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INTERPOLYMER ASSOCIATION OF ACRYLAMIDE COPOLYMERS WITH POLY(ETHYLENEIMINE): STABILITY, THERMODYNAMIC PARAMETERS, AND THEIR CORRELATION WITH THE COPOLYMER MICROSTRUCTURE

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INTERPOLYMER ASSOCIATION OF ACRYLAMIDE COPOLYMERS WITH POLY(ETHYLENEIMINE): STABILITY, THERMODYNAMIC PARAMETERS, AND THEIR CORRELATION WITH THE COPOLYMER MICROSTRUCTURE

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Key Words: Interpolymer Complexation, Acrylamide, Copolymer, Poly(ethyleneimine), Thermodynamic Studies, Osada's Method

ABSTRACT

Acrylamide/vinyl acetate and acrylamide/vinyl propionate copolymers were prepared by solution polymerization using benzoyl peroxide as the initiator. The copolymer composition was determined from the percent nitrogen in the copolymers.

The stability constants and related thermodynamic parameters (e.g., ΔG° , ΔH° , and ΔS°) of the interpolymer complexes with Poly(ethyleneimine) were determined by using Osada's method. These parameters have been correlated with the sequence distribution of monomer units in the copolymer chains which were obtained from $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The sequence distribution of the comonomer units in the copolymer chains influence

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the association between the copolymers and the polyelectrolyte which is reflected on the stability of the interpolymer complexes.

INTRODUCTION

In recent years, the study of interpolymer complexations has gained considerable importance due to the fact that the phenomenon occurring *in vivo* are closely related to the complexation of biopolymers. Therefore, study of interpolymer complexation of synthetic polymers of simpler structure is helpful for understanding the occurrence of similar processes in living cells [1-3]. Intermacromolecular complexation also offers new and effective ways to develop polymer materials with high performance. Experimental studies reveal that the tacticity and sequence distribution of the polymer chains affect the conformation of the chains and the probability of contact between the interacting sites [4, 5], both of which will inevitably influence the stability and various other properties of the interpolymer complexes.

Poly(vinyl acetate) and copolymers of vinyl acetate are widely used in water based paints, adhesives, paper coating and non woven binders. Homopolymers and copolymers of vinyl propionate are used for surface coating applications. The influence of monomer sequence distribution (determined by NMR spectroscopy) on the stability and thermodynamic properties of their interpolymer complexes of Poly(ethyleneimine) (PEI) with acrylamide/methyl acrylate [6] and acrylamide/alkyl acrylate [7] (alkyl = ethyl and butyl) copolymers has been analyzed by us previously. In this article, we report the stability and thermodynamic parameters of the interpolymer complexes of PEI with acrylamide/vinyl acetate (A/V) and acrylamide/vinyl propionate (A/P) copolymers. These systems were studied keeping in view the large industrial applications of both homo and copolymers of vinyl acetate and vinyl propionate, and also due to the fact that these comonomers have specific interactions with PEI. The influence of microstructure of the copolymer chains on the stability of the interpolymer complexes with PEI has also been discussed. The compositional and configurational sequence distribution of the (A/V) and (A/P) copolymers have been determined by both one and two dimensional NMR spectroscopy [8].

EXPERIMENTAL

Vinyl acetate (Central Drug House) and vinyl propionate (Aldrich) were distilled under reduced pressure and stored below 5°C. Acrylamide (Sisco Research Laboratories) was recrystallized twice from chloroform. N,N-dimethyl formamide (DMF) (MERCK) was distilled and dried.

A series of acrylamide/vinyl acetate and acrylamide/vinyl propionate copolymers containing different mole percent of the respective comonomers in feed was prepared by solution polymerization in DMF at 65°C using benzoyl peroxide (0.5 w/v%) as the initiator. The conversion was kept below 10% and the copolymers were precipitated in excess of methanol. The copolymers were further dissolved in DMF and reprecipitated in methanol/acetone (50:50) mixture and vacuum dried at room temperature.

The copolymer composition was determined by estimating the nitrogen content of the copolymers. The C,H and N analyses were done on a Perkin - Elmer 240C Elemental Analyzer. The number average molecular weight (M_n) of PEI (BDH, England) was determined from osmotic pressure measurement by using Polderman's method [9, 11] and found to be 1.5×10^5 g/mol. Measurement of number average molecular weight were carried out by means of Knauer Automatic Membrane Osmometer thermostated at 25°C. The membrane used was Sartorius UFF membrane and for the solvent a 0.01M NaOH/0.01M NaCl solution in water was used.

