Stability Constants and Related Thermodynamic Parameters of Some Quaternary Intermacromolecular Complexes Involving Polyelectrolytes and Nonionic Homopolymers

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STABILITY CONSTANTS AND RELATED THERMODYNAMIC PARAMETERS OF SOME QUATERNARY INTERMACROMOLECULAR COMPLEXES INVOLVING POLYELECTROLYTES AND NONIONIC HOMOPOLYMERS

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ABSTRACT

Stability constants and related thermodynamic parameters (e.g., $\Delta H°$ and $\Delta S°$) of some quaternary intermacromolecular complexes involving polyelectrolytes and nonionic homopolymers were determined at several temperatures. The various interacting forces involved in the complex formation are destabilized at different temperatures which are reflected in the enthalpy and entropy changes of the systems at various temperatures.

INTRODUCTION

The various aspects of polyelectrolyte complex (PEC) formation have been studied since time immemorial, particularly in view of their potential applications in various fields [1, 2]. It is expected that by incorporating various types of nonionic homopolymers in these complexes, their stabilities, properties, and potential applications could be appropriately modified from those of the original complexes. Keeping this object in mind, we have studied the interaction of poly(methacrylic acid) (PMA) with the following components: poly(ethylene imine) (PEI), poly(vinylpyrrolidone) (PVP), and poly(ethylene oxide) (PEO). The components were

added to PMA in a definite sequence and in particular stoichiometric amounts. Simultaneous interaction of various units (EI, VP, and EO) with the PMA chain results in the formation of quaternary interpolymer complexes. Such ternary and quaternary complex formations have been reported in the literature and explained on the basis of closed and open chain mechanisms [3], as well as "all or none" type complex formation mechanism [4]. Since the nature of the interacting forces of the various units (EI, VP, and EO) with PMA are all different, one could predict that the relative proportions of various interacting units present in the complex will influence their stability and other related thermodynamic parameters (e.g., $\Delta H°$ and $\Delta S°$). In other words, enthalpy and entropy changes at various stages of complex formation are likely to be reflected in the stability constants of the complexes since the various interacting forces (e.g., coulombic, H-bonding, ion–dipole interactions, etc.) are destabilized at different temperatures. Therefore, temperature dependence studies on the stability constants of the systems are likely to provide insight into the mechanism of degradation of these complexes. In this report we use Osada's method to calculate the stability constants and related thermodynamic parameters (e.g., $\Delta H°$ and $\Delta S°$) of various quaternary complexes. An excellent correlation was obtained between the stability constants and the relative proportions of various interacting units present in the complexes.

EXPERIMENTAL

Poly(methacrylic acid) (PMA) was prepared by known methods. $\overline{M}_w$ was calculated from viscosity measurements and was found to be $2.5 \times 10^5 \, \text{g} \cdot \text{mol}^{-1}$ [5].

Poly(ethylene imine) (PEI) was supplied by BDH Chemicals Ltd. (Poole, UK) in the form of a 50% viscous aqueous solution [6].

Poly(vinyl pyrrolidone) (PVP) was of commercial origin (Fluka, Switzerland). The $\overline{M}_w$ of the polymer was calculated from viscosity measurements and was found to be $2.4 \times 10^4 \, \text{g} \cdot \text{mol}^{-1}$ [7].

Poly(ethylene oxide) (PEO) was supplied by Iwai Kagaru Co., Japan, and its $\overline{M}_w$ was found to be 1.9×10^4 as calculated from a viscosity equation [8].

*Solvent*: Double distilled water was used for all experimental measurements.

Measurement of pH: The measurement of pH of various solutions of the homopolymer 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 $\pm 0.05°$C by circulating thermostatically controlled water.

The pH was measured at a homopolymer concentration of 5×10^{-3} (unit mole) $\mu\text{m} \cdot \text{L}^{-1}$ in the absence and presence of stoichiometric concentrations of PEI, PVP, and PEO. Complexes did not precipitate at these concentrations.
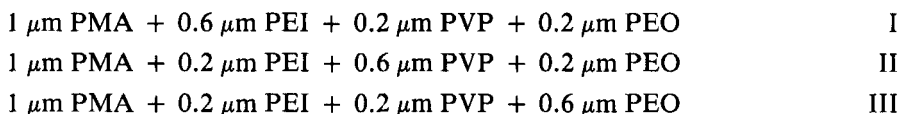
RESULTS AND DISCUSSION

