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Thermodynamic parameters of some multicomponent intermacromolecular complexes in relation to their structure and composition

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SUMMARY

Four component intermacromolecular complexes involving methacrylic acid-acrylamide copolymer, poly(ethylene imine), poly (vinyl pyrrolidone), and poly(methacrylic acid) were prepared. The stability constants and related thermodynamic parameters (e.g. ΔH° and ΔS°) of these complexes were determined at several temperatures. The enthalpy and entropy changes of the systems with temperature have been interpreted in terms of destabilization of the various interacting forces involved in complex formation.

INTRODUCTION

Studies on intermacromolecular complex formation between different macromolecules with complementary binding sites, is an important field in Polymer Science, particularly in view of their potential applications in various industries (1,2). Though, considerable amount of work have been reported in the literature regarding the fundamental studies on polymer-polymer interactions, and applications of intermacromolecular complexes, but detailed thermodynamic studies on these systems are particularly lacking. Keeping this object in mind, we have studied the interaction of a typical acrylic copolymer, e.g. methacrylic acid-acrylamide (MA-AAm) with poly(ethylene imine) (PEI), poly(vinyl pyrrolidone) (PVP) and poly(methacrylic acid) (PMA). Since, both the comonomer units of the copolymer (e.g. MA and AAm) are known to form complexes with each of the above mentioned component polymers (1,2), therefore, by adding varying amounts of component polymers to the acrylic copolymer, one could obtain several multicomponent complexes. The stability constant (K) and related thermodynamic parameters (e.g. ΔH° and ΔS°) of these complexes, will depend on the relative proportion of the various reacting units present in the complexes. In this report, an attempt has been made to correlate the relative enthalpy and entropy changes of the complexes at various temperatures with the possible weakening of different interacting forces between the reacting units of the complexes.

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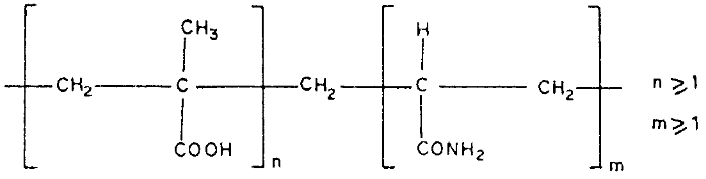
EXPERIMENTAL

Methacrylic acid-Acrylamide Copolymer (MA-AAm) (I)



(I)

The random copolymer(I) was prepared by known methods and characterized (3). It contained 0.58 mol. of MA and 0.42 mol. of AAm units, respectively.

Poly(vinyl pyrrolidone) (PVP) used was of commercial origin (Fluka, Switzerland). The weight average molecular weight ($\bar{M}w$) was calculated from viscosity measurements and was found to be 2.4×10^4 g/mol. (4).

Poly(ethylene imine) (PEI) was supplied by BDH Chemicals Ltd., Poole, England, in the form of 50% viscous aqueous solution (5).

Poly(methacrylic acid) (PMA) was prepared by known methods. $\bar{M}w$ was calculated from viscosity measurements and was found to be 2.5×10^5 g/mol. (6).

Double distilled water was used for all experimental measurements.

The pH measurements of aqueous solutions of the polymer or complex were carried out in a water jacketed cell with "PTA" digital pH meter, using combination electrode. The temperature of sample solution was controlled within ± 0.05°C by circulating thermostatically controlled water.

The pH was measured at copolymer(I) concentration of 5×10^{-3} unit mole/l in absence and presence of stoichiometric concentrations of PVP, PEI and PMA. Complexes did not precipitate at these concentrations.