The pH measurements were carried out with PTA digital pH meter using combination electrode. The pH meter is equipped with a temperature controller which compensates the error in pH measurements due to temperature changes. For thermodynamic studies, the solution was taken in a water jacketed cell and the temperature was controlled within $\pm 0.05^\circ\text{C}$ by circulating thermostatically controlled water. The polymer solutions were prepared in double distilled water at a concentration of 5×10^{-3} um/L (um = unit mole). For pH titrations the concentration of the copolymer solutions were 5×10^{-3} um/L and the concentration of the polyelectrolyte (PEI) (BDH, England) was 2.5×10^{-3} . The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker 300 MHz spectrometer in DMSO- d_6 at 100°C.

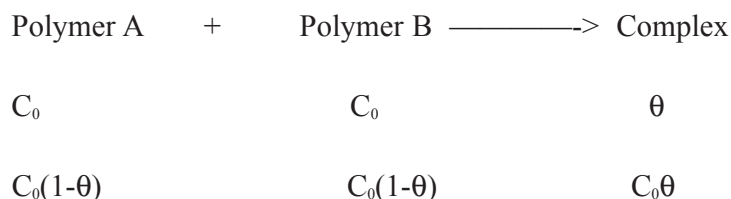
RESULTS AND DISCUSSIONS

The sequence distribution of acrylamide/vinyl acetate [8] and acrylamide/vinyl propionate were determined by both one and two dimensional NMR spec-

trosopy. The respective triad concentrations were determined from the area under the resonance signals from the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the A/V and A/P copolymers. Three different copolymer compositions of both A/V and A/P copolymers were used for complexation studies with PEI. The stability constant (K), degree of linkage (θ) and related thermodynamic parameters (ΔG° , ΔH° , and ΔS°) of these interpolymer complexes have been determined by Osada's method [10]. The method was initially developed for complex formation between poly-acid and non ionic homopolymer, due to hydrogen bonding. It was later extended to other systems also. using the following equations:

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

where $[\text{H}^+]$ and $[\text{H}^+]_0$ are the proton concentrations in the copolymer solution in the presence and absence of complementary polymer (PEI), respectively. These can be calculated from pH measurements of the solution. The process of complexation can be represented as:



where C_0 is the initial concentration of the copolymer in $\mu\text{m/L}$. Thus, the stability constant for the above process can be related to the degree of linkage (θ) by the relation:

Osada and his coworkers [3, 10] calculated the various thermodynamic parameters (ΔG° , ΔH° , and ΔS°) from the temperature dependence of the stability constant (K) using the following equations:

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

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^\circ}{R}; \Delta S^\circ = -\left[\frac{\Delta G^\circ - \Delta H^\circ}{T} \right]$$

The sequence distribution of the comonomer units and the concentration of the triad sequences in the copolymer chains (determined by NMR spec-

trosopy) were then correlated with the stability constant (K) of the complexes calculated using Osada's method.

Acrylamide/Vinyl Acetate (A/V) Copolymers

The A/V copolymers of compositions: (I) $F_A = 0.49$, (II) $F_A = 0.63$, (III) $F_A = 0.71$ (where F_A is the mole fraction of acrylamide in the copolymer) were complexed with PEI. The relative complexation ability of the two comonomer units i.e. A- and V- with PEI in the respective interpolymer complexes IA, IIA and IIIA was determined by studying the variation of pH of the aqueous solutions of the respective copolymers with increasing concentration of the poly-electrolyte, PEI (Figure 1). It is evident from Figure 1 that PEI interacts with both V- and A-

