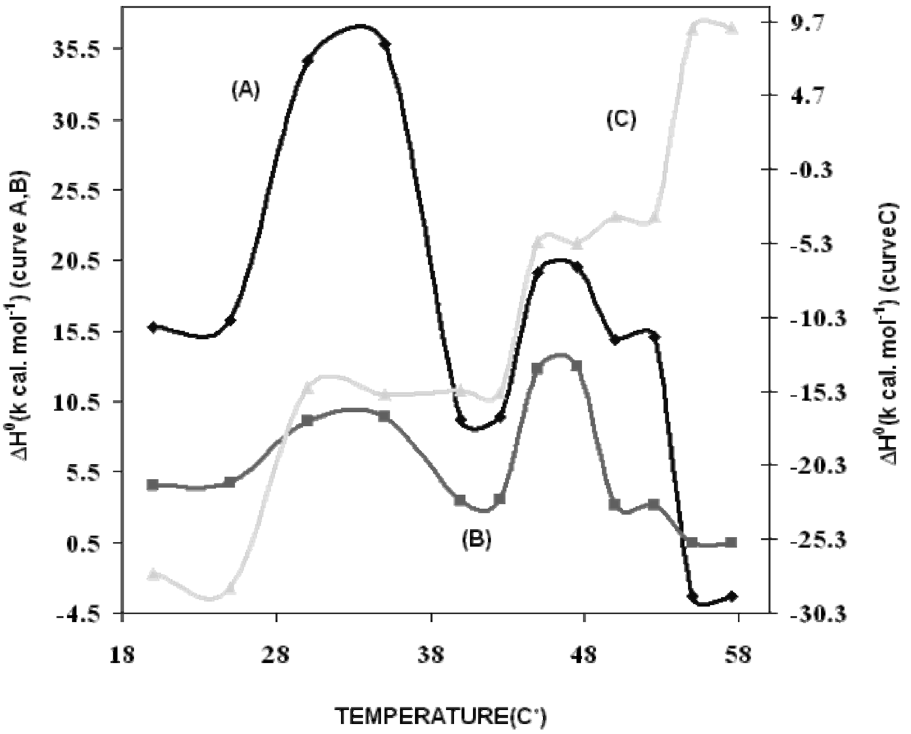


Fig. 2. Temperature dependence of standard enthalpy changes ΔH^0 for complexation systems:I (A), II (B), III (C)

All complexation system ***I, II*** and ***III*** showed two maxima in ΔH^0 vs T curves at 35°C and 45°C respectively. The net enthalpy change (ΔH_M) during interpolymer complex formation consists of at least three steps, namely desolvation (ΔH_1) and its absolute value is related to the strength of the interaction between solvent and each polymer components. The following step is considered to involve complex formation between desolvated polymer components. In this step, hydrogen bonds are formed between polymers (ΔH_2). The final step consists in the conformational change involving complex formation and other factors (ΔH_3). There fore, ΔH_M may be considered as

$$\Delta H_M = \Delta H_1 + \Delta H2 + \Delta H_3 \quad (\mathbf{2})$$

Since the contribution to each step will be different for the various systems, different values for ΔH_M are understandable. This difference of ΔH_M may be caused by the difference hydrogen bonding (i. e proton- accepting) ability and hydrophobicity of PEI, PVP and PEO.

The relatively higher value of ΔS^0 for system ***I*** compared to system ***II*** and ***III*** may be attributed to strong electrostatic interactions and possibly release of more solvated molecules during complexation [1,2].

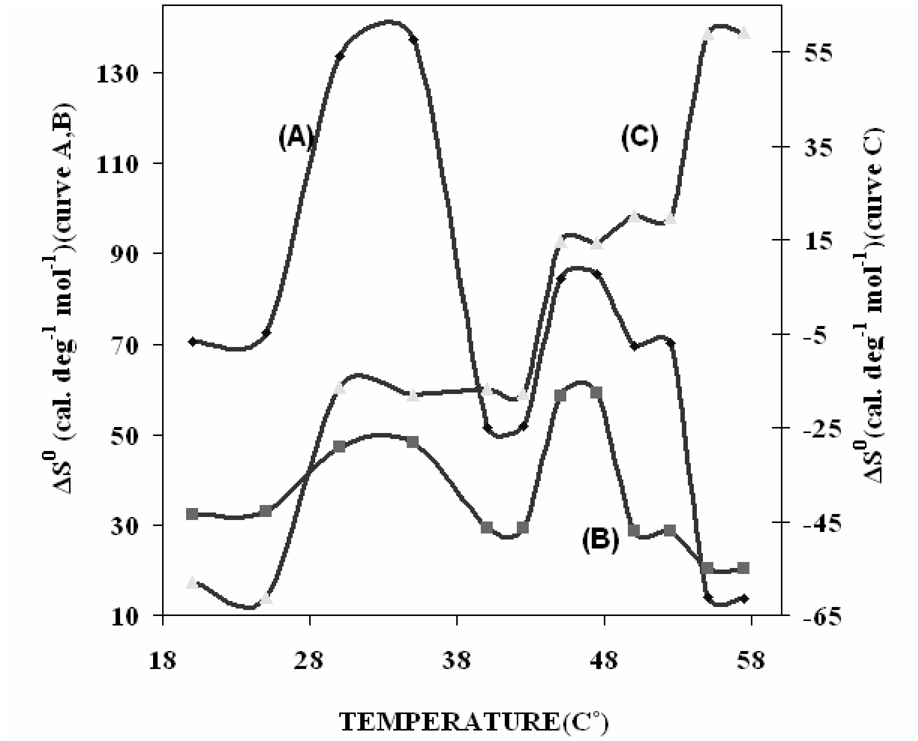


Fig. 3. Temperature dependence of standard entropy changes ΔS^0 for complexation system: I (A), II (B), III (C)

The difference in the change in ΔH^0 and ΔS^0 with temperature for systems ***I-III*** may be attributed to the specific types of interaction forces present in the complex. There fore, as the temperature is increased, destabilization of the hydrogen bond takes place, resulting in weak co-operatively between the binding sites. In the case of polyelectrolyte complexes with increase in temperature coulomb forces are not affected appreciably, resulting in greater co-operative interactions.

It may be concluded that ***K*** of interpolymer complexes of poly (acrylic acid) with other component polymers is influenced by the presence of specific types of interaction force involved. Since interpolymer complex formation involves several process (e. g. hydrogen bonding, electrostatic interactions, ion-dipole and hydrophobic interactions, thermal motion etc.

The contribution of each of these processes is reflected in the temperature dependence of ***K*** and other related thermodynamic parameters.

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