RESULTS AND DISCUSSION

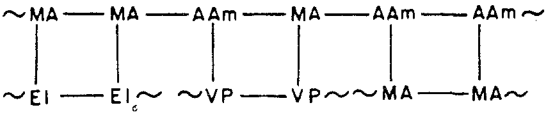
Methacrylic acid-acrylamide (MA-AAm) random copolymer(I) used in this investigation was found to have 0.58 um MA units, and 0.42 um of AAm units. Three multicomponent complexes of MA-AAm copolymer have been prepared by mixing the components in the following stoichiometric proportions :

II : 1 um Cop. MA-AAm + 0.28 um PEI + 0.52 um PVP + 0.20 um PMA

III: 1 um Cop. MA-AAm + 0.10 um PEI + 0.80 um PVP + 0.10 um PMA

IV : 1 um Cop. MA-AAm + 0.48 um PEI + 0.22 um PVP + 0.30 um PMA

The three complexes, II-IV could be represented in general by (V) :



(V)

In these complexes, the nature of interacting forces involved in the various pairs of reacting units (e.g. MA-EI, MA-VP, AAm-VP, AAm-MA) are mostly different (7). For instance, in MA-EI, strong electrostatic interactions, in MA-VP and AAm-MA, strong hydrogen bonding and ion-dipole interactions of different magnitude, and in AAm-VP, weak hydrogen bonding interactions, are involved respectively. Therefore, the relative proportion of these interacting forces in each of these complexes (e.g. II to IV) will depend on the actual composition of the complex. One would expect it to be reflected on the stability constant (K) and related thermodynamic parameters (e.g. ΔH° and ΔS°) of the complexes.

Osada's procedure has been chosen for calculating the stability constant (K) and degree of linkage (θ) (8,9). The degree of linkage, which is defined as the ratio of the binding groups to the total number of potentially interacting groups, could be correlated with K by the following equations (8-10):

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

$$K = \frac{\theta}{C_o(1-\theta)^2}$$

Where C_o is the initial concentration of MA-AAm copolymer (um/l), and $[H^+]$ and $[H^+]_o$ are the proton concentrations in the copolymer solution in presence and absence of complementary polymers (e.g. PEI, PVP and PMA). The value of θ and K have been calculated at several temperatures for the complexaction systems, II to IV. The θ values are presented in Table I.

Table 1: Degree of linkage of complexes at various temperatures

System	Composition of Complex (Unit mole)	Degree of linkage (θ)										
		10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C
II	1.0 Cop.MA-AAm + 0.28 PEI + 0.52 PVP + 0.20 PMA	.583	.583	.602	.637	.698	.725	.760	.791	.826	.862	.880
III	1.0 Cop.MA-AAm + 0.10 PEI + 0.80 PVP + 0.10 PMA	.397	.276	.206	.276	.398	.398	.369	.397	.398	.475	.522
IV	1.0 Cop.MA-AAm + 0.48 PEI + 0.22 PVP + 0.30 PMA	.749	.725	.684	.698	.725	.737	.781	.818	.855	.890	.895

The plots of ln K versus 1/T are shown in Fig.1. The complexation systems II and III, showed an initial fall in ln K upto a certain temperature. The systems II and IV, showed almost a linear increase in ln K beyond 25°C. The nature of curve for system III beyond 25°C was found to be somewhat different. The difference in the nature of ln K vs 1/T curves for the systems II and IV, may be attributed to the presence of relatively larger proportion of electrostatic interactions in these two complexes. These interactions are not much affected at comparatively higher temperature, and simultaneous reinforcement due to hydrophobic interactions may also be possible (2). In complexation systems, where hydrogen bonding predominate (e.g., system III), stability of such complexes will be comparatively less at higher temperature, and one would expect this to be reflected on their stability constant (K), and related thermodynamic parameters.

The thermodynamic parameters (e.g. ΔH° and ΔS°) can be calculated from the temperature dependence of stability constant (K) of the complexes, by using the following relationships (8-10):

$$\Delta F^\circ = -RT \ln K$$

$$d(\ln K)/d(1/T) = -\Delta H^\circ/R$$

$$\Delta S^\circ = -(\Delta F^\circ - \Delta H^\circ)/T$$

where, ΔF° is the standard free energy change and R is the molar gas constant.

The standard enthalpy and entropy change for complexation systems (II to IV) have been calculated on the basis of the above equations at several temperatures, and the corresponding plots have been shown in Figs. 2 and 3. Each of the three complexation systems, (e.g. II-IV), showed three distinct maxima in ΔH° vs T curve, at 27.5°C, 42.5°C and 52.5°C respectively. The maxima value of the three systems are tabulated in Table 2.

