A comparative study of thermodynamic parameters of interpolymer complexes of an acrylic copolymer and a polymer blend with a polyelectrolyte

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SUMMARY :

Interpolymer complexes of poly (ethylene imine) (PEI) with an acrylic copolymer, and a polymer blend with identical structural units have been prepared. The stability constant (K), degree of linkage (Θ), and related thermodynamic parameters (e.g. $\Delta H°$ and $\Delta S°$) of the two complexes have been found to be widely different. The discrepancy has been interpreted in terms of cooperativity, neighbouring group influence, and sequence combination of comonomer units in the copolymer chain.

INTRODUCTION :

Study of interpolymer interactions has already occupied an unique position in the field of polymer science (1-3). Such interaction products have already found wide applications in industries (4,5) and medicine (6). During the last decade, considerable amount of work have been done in this field both from theoretical and practical point of view (1-3). However, relatively few references have been found in the literature regarding interpolymer complexes of copolymers. Obviously, the complexation involving copolymers will be more complicated, in view of the presence of possible non-interacting units in the copolymer chain, as well as different composition and sequence combination of comonomer units of the copolymer. The author's group has reported extensive study on interpolymer complexes of acrylic copolymers and highlighted the various factors which are likely to influence these systems (7-9). The difference of the previous and the present systems will be discussed elsewhere in the text. For the present investigation, an acrylic copolymer (e.g. methacrylic acid - acrylamide) (MA-AAm) of known composition has been chosen, and a polymer blend has been prepared by mixing the two acrylic homopolymers (e.g. PMA and PAAm) in the same proportion as present in the copolymer. Interpolymer complexes of both copolymer and the polymer blend have been prepared with a typical polyelectrolyte (e.g. poly (ethylene imine)(PEI). Using Osada's procedure (10,11), stability constant (K), degree of linkage (Θ), and related thermodynamic parameters (e.g. $\Delta H°$ and $\Delta S°$) of both the complexes have been determined. A comparative study of these parameters of complexes of the copolymer and the polymer blend indicated a very large variation of the values of these parameters. In this report, an effort has been made to interpret these discrepancies in terms of cooperative interaction, sequence combination of comonomer units, and a possible neighbouring group influence in the copolymer chain.

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EXPERIMENTAL :

Methacrylic acid-Acrylamide Copolymer (MA-AAm) (12)
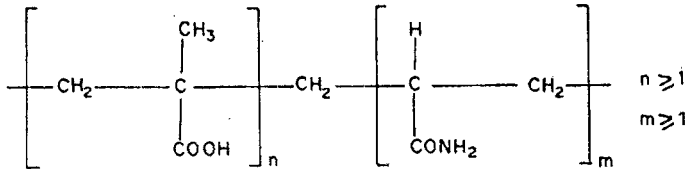
Methacrylic acid (MA) and acrylamide (AAm) monomers were taken in aqueous medium in ratio 9:1 (mole/l) with $K_2S_2O_8$ as initiator and polymerized at 70°C in an atmosphere of nitrogen for 50 minutes. As soon as the product precipitated, it was seperated, dissolved in acetone and reprecipitated with ether. The process was repeated thrice to remove unreacted monomers. The composition of the copolymer was established by electrometric titration techniques (13) and was found to contain 58% and 42% of MA and AAm units respectively.

Poly (methacrylic acid) (PMA) was prepared by known methods. The weight average molecular weight $\overline{Mw}$ was calculated from viscosity measurements and was found to be 2.5×10^5 g/mol. (14).

Poly (acrylamide)(PAAm) was prepared by free radical polymerization of acrylamide monomer using azobisisobutyronitrile (AIBN) as an initiator (15). The polymerization was carried out in acetone medium in N_2 atmosphere at 50°C for 45 minutes. At the end of polymerization, the polymer got seperated as white solid mass that was removed from reaction vessel, washed with acetone and dried to constant weight in vacuo.

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

Double distilled water was used for all experimental measurements.

The pH measurements of aqueous solutions of the copolymer, polymer blend, and their complexes 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 / or polymer blend concentration of 5×10^{-3} unit mole / litre in absence and presence of stoichiometric concentrations of PEI. Complexes did not precipitate at these concentrations.

