Thermodynamic studies on some copolymer–homopolymer–polyelectrolyte interactions

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Some multicomponent interpolymer complexes of methacrylic acid–acrylamide copolymer were prepared by adding polyethyleneimine and polyvinylpyrrolidone in different sequences. The stability constants, and enthalpy and entropy changes of the systems at several temperatures were determined. Interpretations have been sought in terms of the various interacting forces involved in complex formation.

(Keywords: stability constant; thermodynamic parameters; multicomponent complexes; copolymer; polyelectrolyte; non-ionic polymers)

INTRODUCTION

Studies on the interactions between copolymers and homopolymers, as well as between non-ionic polymers and polyelectrolytes, have been extensively reported in the literature[1,2]. However, most of the information available on intermacromolecular complexes is qualitative in nature because of the lack of a suitable theory to interpret the experimental observations[3,4]. Moreover, very little information is available regarding the formation and stability of three-component intermacromolecular complexes. Keeping this in mind, some typical three-component intermacromolecular complexes have been prepared by interacting methacrylic acid–acrylamide (MA-AAm) copolymer with polyethyleneimine (PEI) and polyvinylpyrrolidone (PVP). The system is interesting in view of the fact that both the comonomer units (e.g. MA and AAm) of the copolymer are known to form interpolymer complexes with PEI and PVP[5–7]. Thus, by adding stoichiometric quantities of PEI and PVP in different sequences, one could complex both the comonomer units of the copolymer with either PEI or PVP. Since the nature of the interacting forces between the two comonomer units (e.g. MA and AAm) with PEI and PVP are different[8], one could expect them to influence the stability of these complexes. Determination of stability constants and related thermodynamic parameters [e.g. the change in standard free entropy (ΔS°) and change in standard free enthalpy (ΔH°)], as well as studying the variations of electrochemical properties (e.g. pH, conductance, etc.) during interaction of component polymers may possibly help in understanding the mechanism of complex formation. In this report, an attempt has been made to estimate the degree of linkage (θ), the stability constant (K) and related thermodynamic parameters (e.g. ΔS° and ΔH°) for some of these three-component interpolymer complexes.

EXPERIMENTAL

Polyvinylpyrrolidone

PVP was supplied by Fluka (USA) in the form of a white crystalline powder. The weight average molecular weight ($\bar{M}_w$) of the polymer was calculated from viscosity measurements using the following equation[9]:

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

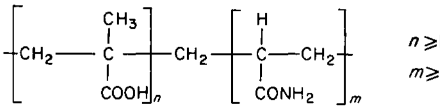
where $[\eta]$ is the intrinsic viscosity and $\bar{M}_w = 2.4 \times 10^4$.

Polyethyleneimine

PEI was supplied by BDH Chemicals Ltd (Poole, UK) in the form of a 50% viscous aqueous solution.

Methacrylic acid–acrylamide copolymer

The MA–AAm copolymer (I) was prepared by free radical polymerization using $K_2S_2O_8$ as initiator[10]. An aqueous medium of MA and AAm monomers (9:1 w/w ratio) with 0.1% $K_2S_2O_8$ was heated in a nitrogen atmosphere at 70°C for 50 min. As soon as the product precipitated, it was separated and dissolved in acetone and reprecipitated with ether. The process was repeated three times to remove unreacted monomers. The copolymer composition was determined by electrometric titration techniques and was found to contain MA and AAm in a 0.56:0.44 mole ratio (i.e. 56% MA and 44% AAm).



$$\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{COOH}}{\mathrm{C}}}\right]_n-\mathrm{CH_2}-\left[\overset{\mathrm{H}}{\underset{\mathrm{CONH_2}}{\mathrm{C}}}-\mathrm{CH_2}\right]_m \qquad n \geqslant 1,\ m \geqslant 1$$

I

Solvent

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

Measurement of pH

The measurement of the pH of various solutions of the copolymer or complex was carried out in a water-jacketed cell with a PTA digital pH meter using a combination electrode. The temperature of the sample solution was controlled within ±0.05°C by circulating thermostatically controlled water.

