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Stability and thermodynamic parameters of some selective intermacromolecular complexation

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Summary

Selectivity in intermacromolecular complex formation has been studied for some three component systems involving poly (ethylene imine) (PEI), poly (ethylene oxide) (PEO) and poly (acrylic acid) (PAA). The stability constant and related thermodynamic parameters of these complexes were determined at several temperatures. The entropy and enthalpy changes of the systems with temperature have been interpreted in terms of destabilization of the various interacting forces involved in complex formation as a result of pH of the medium.

Introduction

Polymer-polymer complexes have been studied extensively during the recent years in view of their potential applications in industry and medical biology [1-17]. Another aspect which has attracted considerable attention is selectivity in their intermacromolecular complexation; this is due to close similarity with substitution reactions in biological systems. Macromolecular chain in biological systems, effectively selects a complementary one to form an intermacromolecular complex. In this way, very specific functionalities become effective [1,2,8,14]. Synthetic polymer can also form intermacromolecular complexes, but the ability of synthetic polymer select one objective polymer as in biological system has not yet realized, except for some specific systems. The inter-macromolecular complex formation of synthetic polymer is controlled by many factors; such as interaction forces, solvent, ionic strength, temperature, pH, etc. Moreover, the cooperative and concerted interactions of each active site play an important role in complex formation. These phenomena suggest that the selective intermacromolecular complexation can be realized under suitable conditions [1,2,8,14,18]. In a system containing a weak poly base e.g. poly (ethylene imine) (PEI) a poly acid e.g. poly (acrylic acid) (PAA) and a proton accepting non ionic polymer e.g. poly (ethylene oxide) (PEO), the selective macromolecular complex formation of different pairs of polymers is governed by pH of the system [1,2]. In this three components system, under acidic condition the hydrogen bond complex is preferentially formed with PAA and PEO, and at neutral pH a polyelectrolyte complex is preferentially formed with PAA and PEI. At alkaline pH neither polyelectrolyte complex nor the complex resulting from hydrogen bonds is formed. This system is interesting in view of the fact that the selective complexation of different pairs of polymers and nature of interacting forces between them is influenced by pH of the system. In the present investigation efforts have been made to determine and compare the corresponding values of the thermodynamic parameters (e.g. ΔH^0 and ΔS^0) and stability constants ***K*** of these three component interpolymer complexes with respect to pH of system.

Experimental

Poly (acrylic acid) (PAA)

Purified acrylic acid (distilled twice in vacuo, b. p. 63°C, 12mmHg) was polymerized with benzoyl peroxide as an initiator in a moist dioxane-methanol mixture [19]. The polymerization time was 2.5h in a 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 $[\eta] = KM_{\eta}^{\alpha}$ [14,20]. The constant K and α in the above equation were equal to 42.2×10^{-3} ml g^{-1} and 0.64, respectively. The viscosity average molecular weight $\overline{M_{\eta}} = 4.0 \times 10^5$.

Poly (ethylene imine) (PEI)

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

Poly (ethylene oxide) (PEO)

PEO was supplied by Iwai Kagaru Co Ltd., Japan. Its 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].

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 by ATI ORION pH meter (model 525A), using a combination electrode (ORION pH Triode 91-57) with auto calibration 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 two hours to compensate for possible electrode drift.

In all experiments the temperature was thermostatically controlled within ± 0.05˚C by circulating water through jacketed glass cell, and the sample solution was continuously stirred using a magnetic stirrer.

The pH was measured at a polymer concentration of 1×10^{-3} mol.L^{-1} in the absence and presence of stoichiometric concentration of PEI and PEO. Complexes did not precipitated at this concentration. In every system the amount of PAA was kept constant as the amount of PEI and PEO was varied during each experiment. The pH of complex solution were between 4–5 for all systems and data which obtained from pH measurements at various temperatures are tabulated in Table 1.