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

System	Composition of the complex (Unit Mole)	Maxima observed in ΔH° (K cal. mol.$^{-1}$)			Maxima observed in ΔS° (cal. deg.$^{-1}$ mol.$^{-1}$)		
		$\Delta H_{(max.)1}$	$\Delta H_{(max.)2}$	$\Delta H_{(max.)3}$	$\Delta S_{(max.)1}$	$\Delta S_{(max.)2}$	$\Delta S_{(max.)3}$
II	1.0 Cop.MA-AAm + 0.28 PEI + 0.52 PVP + 0.20 PMA	16.32	12.52	21.31	68.43	55.65	83.07
III	1.0 Cop.MA-AAm + 0.10 PEI + 0.80 PVP + 0.10 PMA	26.08	6.52	19.15	96.77	31.20	70.00
IV	1.0 Cop.MA-AAm + 0.48 PEI + 0.22 PVP + 0.30 PMA	7.84	16.45	25.11	40.89	68.64	95.64

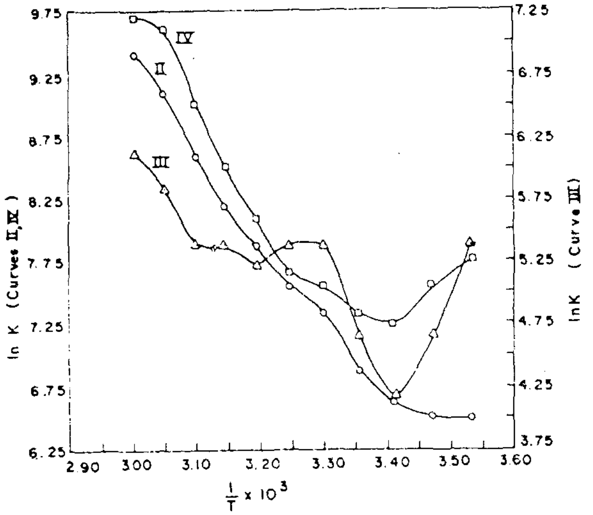


Fig.1. Relationship of In K versus 1/T for complexation systems : II, III and IV.

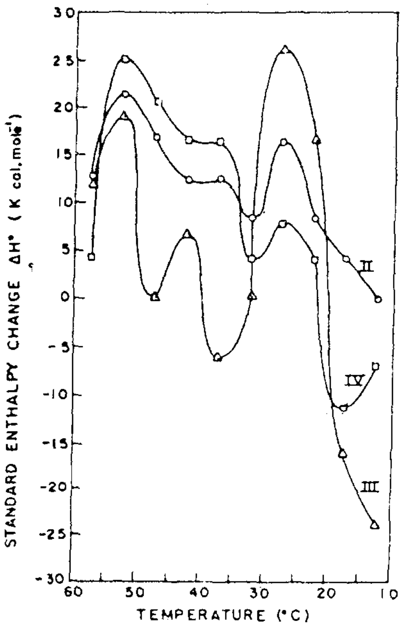


Fig.2. Temperature dependence of standard enthalpy change ΔH°for complexation systems: II, III and IV.

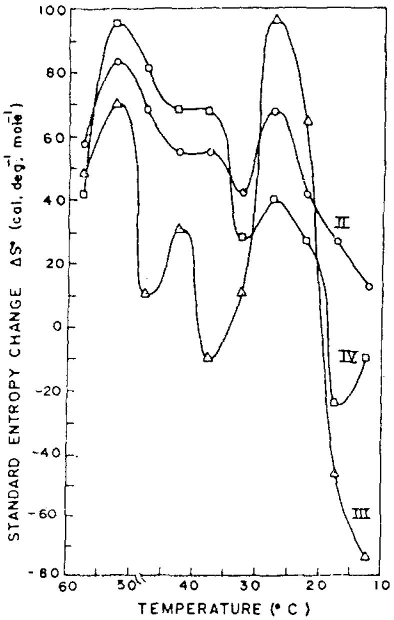


Fig.3. Temperature dependence of standard entropy change ΔS° for complexation system: II, III and IV.