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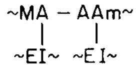
The pH was measured at a copolymer concentration of 5×10^{-3} unit mole (um) l^{-1} in the absence and presence of an equal concentration of PVP and PEI. Complexes did not precipitate at these concentrations.

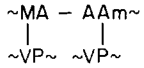
RESULTS AND DISCUSSION

Poly(methacrylic acid) (PMA) homopolymer is known to interact with PEI and PVP, respectively, to form interpolymer complexes[6,8]. It is also reported that AAm units when present in a copolymer can interact with PEI and PVP, perhaps due to neighbouring group influence[11]. Keeping this in mind, an acrylic copolymer (e.g. I) was prepared and characterized[10]. Since, both the component polymers (e.g. PEI and PVP) are known to form complexes with each of the comonomer units (e.g. MA and AAm), a series of three-component interpolymer complexes could be prepared by adding in different sequences stoichiometric quantities of PEI and PVP. The following 1:1 (unit molar ratio) interpolymer complexes have been prepared in aqueous solution:



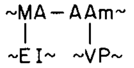
$$\begin{matrix}\sim\mathrm{MA} - \mathrm{AAm}\sim \\ | \quad\quad | \\ \sim\mathrm{EI}\sim \ \sim\mathrm{EI}\sim\end{matrix}$$

II



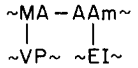
$$\begin{matrix}\sim\mathrm{MA} - \mathrm{AAm}\sim \\ | \quad\quad | \\ \sim\mathrm{VP}\sim \ \sim\mathrm{VP}\sim\end{matrix}$$

III



$$\begin{matrix}\sim\mathrm{MA} - \mathrm{AAm}\sim \\ | \quad\quad | \\ \sim\mathrm{EI}\sim \ \sim\mathrm{VP}\sim\end{matrix}$$

IV



$$\begin{matrix}\sim\mathrm{MA} - \mathrm{AAm}\sim \\ | \quad\quad | \\ \sim\mathrm{VP}\sim \ \sim\mathrm{EI}\sim\end{matrix}$$

V

It is known that the interacting forces involved in the four pairs of monomer units (e.g. MA–EI, MA–VP, AAm–EI and AAm–VP) are all different[8]. For instance, in MA–EI strong electrostatic interactions, in MA–VP hydrogen bonding interactions, and in AAm–EI and AAm–VP, weak electrostatic and weak hydrogen bonding interactions, respectively, are involved. On the basis of these arguments, one could predict that the K values and the related thermodynamic parameters (e.g. ΔH° and ΔS°) of the four complexes (II–V) will be different.

The procedure chosen for the calculation of θ and K of the interpolymer complex is the same as that used in an earlier paper[3]. The degree of linkage is defined as the ratio of the binding groups to the total number of potentially interacting groups, and is related to K of the interpolymer complex by the following equation[3,12,13]:

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

$$K = \frac{\theta}{c_0(1-\theta)^2}$$

where c_0 is the initial concentration of polycarboxylic acid (mol l^{-1}), and $[\mathrm{H}^+]$ and $[\mathrm{H}^+]_0$ are the proton concentrations in the polycarboxylic acid solution in the presence and absence of proton-accepting polymer, respectively.

The values of θ and K have been determined at several temperatures for the complexation systems II–V and are presented in *Table 1*.

The corresponding plots of ln K *versus* $1/T$ are shown in *Figure 1*. For systems II, IV and V K increases abruptly in the temperature range of 10–30°C (cf. curves II, IV and V in *Figure 1*). However, in the case of system III, the increase in K is more or less linear (cf. curve III in *Figure 1*). The plots of ln K *versus* $1/T$ also indicate two distinct inflections in the temperature ranges 20–30°C and 40–50°C (cf. curves II, IV and V in *Figure 1*). This perhaps indicates the two distinct stages of interactions in the three-component complexation systems. Of course, no such inflection was observed in the case of system III (cf. curve III in *Figure 1*).