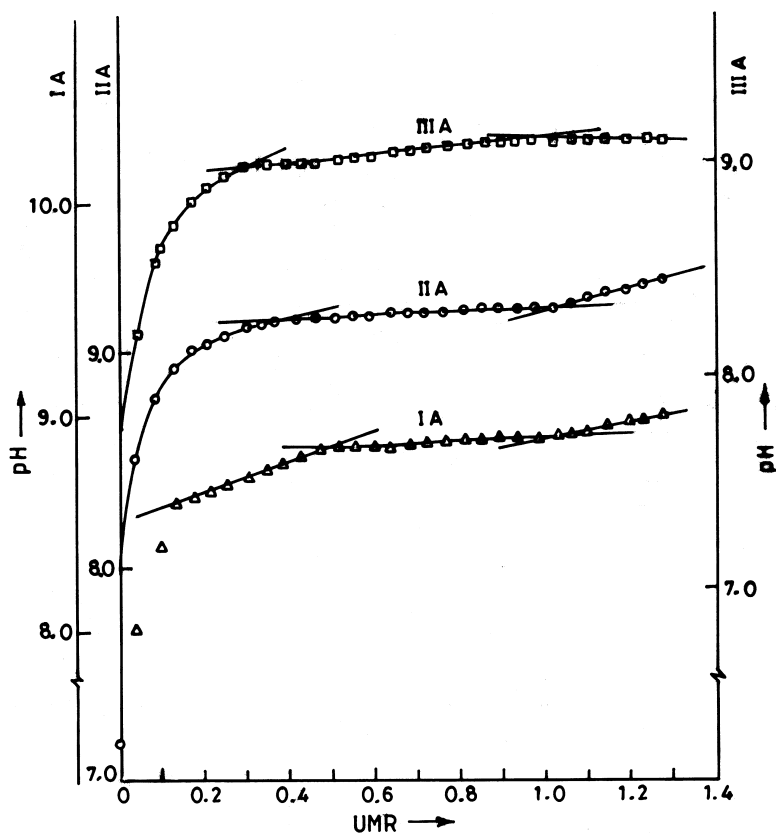


Figure 1. Variation of pH with unit mole ratio (umr) for complexation systems IA, IIA, and IIIA.

comonomer units in two distinct steps. The first break in all the three pH curve coincides with the stoichiometric amount of V- unit in the respective copolymer chains (copolymer composition F_v) which clearly indicates that PEI interacts with the V- units in preference to the A- unit. Subsequently, the polyelectrolyte interacts with A- comonomer units and the second break in all the three curves coincides with the stoichiometric amount of A- unit in the respective copolymer chains.

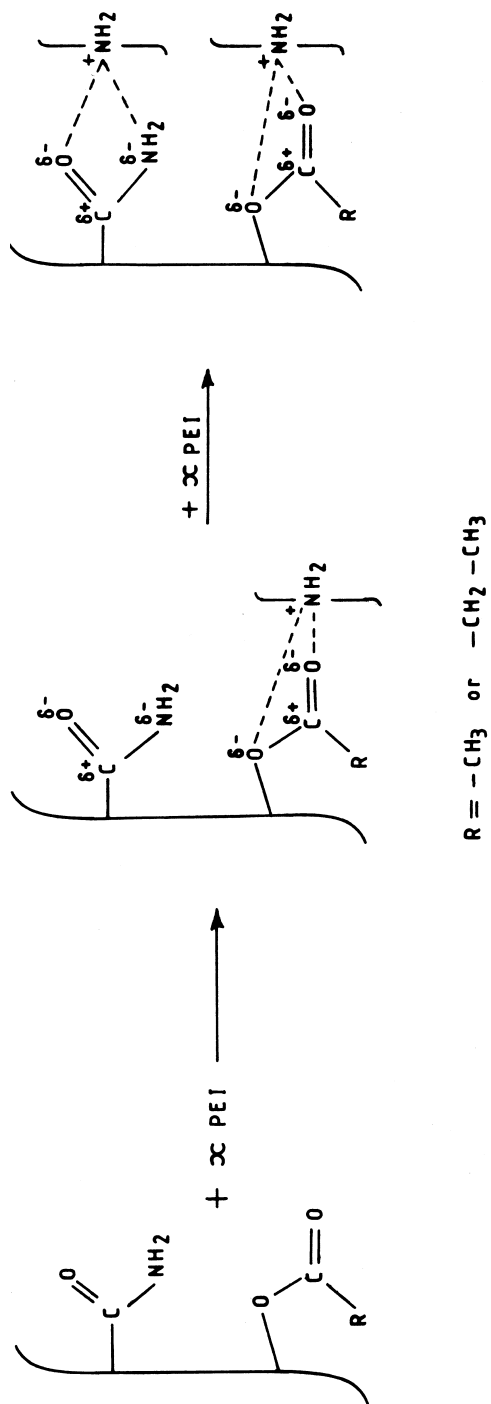
The relatively higher complexation ability of the V- comonomer units as compared to the A- units with respect to PEI can be interpreted from the complexation mechanism presented in Scheme 1. The secondary forces involved in the interaction between the various units are likely to be ion- dipole interactions. Due to the presence of two highly electronegative O atoms, the V- unit interacts more strongly with PEI through ion - dipole forces as compared to the A- units which has only one O atom and one comparatively less electronegative N atom. The presence of a methyl group in the V- units may possibly give rise to additional hydrophobic interactions which further contribute to the higher complexation ability of the V- units with respect to PEI.