RESULTS AND DISCUSSION :

Methacrylic acid - acrylamide (MA-AAm) copolymer has been prepared and characterized by known methods (13). The copolymer has been found to have MA and AAm units in the ratio of 0.58 unit mole (um) and 0.42 um, respectively. A polymer blend of the same composition as the copolymer has also been prepared by mixing the two acrylic homopolymers (e.g. PMA

and PAAm) in the ratio of 0.58 um (PMA) : 0.42 um (PAAm). Interpolymer complexes of the copolymer and the polymer blend have been prepared with a typical polyelectrolyte (e.g. poly (ethylene imine)(PEI)), by mixing them in the following stoichiometric proportions in aqueous solution:

Interpolymer Complex I   :   1 um of MA-AAm copolymer + 1 um PEI.
Interpolymer Complex II   :   0.58 um PMA + 0.42 um PAAm + 1 um PEI.

The copolymer as well as the component polymers were above the critical chain length required for the interpolymer complexation. It may be mentioned that the main difference between the present systems and the systems studied earlier, is the nature of secondary forces between the interacting pairs of units. In the earlier work (7-9), on stability constants and thermodynamic parameters of acrylic copolymer complexes of PVP, PAAm and PEO, only hydrogen bonding and ion-dipole interactions were involved, whereas, in the present systems coulombic (electrostatic) interactions are predominant.

In order to give a quantitative analysis of cooperative interactions, Osada developed a method of determining stability constant both for hydrogen bonding (10,11) and polyelectrolyte (16) complexes. Since, we have used successfully Osada's method for determining stability constant and related thermodynamic parameters of hydrogen bonding complexes, therefore, we thought the same method could also be used for polyelectrolyte complexes as well. The physical significance of stability constant (K) of such complexes could be explained on the basis of several contributing factors, such as free energy change through (i) electrostatic interaction of specific groups, (ii) hydrophobic interactions, (iii) ion-dipole and hydrogen bonding interactions. The free energy changes due to all these factors, naturally contribute to the absolute value of stability constant (K). It may also be mentioned that the system (II), in fact, is a mixture of two homopolymer complexes (e.g. (i) PMA + PEI, and (ii) PAAm + PEI). In the first complex (i), only coulombic interactions are involved, and in the second (ii), hydrogen bonding and ion-dipole interactions are involved. Therefore, the overall stability constant (K) of system (II), may be considered as the sum of the contributions from each of the two homopolymer complexes (e.g. (i) and (ii)). Osada's method (10, 11, 16) is known to be valid for both the types of complexes.

Keeping these facts in mind, we have used Osada's procedure (10,11,16) to determine the stability constant (K), degree of linkage (Θ), and the other thermodynamic parameters (e.g. standard enthalpy change ΔH°, and standard entropy change ΔS°) of the two interpolymer complexes (e.g. I and II). The degree of linkage (Θ), which is defined as the ratio of binding groups to the total numbers of potentially interacting groups, could be correlated with K by the following equations:

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

$$K = \frac{\Theta}{C_0 (1-\Theta)^2}$$

where C_0 is the initial concentration of the copolymer/or polymer blend, and (H^+) and $(H^+)_0$ are the proton concentrations in the copolymer/or polymer blend solution in the presence and absence of complimentary polymer (e.g. PEI). The value of Θ and K have been calculated at several temperatures for the complexes I and II. The ln K values of the two complexes have been plotted against I/T, and shown in Fig. I.

The two curves (i.e. for the copolymer complex and the polymer blend complex), showed an absolutely contrasting behaviour (cf. curve I and II of Fig.1). In the case of copolymer complex, ln K falls with increasing temperature, and in the case of polymer blend complex, ln K increases with increase of temperature. This may possibly be interpreted on the following lines: The secondary binding forces involved in the interaction of the two comonomer units (e.g. MA and AAm) of the copolymer with PEI, are electrostatic and ion-dipole interactions, respectively. On increasing the temperture, one would expect destablization of the copolymer complex due to cooperative character in such interactions, and neighbouring group influence. A fall in ln K values with temperature could thus be anticipated.