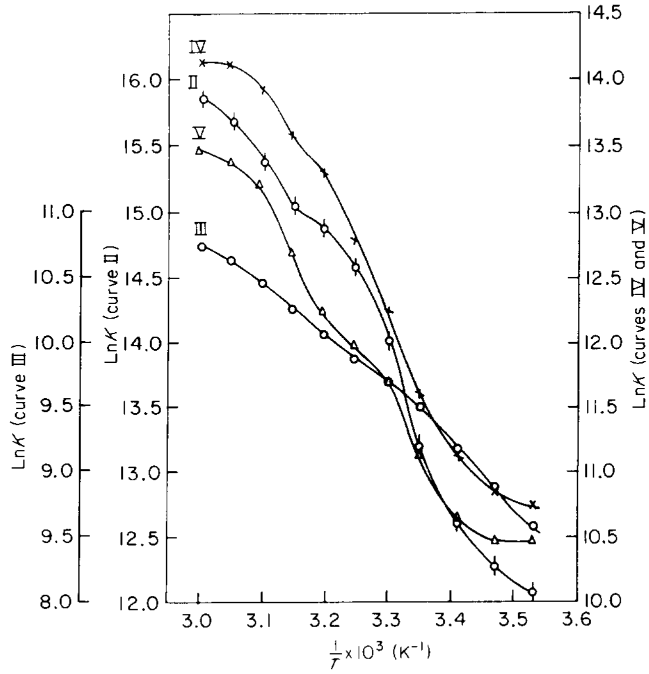


Figure 1 Relationship between ln K *versus* $1/T$ for various complexation systems: (II) 1 um MA–AAm + 1 um PEI; (III) 1 um MA–AAm + 1 um PVP; (IV) 1 um MA–AAm + 0.56 um PEI + 0.44 um PVP; (V) 1 um MA–AAm + 0.56 um PVP + 0.44 um PEI

Table 1 Degree of linkage of the complexes at various temperatures

Complexation systems	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C
II 1 um MA–AAm + 1 um PEI	0.967	0.970	0.975	0.981	0.987	0.990	0.992	0.993	0.994	0.995	0.995
III 1 um MA–AAm + 1 um PVP	0.826	0.848	0.868	0.885	0.895	0.904	0.913	0.921	0.928	0.934	0.939
IV 1 um MA–AAm + 0.56 um PEI + 0.44 um PVP	0.937	0.920	0.948	0.958	0.970	0.977	0.982	0.984	0.987	0.988	0.988
V 1 um MA–AAm + 0.56 um PVP + 0.44 um PEI	0.928	0.928	0.934	0.948	0.960	0.965	0.970	0.976	0.981	0.983	0.983

The values of ln K for the systems II–V at 25°C and 45°C (i.e. where inflections have been observed), are in the following order: II > IV > V > III.

This trend could be anticipated in view of the fact that in system II, interaction in both pairs of monomer units (e.g. MA–EI and AAm–EI) involves electrostatic forces, whereas in system IV, interactions involve both electrostatic forces and weak hydrogen bonding among the two reacting unit pairs (e.g. MA–EI and AAm–VP). The relative stability of IV being greater than V may also be due to the higher proportion of MA units in the copolymer, resulting in a larger contribution of strong electrostatic forces towards complex formation. In system V, the two pairs of reacting units (e.g. MA–VP and AAm–EI) form a complex through hydrogen bonding and ion-dipole interactions, and by weak electrostatic forces. In contrast, in system III, the secondary interacting forces are hydrogen bonding and ion-dipole interactions for the MA–VP pair, and very weak hydrogen bonding for the AAm–VP pair[8]. The resultant effect of these interacting forces between the various pairs of reacting units is reflected in the K values of these three-component complexes.

The thermodynamic parameters (e.g. ΔS° and ΔH°) for the interpolymer complexation process can be calculated from K and its temperature dependence[3,4]:

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

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

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

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

The standard enthalpy and entropy changes for the complexation systems (II–V) have been calculated on the basis of the above equations; the corresponding values have been plotted against temperature in *Figures 2* and *3*. *Figures 2* and *3* indicate two maxima for ΔH° and ΔS° for systems II–V. It is evident from *Figures 2* and *3* that the first maxima values (ΔH_1° and ΔS_1°) are in the following order: II > IV > V > III. The trend is the same as that observed in the case of the K values for the complexes II–V. However, the second maxima values (ΔH_2° and ΔS_2°) for the systems II–V follow an entirely different trend: V > IV > II > III.