The interpolymer associations through secondary binding forces are likely to be affected by an increase in temperature. Therefore, one would expect that as the temperature of the system is raised, various interacting forces get destabilized and the destabilization temperature depends on the nature of the secondary binding forces involved in the interacting pair of units. The stability constant (K) of the interpolymer complexes (IA to IIIA) have been determined at various temperatures using Osada's method and the respective $\ln K$ values are summarized in Table 1. The following trend has been observed for the three complexes, IA, IIA and IIIA:

$$\ln K_{IA} > \ln K_{IIA} > \ln K_{IIIA}$$

The observed trend further confirms the fact that the V- units interact more strongly with PEI as compared to A- units. A similar trend was observed during interpolymer complexation of acrylamide/methyl acrylate (A/M) and acrylamide/ethyl acrylate (A/E) where the M- and the E- units in the two copolymer systems were found to complex more strongly with PEI as compared to the A- units [6, 7]

The percentage of triads containing V- units in the three copolymers (I to III) involved in complexation are shown in Table 2. It is evident that as the sum of $\%(VVV) + \%(VVA + VAV)$ triads decreases the $\ln k$ values decreases at all



Scheme 1. Mechanism of complexation of acrylamide/vinyl acetate (A/V) and acrylamide.

TABLE 1. $\ln K$ (Lum^{-1}) Values of the Complexes of AN Copolymer with PEI at Various Temperatures

Complex*	20°C	25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C	70°C
IA (0.49)	21.9	19.2	16.6	14.9	13.4	12.6	12.0	11.8	11.2	10.9	11.1
IIA (0.63)	21.9	19.2	16.6	13.9	11.9	11.0	10.5	9.7	9.0	8.9	9.0
IIIA (0.71)	19.4	17.0	14.8	12.6	10.9	10.0	8.9	7.9	8.0	8.0	8.1

* The values given in brackets are copolymer compositions (F_A)

TABLE 2. Percentage of Triads Containing V Units in A/V Copolymers Involved in Complexation

Copolymer*	(VVV)% + (VVA + VAV)%	(VAA + AVA)% + (AAA)%
I (0.49)	55.0	45.0
II (0.63)	30.0	70.0
III (0.71)	19.0	81.0

* The values given in brackets are copolymer compositions (F_A).

temperatures. This is due to the fact that in the VVV and (VVA + VAV) triad fractions, there are 100% and 66% contribution of the stronger complexing V- units towards complexation with PEI and therefore a decrease in the sum of their concentration decreases the stability of the interpolymer complexes. However, in case of the AAA and (AAV + AVA) triad fractions, it is observed that as the sum of their percentage increases, the stability constant decreases. This is due to the fact that for these triad fractions, the contribution of the relatively weaker complexing A- unit is higher (ie 100% and 66%, respectively) and therefore an increase in the sum of their concentration decreases the stability of the interpolymer complexes.

Thus, it is evident that the stability of the interpolymer complexes (IA to IIIA) is governed by the relative concentration of the V- units in the copolymer chains.

Figure 2 shows the variation of standard enthalpy change (ΔH°) with temperature for the three complexation systems (IA to IIIA). Two distinct maxima are observed in all the three curves which corresponds to a single stage destabilization of A-EI and V-EI pairs of interacting units. A single stage interaction of V-EI and A-EI pair of units could also be seen from the pH versus umr plots (Figure 1). The maxima observed at higher temperature in all the three curves may be attributed to the destabilization of the stronger interacting V-EI units. It is also observed that as the concentration of the V- unit in the respective copolymers increases, the maximum corresponding to the destabilization of V-EI interacting pair shifts to a higher temperature ie. from 42.5°C (IIIA) to 47.5°C (IIA) to 52.5°C (IA). The maximum observed at lower temperature in all the three