However, in the case of interpolymer complex II of the polymer blend, ln K values increases with temperature (cf. curve II of Fig. 1). In the case of polymer blend, each pair of interacting chains (e.g. PMA + PEI and PAAm + PEI), is likely to contribute towards the stability constant of the complex (e.g. II). the electrostatic interactions involved in (PMA + PEI), which is not very much affected by increase of temperature, as well as enhanced hydrophobic interactions, will contribute to the increased stability of the complex II with temperature. The contribution of the other pair of chains (e.g. PAAm + PEI) towards stability will be less due to its relatively lower proportion in the polymer blend. Moreover, in the polymer blend complex [e.g. (PMA + PEI), (PAAm + PEI)], the effects of cooperativity and neighbouring group influence will be much less compared to the interpolymer complex of the copolymer (e.g.I). This is due to the fact that system II is a mixture of two homopolymer complexes, where all the neighbouring groups are indentical, whereas in copolymer complex system I, dissimilar neighbouring groups [e.g. MA and AAm] are present in the copolymer chain, which may be have its influence on subsequent interactions. In other words, cooperative interaction is likely to be more favourable in copolymer than in homopolymer chains.

Therefore, the increase of ln K values with temperature for complex II, could be anticipated. It may also be pointed out that the absolute values of ln K of the polymer blend complex (e.g. II) is much grater than the copolymer complex (e.g. I) at all temperatures. This observation is also in conformity with the above arguments.

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

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

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

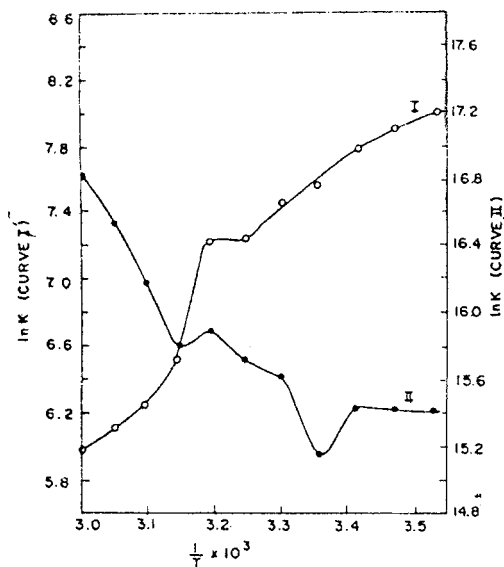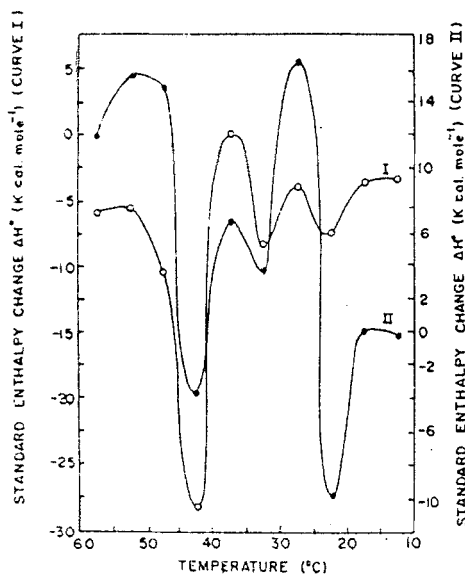Fig.1. Relationship of ln K vs 1/T for complexation systems, I & li.

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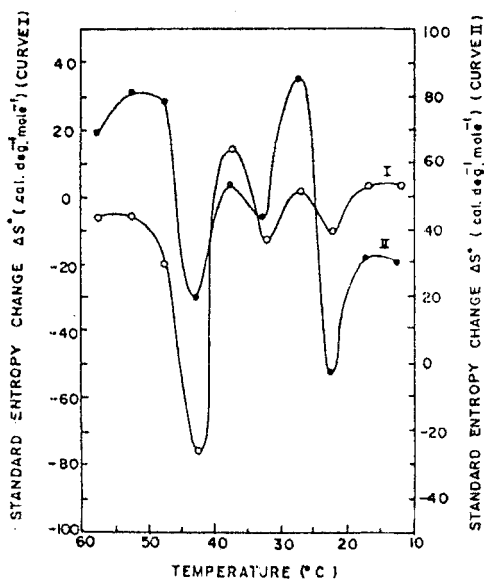

Fig.3. Temperature dependence of standard entropy change, ΔS° for complexation system I and II.