The two different trends observed for the two maxima in ΔH° and ΔS° are obviously related to the difference in the nature of interactions involved in the two pairs of reacting units for each system. The total enthalpy change (ΔH_M) during interpolymer complex formation consists of three basic steps, e.g. desolvation (ΔH_1), complex formation by electrostatic, ion-dipole or hydrogen bonding interactions (ΔH_2) and conformational change involving complex formation (ΔH_3). Therefore, ΔH_M is the sum of these contributions[1]:

$$\Delta H_\mathrm{M} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Since complex formation in each of the systems (II–V) involves two different pairs of reacting units, contribution due to each of the above factors will be different for the respective stages of interaction in a given system. Therefore the difference in the trend of the first and second maxima for the systems, as well as the difference in their absolute values, could possibly be interpreted in terms of specific interaction forces involved in a particular pair of reacting units. It may also be mentioned that as the temperature is increased, destabilization of the hydrogen bond takes place, whereas coulombic forces are not affected appreciably[1]. Therefore, at higher temperature, the contribution due to conformational change towards ΔH° and ΔS°, will perhaps be more in the case of V compared to IV, as the former contains relatively more hydrogen-bonded complex than the latter. Due to very strong electrostatic interactions, conformational change in II is expected to be comparatively low at higher temperature, whereas in III the hydrogen-bonded complex may completely break down at higher temperature. Thus the observed trend of the second maxima could be anticipated. Of course, hydrophobic interactions are likely to play a significant

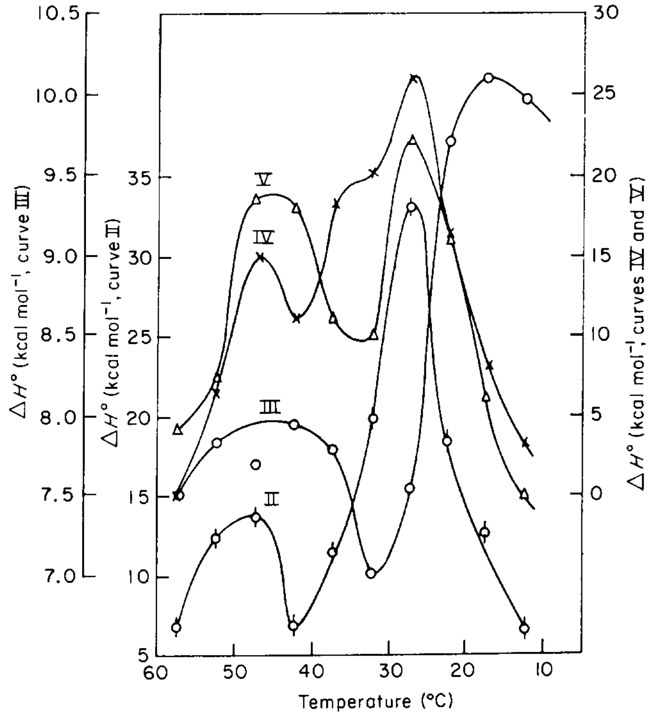


Figure 2 Temperature dependence of standard enthalpy changes for complexation systems. Systems II–V as in *Figure 1*

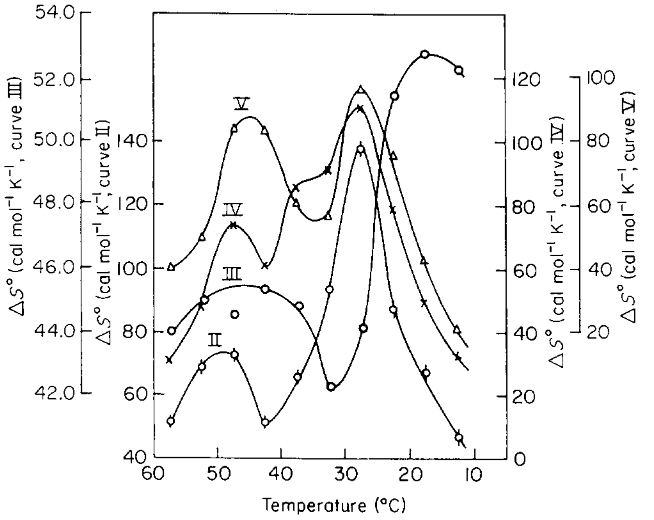


Figure 3 Temperature dependence of the standard entropy changes for complexation systems. Systems II–V as in *Figure 1*