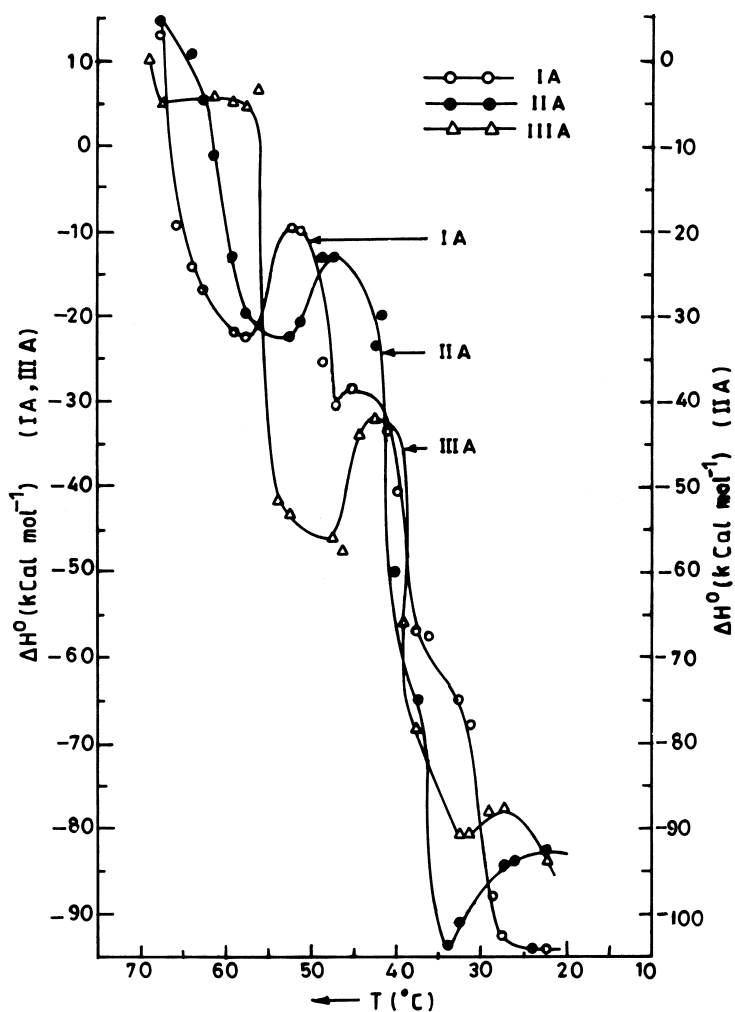


Figure 2. Temperature dependence of standard enthalpy change (ΔH°) for complexation systems IA, IIA, and IIIA.

curves (i.e., 27.5°C for IIA and IIIA and 32.5°C for IA) corresponds to the destabilization of the relatively weaker interacting A-EI pair of units.

The maxima assigned to the destabilization of the same interacting pair in the three complexation systems have different absolute values of ΔH° . This may be attributed to the fact that the overall ΔH_M results from the contributions from several processes, such as desolvation, complex formation by hydrogen

bonding or ion-dipole interaction, and conformational changes as a result of complex formation [6]. Each of these processes is likely to contribute to different extent to the overall value of ΔH_M . The sharp changes in ΔH° within a narrow range of temperature are far greater than the calculated experimental error. The experimental error is ± 0.01 in the pH scale and the observed and corrected data differ within 1-3% which is very much lower compared to the actual variation of ΔH° with temperature.

Acrylamide/Vinyl Propionate (A/P) Copolymer

Copolymer compositions (IV) $F_A = 0.53$, (V) $F_A = 0.72$, (VI) $F_A = 0.78$ were chosen for complexation with PEI and the stability constant and related thermodynamic parameters of the respective complexes (IVA, VA and VIA) at various temperature were calculated using Osada's method [10]. By measuring the variation of pH of the copolymer solutions with increasing concentration of the polyelectrolyte, the relative complexation ability of the two comonomer units with PEI was ascertained (Figure 3). Similar to the previous system (A/V), the first break in all the three curves coincides with the stoichiometric amount of vinyl propionate in the three copolymer systems (F_P), indicating that the interaction of PEI with P- units are relatively stronger than the A- units. As soon as the interaction of P and EI units is complete, the A- units starts interacting with the EI units. A single stage interaction of PEI with both P- and A- units was observed for all the three copolymer systems.