PMA is known to form interpolymer complexes with PEI through coulombic interactions [9], with PVP through H-bonding and ion–dipole interactions [10], and with PEO through H-bonding [11]. Since the strengths of these interacting forces differ widely, the stability of the complexes will depend on the relative pro-

portions of various interacting units present in them. One can possibly prepare quaternary complexes of PMA by adding stoichiometric amounts of various complementary homopolymers (e.g., PEI, PVP, and PEO). The probable structure of such a complex may be represented as
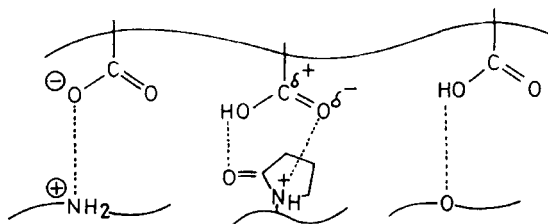
Three quaternary interpolymer complexes of PMA have been prepared by mixing the components in the following stoichiometric proportions:

$$1 \mu m \text{ PMA} + 0.6 \mu m \text{ PEI} + 0.2 \mu m \text{ PVP} + 0.2 \mu m \text{ PEO} \qquad \text{I}$$

$$1 \mu m \text{ PMA} + 0.2 \mu m \text{ PEI} + 0.6 \mu m \text{ PVP} + 0.2 \mu m \text{ PEO} \qquad \text{II}$$

$$1 \mu m \text{ PMA} + 0.2 \mu m \text{ PEI} + 0.2 \mu m \text{ PVP} + 0.6 \mu m \text{ PEO} \qquad \text{III}$$

In these complexes the relative proportions of various pairs of reacting units (MA–EI, MA–VP, and MA–EO) are different. On the basis of the nature of the interacting forces (e.g., coulombic, H-bonding, ion–dipole, etc.), and their relative proportions in the complexes, one can predict their stabilities and relative thermodynamic parameters (e.g., $\Delta H°$ and $\Delta S°$).

Stability constants (K) of the complexes (I to III), have been calculated by using Osada's procedure [12–14]. The basic assumption of this approach is that complexation is produced only by the carboxyl groups in the undissociated state for a weak acid with a dissociation constant K_a and a concentration C. For $K_a/C << 1$, we have $[H^+] = (K_a C)^{0.5}$. This relation holds for the polymeric acid in both the presence and absence of component polymers. Expressing the free carboxyl concentrations for these two cases as C and C_0, we obtain the degree of linkage, θ, which is defined as the ratio of the binding groups to the total number of potentially interacting groups, and which can be correlated with K by the following equations:

$$\theta = 1 - C/C_0$$

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

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

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

where $[H^+]$ and $[H^+]_0$ are the proton concentrations in the polyelectrolyte solution in the presence and absence of complementary homopolymers (PEI, PVP, and PEO). The θ values are presented in Table 1.

Plots of $\ln K$ vs $1/T$ for the systems (I to III) are shown in Fig. 1. The maximum error which could be introduced in the value of θ, and consequently in $\ln K$, has been calculated on the basis of experimental error (e.g., ±0.01 pH). There

TABLE 1. Degree of Linkage (θ) of Complexes at Various Temperatures

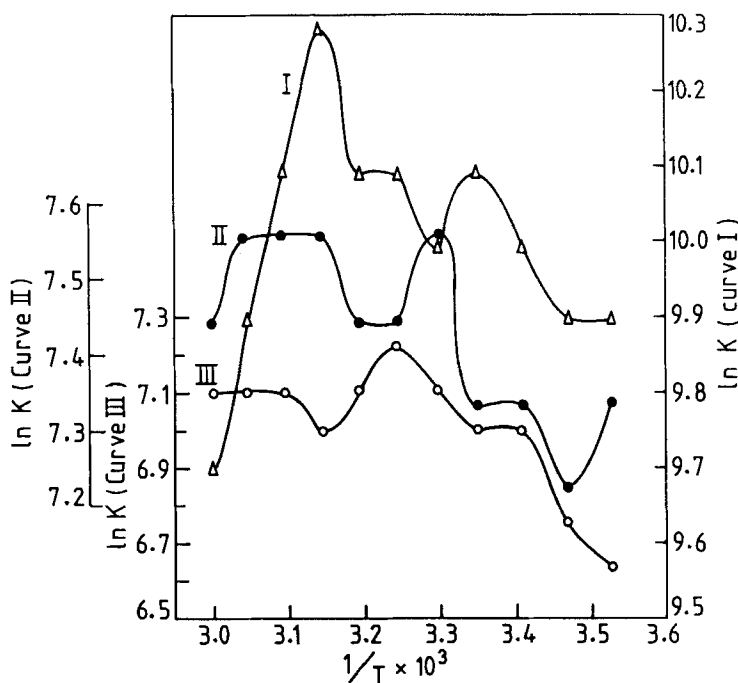| System	Composition of complexes, μm	Temperature, °C											
		10	15	20	25	30	35	40	45	50	55	60
I	1.0 PMA + 0.6 PEI 0.2 PVP + 0.2 PEO	.905	.905	.909	.913	.909	.913	.913	.921	.913	.905	.895
II	1.0 PMA + 0.2 PEI 0.6 PVP + 0.2 PEO	.698	.684	.698	.698	.725	.712	.712	.725	.725	.725	.712
III	1.0 PMA + 0.2 PEI 0.2 PVP + 0.6 PEO	.602	.620	.653	.653	.667	.684	.653	.653	.667	.667	.667