The standard enthalpy and entropy change (ΔH° and ΔS°) for the interpolymer complexes I and II, have been calculated on the basis of above equations at several temperatures, and the corresponding plots have been shown in Figs. 2 and 3, respectively. The ΔH° vs T curve for both the complexes, I and II, showed four distinct peaks (cf. curve I and II of Fig.2). However, there are only two interacting pairs in both the complexes (e.g. MA-EI and AAm-EI). Obviously, it indicates that the two pairs of interacting units are complexing in 2:1 and 1:1, unit mole ratio (umr). Some evidence of this interpretation will be provided in the later part of the discussion on electrochemical studies. The observed values of ΔH° and ΔS° at the four maxima in ΔH° vs T, and ΔS° vs T curves are summarized in Table 1.

Table 1 : The maximum values of ΔH° and ΔS° observed for complexation systems, I and II (cf Figs. 2 and 3)

System	Composition of the complex (unit mole)	Maxima observed in ΔH° [K cal. mole^{-1}]				Maxima observed in ΔS° (cal.deg.$^{-1}$ mole^{-1})			
		ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔS_1	ΔS_2	ΔS_3	ΔS_4
I	1.0 Cop.MA-AAm+ 1.0 PEI	-3.5	-3.75	0.5	-5.2	4	2	15	-5
II	0.58 PMA+0.42 PAAm 1.0 um PEI	0	16.5	6.8	16	32	85	54	81

The four maximas (e.g. ΔH_1, ΔH_2, ΔH_3 and ΔH_4), may be assigned to the destabilization of the following interacting pairs in different stoichiometries: AAm-EI (2.1), AAm-EI (1:1), MA-EI (2:1) and MA-EI(1:1), respectively. On comparing the values of ΔH_1, ΔH_2, ΔH_3 and ΔH_4 of the copolymer complex (I) with that of the polymer blend complex (II), a striking disparity could be seen (cf. Table-I) In the case of copolymer complex (I), these values are mostly small and negative, whereas the corresponding values for the polymer blend complex (II), are comparatively much higher and positive. Similar discrepancies could also be seen in ΔS_1, ΔS_2, ΔS_3 and ΔS_4 values for the complexes I and II (cf. Fig.3).

The difference in the absolute values of ΔH_1 .... ΔH_4 and ΔS_1 .... ΔS_4, for the complexes I and II, could be interpreted on the following lines: The total enthalpy change during complex formation (ΔH_M), could be considered as the sum of ΔH_A (desolvation), ΔH_B (complex formation by secondary binding forces) and ΔH_C (conformational change as a result of complex formation) (17), i.e.

$$\Delta H_M = \Delta H_A + \Delta H_B + \Delta H_C$$

It is most likely that the individual contribution of ΔH_A, ΔH_B and ΔH_C for the complexes I and II, will be different, and obviously, the overall ΔH_M for the complexes I and II, will also differ. Thus, the very large differences in the observed values of ΔH_1 ....ΔH_4 and ΔS_1 ....ΔS_4 for

the copolymer complex (I) and the polymer blend complex (II) is understandable. Moreover, the neighbouring group influence as well as particular sequence combination of comonomer units in the copolymer chain, may also contribute towards the absolute values of ΔH° and ΔS°, at the various stages of destabilization of the complexes.

Some of the interpretations given in the thermodynamic studies, could possibly be substantiated from electrochemical studies during complex formation. In Figs. 4 and 5, are presented the variations of specific conductance and pH of the copolymer and the polymer blend solutions on the addition of PEI in small instalments, respectively.
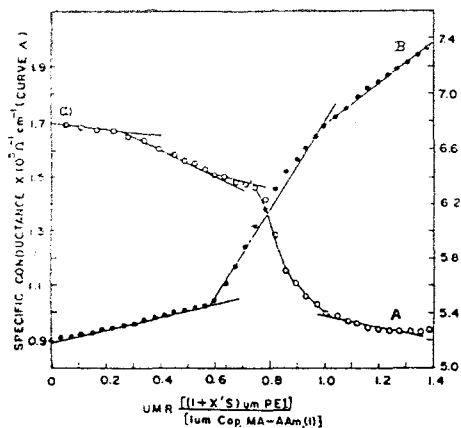