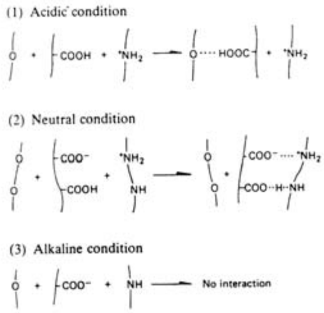
Table 1: pH data for PAA and PAA-PEI-PEO complex systems at various temperature

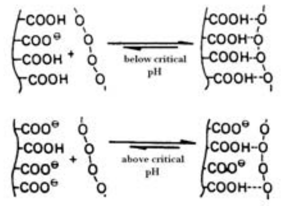
System	Composition (unit mole)	pH						
		20ºC	30ºC	40ºC	45ºC	50ºC	55ºC	60ºC
I	1.0 PAA	4.320	4.355	4.400	4.425	4.435	4.470	4.470
II	1.0 PAA + 0.6 PEI + 0.4 PEO	5.305	5.270	5.339	5.390	5.439	5.440	5.442
III	1.0 PAA + 0.5 PEI + 0.5 PEO	5.419	5.369	5.429	4.459	5.490	5.519	5.530
IV	1.0 PAA + 0.4 PEI + 0.6 PEO	5.040	5.000	4.919	4.879	4.859	4.840	4.810
V	1.0 PAA + 0.2 PEI + 0.8 PEO	4.710	4.740	4.680	4.666	4.635	4.633	4.632

Result and Discussion

It is known that the PAA interact with PEI through strong electrostatic interaction [1,2,8-11,14]. PAA forms an interpolymer complex with PEO in dilute aqueous solutions through hydrogen-bonding interaction between carboxylic acid groups of PAA and ether oxygen of PEO [1,2,10,11,21-23]. Moreover, the PAA / PEO complex is also stabilized by hydrophobic interaction [1,2,10,11,21-23]. This complexation strongly depends on pH of the system; i.e. the degree of dissociation of PAA [21-34]. Dissociation of PAA is suppressed in the presence of PEO. The existence of a certain number of undissociated carboxyl groups is necessary for PAA and PEO to form stable complex through H-bonds. This condition is satisfied at critical pH. At higher pH as the number of active sites is extremely insufficient, it is assumed that the enthalpy afforded by hydrogen bonds is not compensated by the decrease in enthalpy [2,13,21-34].

In a system containing PAA, PEO and PEI, the selective intermacromolecular complex formation of different pairs of polymer is governed by the pH of the system. Under acidic condition, weak poly base PEI is almost all protonated but PAA is scarcely dissociated. Thus the complex of PAA with proton-accepting polymer PEO, which may form hydrogen bonds with PAA, is preferentially formed. At neutral pH, both weak poly acid PAA and a weak poly base PEI are partially ionized, resulting in the formation of the polyelectrolyte complexes. At alkaline pH, a weak poly acid is almost completely dissociated while poly base are not protonated. Thus neither the polyelectrolyte complexes, nor the complexes resulting from hydrogen bonding are formed [1,2].





Hence it was considered of interest to prepare some three-component intermacromolecular complexes of PAA, PEO and PEI, by mixing the components in the following stoichiometric proportions.

II) 1.0 unit mole of (PAA) + 0.6 unit mole (PEI) + 0.4 unit mole (PEO)
III) 1.0 unit mole of (PAA) + 0.5 unit mole (PEI) + 0.5 unit mole (PEO)
IV) 1.0 unit mole of (PAA) + 0.4 unit mole (PEI) + 0.6 unit mole (PEO)
V) 1.0 unit mole of (PAA) + 0.2 unit mole (PEI) + 0.8 unit mole (PEO)

In these complexes, the nature and magnitude of interacting forces involved in the various reacting units (e.g. AA-EI, AA-EO) as stated above expected to be different, in acidic medium [2,11,14]. Thus one could predict that the ***K*** values and the related thermodynamic parameters (e.g. ΔH^0 and ΔS^0) of the four complexes II-V will be different. The procedure has been chosen for the calculation of the stability constant ***K*** and degree of linkage ***θ*** of interpolymer complexes is same as that used in earlier communications [11,18,25,36]. The degree of linkage ***θ*** defined as the ratio of the binding groups to the total number of potentially interacting groups, and it is related to the stability constant ***K*** of the inter-polymer complex by the following equation:

$$\theta = 1 - \left([\mathrm{H}^+]/[\mathrm{H}^+]_0\right)^2 \qquad (\mathbf{1})$$

$$\mathrm{K} = \frac{\theta}{\mathrm{C}_0(1-\theta)^2} \qquad (\mathbf{2})$$

Where C_0 is the initial concentration of poly carboxylic acid (mol.L^{-1}), $[H^+]$ and $[H^+]_0$ are the proton concentrations in the polymer solution in presence and absence of complementary polymer, (e.g. PEI and PEO). The values of ***θ*** have been calculated at several temperatures for the complexation systems, II to V are presented in Table 2. The corresponding plots of LnK versus reciprocal temperature are shown in figure. 1. The stability of these three components inter polymer complexes at higher temperature is likely to be influenced by the relative amount of PEI and PEO presence.

Table 2: Degree of the linkage of complexes at various temperatures

System	Composition of complex (unit mole)	Degree of linkage (θ)						
		20°C	30°C	40°C	45°C	50°C	55°C	60°C
II	1.0PAA + 0.6 PEI + 0.4 PEO	0.9892	0.9852	0.9868	0.9882	0.9902	0.9884	0.0988
III	1.0PAA + 0.5 PEI + 0.5 PEO	0.9936	0.9906	0.9913	0.9914	0.9922	0.9920	0.9924
IV	1.0PAA + 0.4 PEI + 0.6 PEO	0.9636	0.9487	0.9088	0.8769	0.8587	0.8180	0.7911
V	1.0PAA + 0.2 PEI + 0.8 PEO	0.8340	0.8138	0.7246	0.6611	0.6020	0.5213	0.5322

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. In addition to the above mentioned interacting forces, hydrophobic interactions play a significant role in the stability of inter polymer complex. It is known that hydrophobic interactions are reinforced with increasing temperature in an aqueous medium [1,2,10,11]. Moreover the effect of hydrophobic interactions on the stabilization of hydrogen bond containing complex may be stronger than on stabilization of the polyelectrolyte complex.

On comparing plot of Ln***K*** versus 1/T, it can be seen for system II in acidic medium, there is fall in Ln***K*** with increase in temperature (cf. curve A in Fig. 1) up to 30°C and then increase up to 50°C. This trend could be anticipated in view of the fact that in acidic medium as explained above selective interaction is preferably involved hydrogen bonding between (PAA-PEO), but the amount of PEI in this system is more (0.6 unit mole) as compared to PEO (0.4 unit mole), therefore polyelectrolyte complexes between (PAA-PEI) is also expected.

The hydrogen bonded complex destabilized with increase in temperature, where as the polyelectrolyte complexes are only slightly affected. The increase of stability constant ***K*** of the complexes with temperature may be attributed to strong electrostatic interaction between (PAA-PEI), it is perhaps due to hydrophobic interaction affect at higher temperature.

The corresponding plots of Ln ***K*** versus 1/T for system III is almost similar to system II except that after destabilization of hydrogen bonded complex, there is a gradual increase in ***K*** (cf. curve B in Fig. 1) which is due to amount of PEI in the complex (i.e. 0.5 unit mole). For system IV and V there is almost continuous fall in ***K*** with increase in temperature. This is in view of the fact that the relative amount of PEO is more (cf. curve C and D in Fig. 1).