FIG. 1.   Variations of ln K with $1/T$ for complexation systems I, II, and III.

seems to be very little difference between θ_{obs} and θ_{corr}. The discontinuities in the plots have been found to exist even when ln K_{corr} is plotted instead of ln K_{obs}. Therefore, these features may possibly be attributed to destabilization of the complexes in distinct stages at specific temperatures. Moreover, even after considering the experimental error, the absolute values of ln K (or K) for the three complexation systems (I to III) within the temperature ranges studied follow the order

$$\ln K_{(I)} > \ln K_{(II)} > \ln K_{(III)}$$

This is understandable in view of the fact that complex I has more coulombic interactions due to the presence of relatively larger proportion of EI units from PEI. Complex II has a smaller proportion of EI units, but this is partly compensated for by the presence of a larger proportion of VP units from PVP. The comparatively weaker H-bonding and ion–dipole interactions as well as hydrophobic interactions of the MA–VP pair are not able to fully compensate for the strong coulombic interactions of the MA–EI reacting pair. The relatively small stability constant (K) of II compared to I could thus be accounted for. Complex III has a relatively large proportion of MA–EO reacting pairs, which involve only very weak H-bonding. Thus, the relatively lower value of the stability constant of complex III compared to I and II could be explained on the basis of the above arguments.

The simultaneous presence of several complementary reacting units (EI, VP, and EO) on the same PMA chain may involve cooperation as well as neighboring group influence. Both these factors are likely to influence the stability constants of the quaternary complexes (I to III), which in fact is reflected in the actual values of

K for the various complexes. Moreover, the temperature effect on coulombic forces is much less compared to other weaker forces, e.g., H-bonding and ion–dipole interactions [1].

The changes of conformation and microenvironment in the domain of the polymer chain may also affect the stability of the complexes in different ways [1].

Changes in free energy, enthalpy, and entropy ($\Delta F°$, $\Delta H°$, and $\Delta S°$) can be calculated from the stability constant (K) and its temperature dependence. The thermodynamic parameters are related by the following equations:

$$\Delta F° = -RT \ln K$$
$$d(\ln K)/d(1/T) = -\Delta H°/R$$
$$\Delta S° = -(\Delta F° - \Delta H°)/T$$

The $\Delta H°$ and $\Delta S°$ for complexes I to III have been calculated on the basis of the above equations, and their variations with temperature are shown in Figs. 2 and 3 for the three systems.

The difference in the values of $\Delta H°_{obs}$ and $\Delta H°_{corr}$ (calculated on the basis of ln K_{obs} and ln K_{corr}, respectively) was found to be within 1 to 3%. Obviously, the
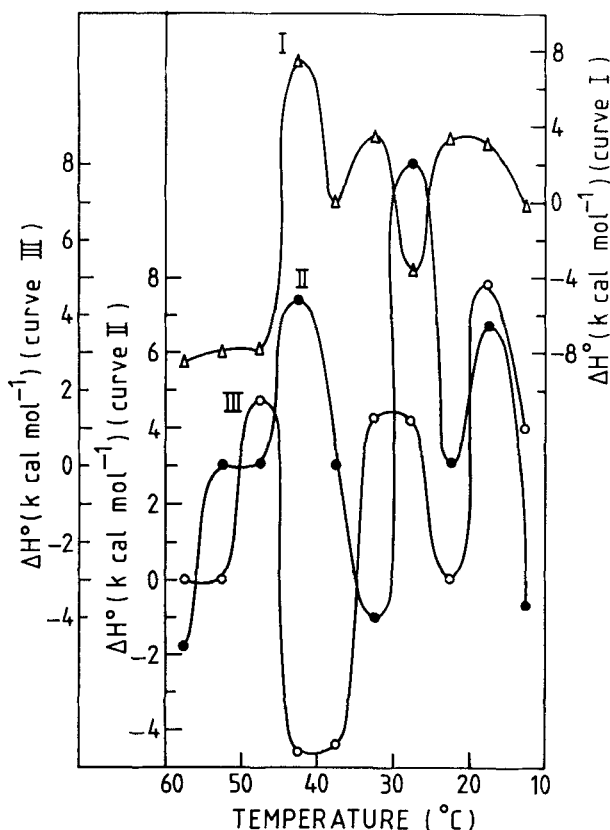