The probable mode of interaction between the two comonomer units (e.g. P and A) and the polyelectrolyte is expected to be through ion-dipole forces as shown in Scheme 1. These forces are likely to be stronger for P-EI interacting pair than involved in the A-EI interactions. The reasons for the P-EI interaction being stronger are similar to those mentioned in case of vinyl acetate for the complexation of A/V with PEI.

The stability constant (K) of the three complexes (IVA to VIA) was calculated at various temperatures and the corresponding $\ln K$ values are summarized in Table 3. The following trend was observed at all temperatures:

$$\ln K_{IVA} > \ln K_{VA} > \ln K_{VIA}$$

The above trend gives a direct evidence of the fact that the relative complexation ability of the P- units with respect to PEI is larger as compared to the A- units.

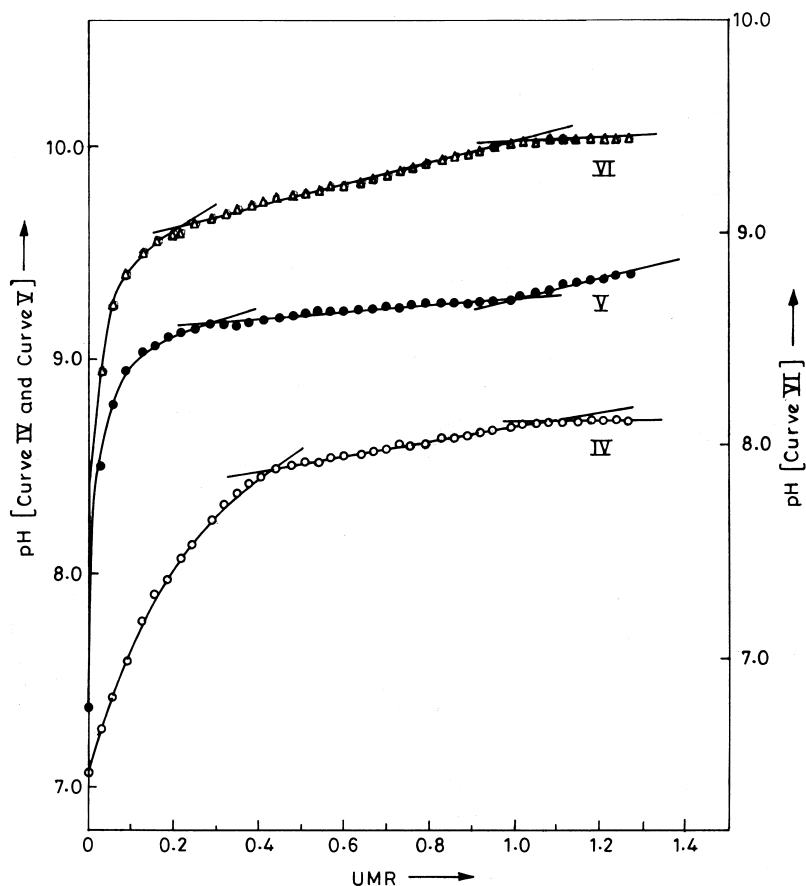


Figure 3. Variation of pH with unit mole ratio (umr) for complexation systems IVA, VA, and VIA.

Table 4 shows the percentage of triads containing P- units for all the three copolymer systems. It is evident that the stability of the respective complexes decreases with the decrease in the concentration of the triads containing higher percentage of P- units. As the $\%(PPP) + \%(PPA + PAP)$ (where there is 100% and 66% contribution of the P- units in complexation) in the copolymer system decrease, the $\ln K$ values decrease at all temperatures. However, an increase in the $\%(AAA) + \%(APA + AAP)$ in the copolymer chains decreases the stability of the interpolymer complexes. This is due to the fact that in these triad fractions the P- units contribute only 0 and 33%, respectively, while the weaker complexing A- units contribute 100% and 66%, respectively to interpolymer com-

TABLE 3. $\ln K$ (Lum^{-1}) Values of the Complexes of A/P Copolymer with PEI at Various Temperatures

Complex*	20°C	25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C	70°C
IVA (0.53)	21.1	18.5	15.8	13.4	11.4	10.1	9.1	8.4	8.5	9.2	9.6
VA (0.72)	19.3	17.1	14.6	12.6	11.3	10.0	9.0	8.3	8.1	7.2	7.3
VIA (0.78)	15.8	13.8	11.2	9.6	8.4	7.3	6.9	7.9	8.1	8.6	9.1

* The values given in brackets are copolymer compositions (F_A).