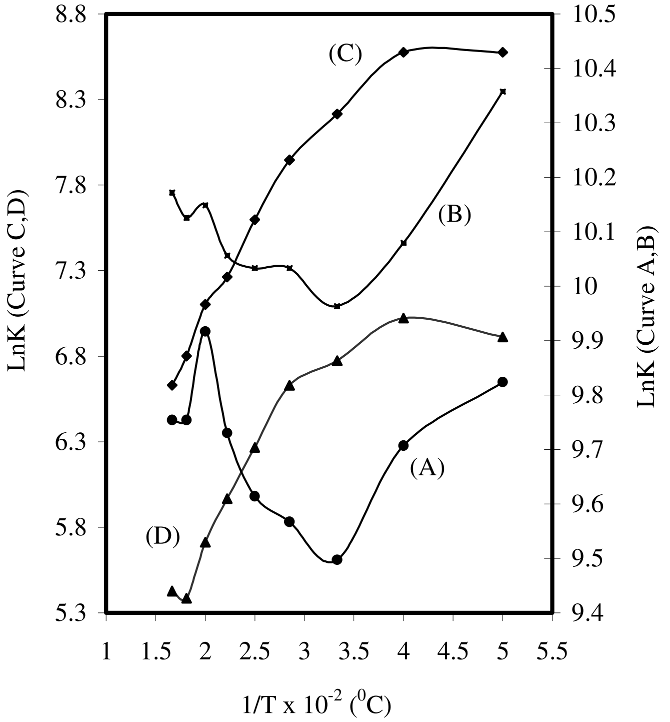


Fig. 1. Relationship of Ln K versus 1/ T for complexation system: (II) (A), (III) (B), (IV) (C), (V) (D).

The enthalpy and entropy change for the intermacromolecular complexation process can be calculated from the stability constant and its temperature dependence.

The stability constant ***K*** and thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) are related with each other by the following equations:

$$\Delta G^0 = -RTLnK \tag{3}$$

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

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

Where ΔG^0 is the change in standard free energy and (R) is the molar gas constant. The standard enthalpy and entropy change for complexation system II-V in acidic medium have been calculated on the basis of the above equation at several temperatures, and the corresponding plots have been shown in Figures 2 and 3.

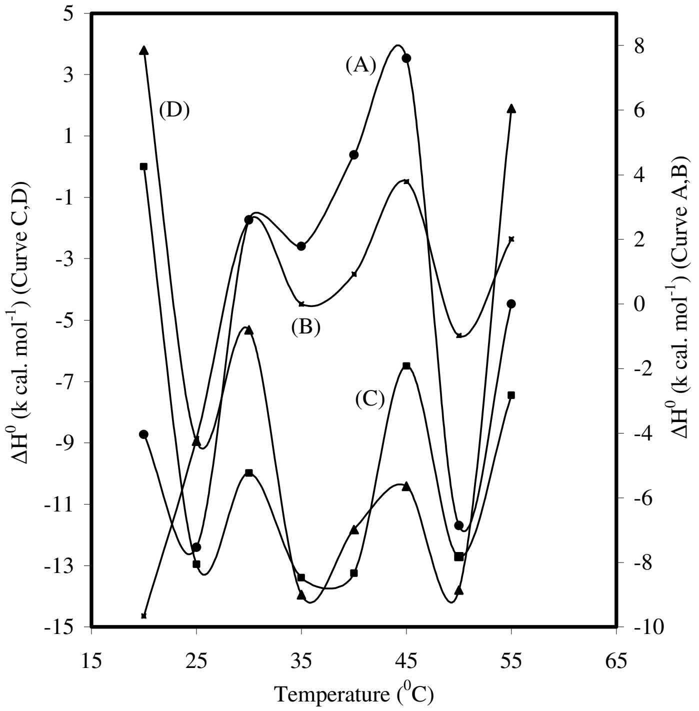


Fig. 2. Temperature dependence of standard enthalpy changes ΔH^0 for complexation system: (II) (A), (III) (B), (IV) (C), (V) (D).

The complexation systems showed an initial fall up to certain temperature and two maxima for ΔH^0 and ΔS^0 for all systems at 30°C and 45°C.

It is evident from figures 2 and 3 that the first maxima values ($\Delta H_{(max.)1}$ and $\Delta S_{(max.)1}$) are in the following order:

II > III > V > IV

However the second maxima values ($\Delta H_{(max.)2}$ and $\Delta S_{(max.)2}$) for system II-V follow a different trend

II > III > IV > V

The maxima values of the four systems are tabulated in Table 3.

As explained above, since in these systems in acidic medium hydrogen bonding interactions are preferable, therefore, during the initial increase in temperature, hydrophobic interactions are likely to reinforce the hydrogen bonded complexes, resulting in abrupt rise in ΔH^0 value [2,10,11,18].