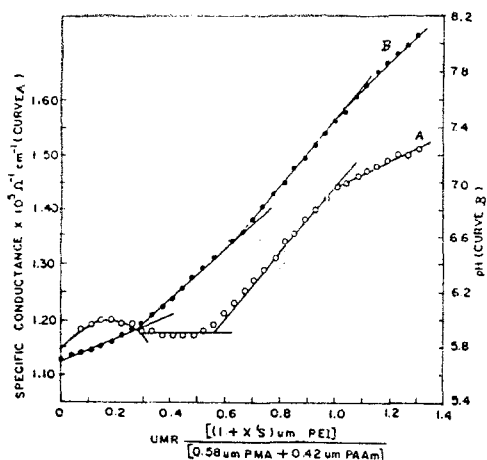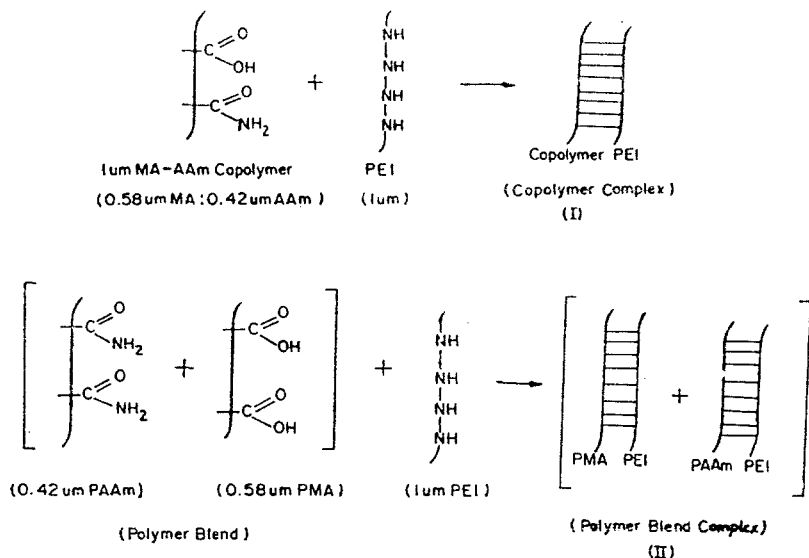Fig.4. Variation of, (A) Specific conductance, and (B) pH with unit mole ratio for complex I.

Fig.5. Variation of, (A) specific conductance, and (B) pH with unit mole ratio for complex II.

The conductance curve during copolymer – PEI complex formation, indicated four distinct breaks, which could be assigned to the formation of MA-EI(2:1), MA-EI (1:1), AAm-EI (2:1), and AAm-EI (1:1) (umr) complexes (cf. curve A of Fig.4). However, the corresponding pH curve, indicated only two distinct breaks which correspond with the formation of MA-EI (1:1), and AAm-EI (1:1) (umr), complexes (cf. curve B of Fig.4). The fall in conductance of the copolymer solution throughout the addition of PEI, indicates the formation of compact structure during complex formation (cf. curve A of Fig.4). Interestingly enough, the conductance curve during complex formation of polymer blend with PEI, did not indicate any such fall in conductance at any stage. Obviously, the neighbouring group influence which will be much less in the polymer blend compared to the copolymer, may possibly be responsible for the difference in the nature of conductance curves of the two complexes (cf. compare curve A of Figs. 4 and 5).

On the basis of arguments based on the various observations, the following scheme may be suggested to explain the mode of interaction of the copolymer (MA-AAm), and the polymer blend (PMA + PAAm) with PEI.

lum MA-AAm Copolymer   PEI   Copolymer PEI

(0.58umMA:0.42umAAm)   (lum)   (Copolymer Complex)

(I)

(0.42 um PAAm)   (0.58um PMA)   (lum PEI)   PMA PEI   PAAm PEI

(Polymer Blend)   (Polymer Blend Complex)

(II)

In conclusion, it can be said that thermodynamic parameters of interpolymer complexes of PEI with a copolymer, and a polymer blend with identical structural units, are entirely' different. This is attributed to the effects of cooperativity, neighbouring group influence, and particular sequence combination of comonomer units in the copolymer chain.

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