Table 2 Breaks observed and probable stoichiometries assigned to various complexes

Complexation	Breaks (umr)^a	Probable stoichiometry/and unreacted units in the complex
1 um MA-AAm + 1 um PEI + excess PVP (*Figure 4*)	0.55	1:1 (MA units of copolymer:PEI)
	1.02	1:1 (AAm units of copolymer:PEI)
1 um MA-AAm + 1 um PMA + 1.5 um PEI + excess PVP (*Figure 5*)	0.43	1:1 (AAm units of copolymer: MA units of PMA)
	1.00	(MA units of copolymer and unreacted PMA)
	2.10	1:1 (MA units of copolymer and unreacted PMA:PEI)
	2.55	Excess PVP

^{a}umr, unit mole ratio

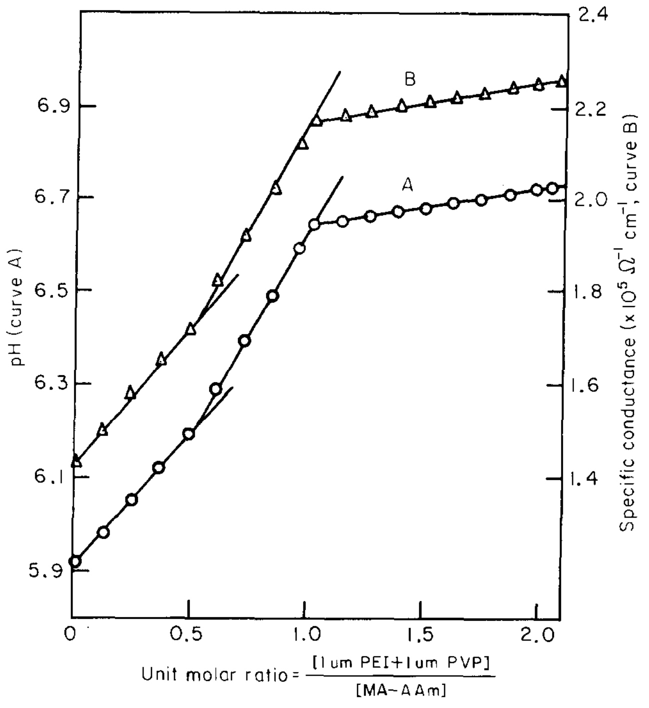


Figure 4 Variation of pH and conductance with unit mole ratio for the MA-AAm/PEI/PVP complexation system: (A) pH; (B) conductance