It can be seen from table 2 that $\Delta H^\circ_{(max.)1}$, $\Delta H^\circ_{(max.)2}$ and $\Delta H^\circ_{(max.)3}$, values follow different trends in complexation systems II to IV.

The $\Delta H_{(max.)}1$ values were found to be in the following order :

III > II > IV

This trend is in accordance with the relative proportion of VP units in the respective complexes. (cf. Table-2). Since, in system III, the relative proportion of hydrogen bonding reacting units (e.g. MA-VP and AAm-VP) is largest, therefore, during the initial increase in temperature, hydrophobic interactions are likely to reinforce the hydrogen bonded complexes, resulting in abrupt rise in ΔH° value. However, around 30°C, these interactions get destabilized, and an abrupt fall in ΔH° has been observed (cf. Fig. 2, Curve III). This may be attributed to abrupt conformational change, which is likely to contribute to overall change in ΔH°. When the relative proportion of these hydrogen bonding units (i.e. VP units) are reduced, e.g. in complex II, ΔH° showed a maximum almost at the same temperature, but the height of the maxima (e.g. $\Delta H^\circ_{(max.)1}$) is relatively lower. In system IV, where these h-bounded units (i.e. VP units) are present in still smaller proportion, the height of the first maxima is lowest. In other words, conformational change at this temperature is expected to be largest in III, followed by II and IV. In fact, the absolute value of $\Delta H^\circ_{(max.)1}$, for the three systems are proportional to the amount of VP units in the complexes.

The second maxima value, $\Delta H_{(max.)2}$ observed at 42.5°C, for the three systems, (e.g. II to IV) indicates the following trend (cf. Fig. 2 and Table-2) :

IV > II > III

The subsequent fall or increase in ΔH° beyond 42.5°C, may be attributed to destabilization of MA-AAm bond in the complexes (V). The height of this maxima (e.g. $\Delta H_{(max.)2}$) is again in accordance with the relative amount of PMA added to form the respective complexes (cf. Table-2).

The third and final maxima, $\Delta H_{(max.)3}$ observed at 52.5°C also follows the same trend as in the case of $\Delta H_{(max.)2}$, i.e.

IV > II > III

This is understandable in view of the presence of relatively larger proportion of MA-EI reacting pairs in IV as compared to II, and III contains reltively lesser proportion of such unit pairs compared to II. The complex becomes more stable because electrostatic interactions (e.g. MA-EI) are not much affected by temperature and also due to additional enhancement of hydrophobic interactions at higher temperature (2). The absolute value of $\Delta H_{(max.)3}$ is also proportional to the relative amount of MA-EI reacting unit pairs in the respective complexes (cf. Table-2). Beyond this temperature (e.g. 52.5°C), the fall in $\Delta H°$ is also more pronounced in IV as compared to II and III. This is expected in view of the destabilization of relatively larger number of MA-EI bonds in IV compared to II and III.

The threee maxima observed in $\Delta S°$ vs T plots (cf. Fig.3), for the three complexation systems, also indicated similar trend as in $\Delta H°$ vs T curves (cf. compare Fig. 2 with Fig. 3). The overall change in entropy ($\Delta S°$) at different temperatures is obviously related to : (a) desolvation, (b) complex formation by electrostatic, hydrogen bonding or ion-dipole interactions, and (c) configurational change of the complexes as a result of destabilization of interaction forces within reacting pairs at different temperatures (2). 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 $\Delta S_{(max.)1}$, $\Delta S_{(max.)2}$, and $\Delta S_{(max.)3}$ for the complexation systems II to IV.

It may be concluded that multicomponent intermacromolecular complex formed as a result of secondary binding forces, such as, electrostatic, hydrogen bonding, ion-dipole interactions, gets destabilized in distinct stages at various temperatures. The extent of destabilization of these complexes could be correlated with thermodynamic parameters (e.g. $\Delta H°$ and $\Delta S°$) at different temperatures by suitably changing the proportion of reacting units responsible for electrostatic, hydrogen bonding, and ion-dipole interactions.

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