Table 3: The maxima 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})	
		$\Delta H_{(max.)1}$	$\Delta H_{(max.)2}$	$\Delta S_{(max.)1}$	$\Delta S_{(max.)2}$
(II)	1.0 PAA+0.6 PEI+0.4 PEO	2.599	7.6006	27.378	43.0493
(III)	1.0 PAA+0.5 PEI+0.5PEO	2.5851	3.7903	28.259	31.8078
(IV)	1.0PAA+0.4 PEI+0.6PEO	-9.976	-6.4956	-16.3295	-5.8398
(V)	1.0PAA+0.2 PEI+0.8PEO	-5.31	-10.412	-3.9557	-20.632

The largest values of $\Delta H_{(max.)1}$ and $\Delta H_{(max.)2}$ for system II and III is due to larger amount of PEI in these systems, which results in strong electrostatic interactions in addition to strong hydrogen bonding due to hydrophobic interactions.

However, around 30˚C, these interactions get destabilized, and an abrupt fall in ΔH^0 has been observed, (cf. Fig. 2). This may be attributed to abrupt conformational change, which is likely to contribute to overall change in ΔH^0. In system V the height of first maxima is more as compare to system IV, this is perhaps due to conformational change at this temperature in which expected to be more for system V. The second maxima value $\Delta H_{(max.)2}$ observed at 45˚C-50˚C for all complex system. This may be attributed to the relative amount of PEI which make stronger interactions as a result of electrostatic interactions, which are not much affected by temperature and also due to additional enhancement of hydrophobic interactions at higher temperature [2,10,11,16,18,34].

The two maxima observed in ΔS^0 vs. T plots(cf. Fig. 3), for the three complexation systems, also indicated similar trend as in ΔH^0 vs. T curves(cf. compare Fig. 2 with Fig. 3).

The overall change in entropy ΔS^0 and enthalpy ΔH^0 at different temperature is obviously related to: (a) desolvation, (b) complex formation by electrostatic, hydrogen bonding, and (c) configurational change of the complexes as a result of destabilization of interaction forces within reacting pairs at different temperature [2,10]. Therefore, on the basis of arguments put forward earlier, and due to the presence of different proportions of various reacting unit pairs in the respective complexes, one can justify the relative values of $\Delta S_{(max.)1}$ and $\Delta S_{(max.)2}$ for the complexation systems II-V.

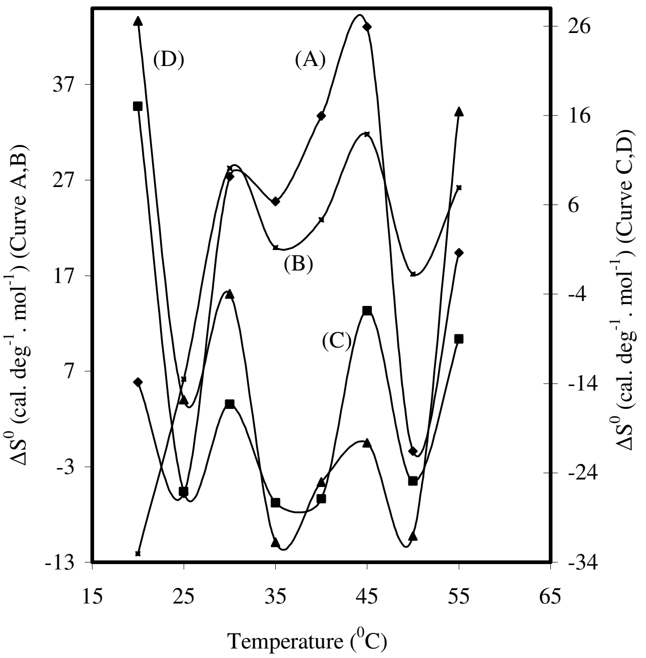


Fig. 3. Temperature dependence of standard entropy changes ΔS^0 for complexation system: (II) (A), (III) (B), (IV) (C), (V) (D).

It may be concluded that selective multicomponent intermacromolecular complex formed in acidic medium as a result of secondary binding forces, such as, hydrogen bonding and electrostatic interactions, gets destabilized in distinct stages at various temperatures. The extent of destabilization of these complexes could be correlated with thermodynamic parameters (e.g. ΔH^0 and ΔS^0), at different temperatures.

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