TABLE 4. Percentage of Triads Containing P Units in A/V Copolymers Involved in Complexation

Copolymer*	(PPP)% + (PPA + PAP)%	(PAA + APA)% + (AAA)%
I (0.53)	40.0	60.0
II (0.72)	19.0	81.0
III (0.78)	7.0	93.0

*The values given in brackets are copolymer compositions (F_A).

plexation. It is evident from these results that the relative concentration of the P-units in the various triad fractions are reflected on the stability of these complexes.

The variation of standard enthalpy change (ΔH_o) with temperature for the three complexes (IVA to VIA) is shown in Figure 4. The first maximum appearing at relatively lower temperature (ie. at 37.5°C for VA and VIA and at 47.5°C for IVA) could be attributed the destabilization of the relatively weaker A-EI interacting pair of units. The three maxima appearing at relatively higher temperatures for all the three systems could be attributed to the destabilization of the stronger P-EI interacting pair of units. It is also clear that as the concentration of the P- units in the copolymer chains increases, the second maxima shifts to a higher temperature ie. from 52.5°C (VIA) to 62.5°C (VA) to 67.5°C (IVA).

CONCLUSION

The stability and the related thermodynamic properties of the interpolymer complexes of PEI with acrylamide/vinyl acetate and acrylamide/vinyl propionate were found to depend on the microstructure of the respective copolymer chains. It was observed that vinyl acetate and vinyl propionate comonomer units complexes more favorably with respect to PEI as compared to acrylamide in A/V and A/P copolymer systems, respectively.

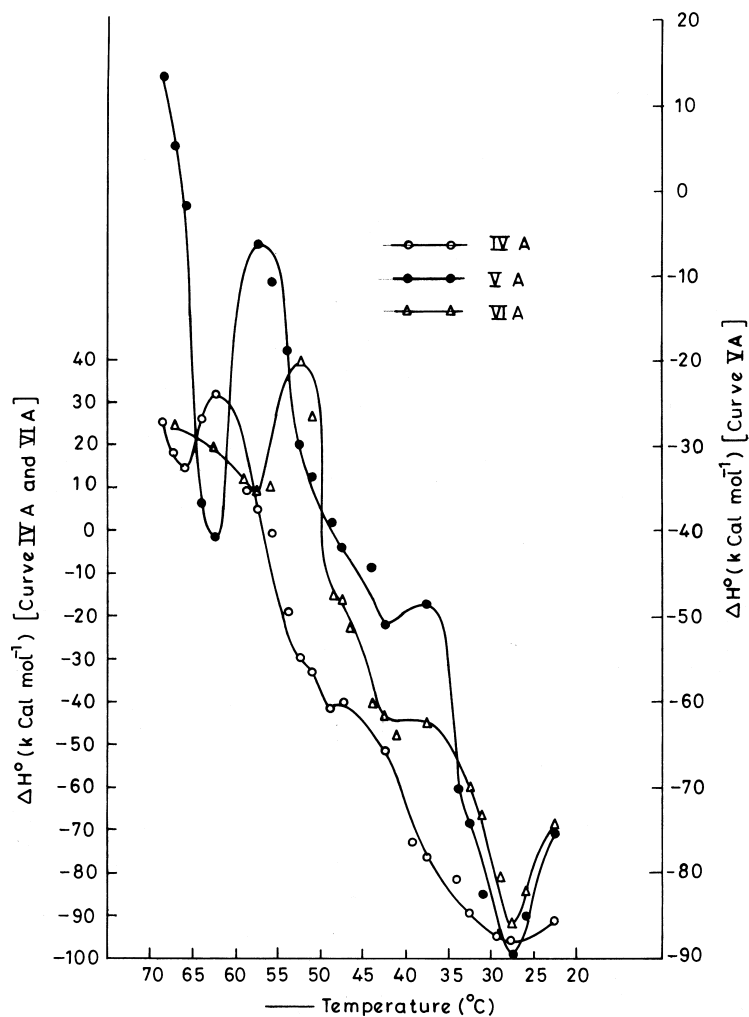


Figure 4. Temperature dependence of standard enthalpy change (ΔH°) for complexation systems IVA, VA, and VIA.

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