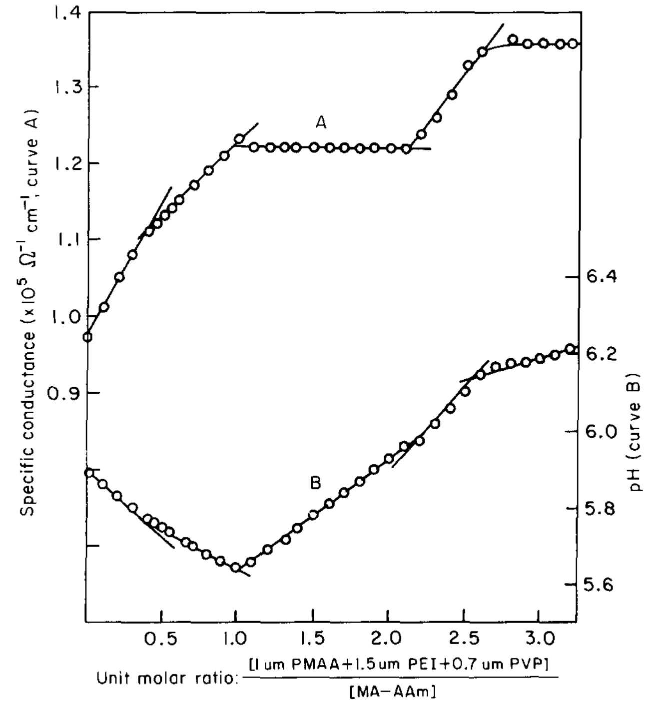


Figure 5 Variation of conductance and pH with unit mole ratio for the MA-AAm/PMA/PEI/PVP complexation system: (A) conductance; (B) pH

role at higher temperature. Also at higher temperature, one could expect greater co-operative interactions in polyelectrolyte-type complexes compared to hydrogen bonding complexes[1].

In order to substantiate some of these arguments, some substitution reactions were carried out using standard electrochemical techniques[14]. *Figure 4* shows variations of pH and conductance of 1 um MA-AAm copolymer solution on addition of 1 um PEI and excess PVP solution in small instalments. The MA-AAm copolymer has 0.56 m and 0.44 m MA and AAm units, respectively. Two distinct breaks in both the curves (cf. curves A and B in *Figure 4*), indicated the interaction of MA and AAm with PEI, respectively. Subsequent addition of excess PVP solution did not show any break in the titration curve, which obviously indicates that the relative complexation ability of PEI is greater than PVP with respect to MA and AAm units.

Further unequivocal proof of this substitution reaction has been obtained from the following observation. The variations of pH and conductance of 1 um MA-AAm copolymer solution on addition of 1 um PMA, 1.5 um PEI and excess PVP are shown in *Figure 5*. The distinct breaks observed at various unit mole ratios, and the probable stoichiometries assigned to various complexes are summarized in *Table 2*. It is evident from the substitution reactions that PVP is not able to replace PEI in either of the comonomer units in the copolymer chain.

It may be concluded that K of the three-component interpolymer complexes depends on the relative contribution of each of the interacting forces, e.g. hydrogen bonding, electrostatic, ion-dipole and hydrophobic interactions. The temperature dependence of K and other related thermodynamic parameters is influenced by the specific type of reacting units involved in the formation of a particular complex.

REFERENCES

1 Tsuchida, E. and Abe, K. *Adv. Polym. Sci.* 1983, **45**, 1
2 Bekturov, E. A. and Bimendina, L. A. *Adv. Polym. Sci.* 1981, **41**, 99
3 Osada, Y. *J. Polym. Sci., Polym. Chem. Edn* 1979, **17**, 3485
4 Osada, Y. and Sato, M. *J. Polym. Sci., Polym. Lett. Edn* 1976, **14**, 129
5 Chatterjee, S. K., Yadav, D., Ghosh, S. and Khan, A. M. *J. Polym. Sci., Polym. Chem. Edn* 1989, **11**, 3855

6 Chatterjee, S. K., Sethi, K. R. and Yadav, D. *Polymer* 1987, **28**, 519

7 Chatterjee, S. K. and Malhotra, A. *Angew. Makromol. Chem.* 1984, **126**, 153

8 Abe, K., Koida, M. and Tsuchida, E. *Macromolecules* 1977, **10**, 1259

9 Levy, G. B. and Frank, H. P. *J. Polym. Sci.* 1955, **17**, 247

10 Pinner, S. H. *J. Polym. Sci.* 1953, **10**, 379

11 Chatterjee, S. K. and Malhotra, A. *J. Macromol. Sci. Chem. Edn* 1984, **A21**, 765

12 Chatterjee, S. K., Yadav, J. B. and Sethi, K. R. *Angew. Makromol. Chem.* 1985, **130**, 55

13 Chatterjee, S. K., Yadav, J. B. and Sethi, K. R. *Angew. Makromol. Chem.* 1987, **154**, 121

14 Chatterjee, S. K., Sethi, K. R. and Pachauri, L. S. *J. Polym. Sci., Polym. Chem. Edn* 1983, **21**, 1045