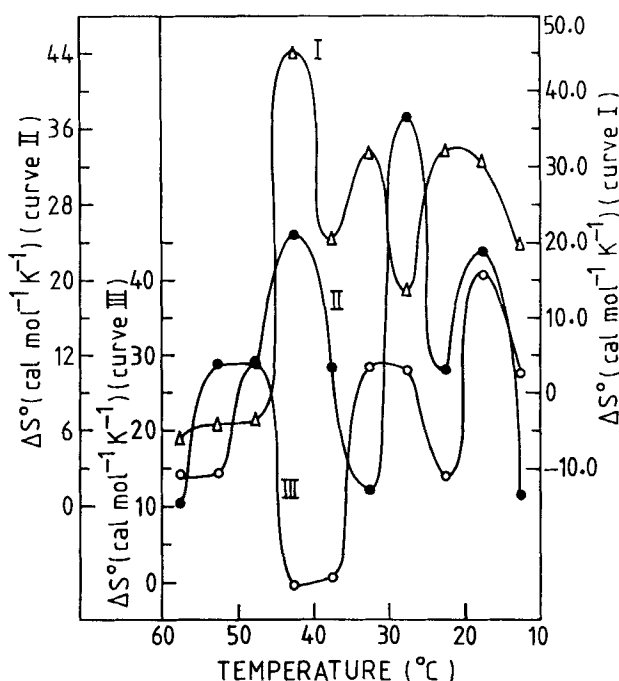FIG. 2. Temperature dependence of standard enthalpy change ($\Delta H°$) for complexation systems I, II, and III.

FIG. 3. Temperature dependence of standard entropy change ($\Delta S°$) for complexation systems I, II, and III.

observed variations in $\Delta H°$ and $\Delta S°$ with temperature are much larger than the experimental error. Therefore, the three distinct peaks observed in $\Delta H°$ vs T and in $\Delta S°$ vs T plots may possibly be interpreted in terms of stepwise destabilization of the complexes.

On comparing the enthalpy and entropy curves of the three systems (Curves I, II, and III of Figs. 2 and 3), it can be seen that peak height is directly proportional to the relative proportion of the interacting units (EI, VP, and EO) present in the complexes. This, in fact, is authentic evidence of the assignment of different peaks to destabilization of various pairs of interacting units (MA–EO, MA–VP, MA–EI) at different temperatures.

It is evident from Table 2 that complex I has the largest values of ΔH_3 and ΔS_3, which may be attributed to the presence of a relatively large proportion of EI units in I, whereas the large values of ΔH_2 and ΔS_2 for complex II and the corresponding large values of ΔH_1 and ΔS_1 for complex III may be attributed to the relatively large proportion of VP and EO units present in complexes II and III, respectively. Obviously, the assignment of the three peaks of $\Delta H°$ and $\Delta S°$ vs T curves to destabilization of MA–EO, MA–VP, and MA–EI interacting pairs can be justified on the basis of the relative strengths of different interacting forces and the composition of the complexes. The absolute values of $\Delta H°$ and $\Delta S°$ due to destabilization of specific interacting pairs may vary in different complexes (cf. Table 2) although the complexes may have identical proportions of these pairs. This is understandable in view of the fact that the net enthalpy or entropy change during

TABLE 2.   The Three Maximum Values of ΔH° and ΔS° Corresponding to Three Peaks of Complexes I to III

System	Composition of complexes, μm	ΔH_1	ΔH_2 (kcal·mol^{-1})	ΔH_3	ΔS_1	ΔS_2 (cal·deg^{-1}·mol^{-1})	ΔS_3
I	1.0 PMA + 0.6 PEI 0.2 PVP + 0.2 PEO	3.5	3.6	7.7	32.0	32.0	44.5
II	1.0 PMA + 0.2 PEI 0.6 PVP + 0.2 PEO	3.7	8.0	4.4	27.3	41.4	29.0
III	1.0 PMA + 0.2 PEI 0.2 PVP + 0.6 PEO	7.8	4.3	4.7	40.7	28.2	28.6

interpolymer complex formation may involve several steps, such as desolvation, complex formation by H-bonding, ion–dipole and electrostatic interactions, and conformational changes. Since the contribution of each step will be different for each of the complexes, a small difference in ΔH° and ΔS° should be anticipated.

Some of the arguments regarding the stepwise formation of the quaternary complexes I to III could be substantiated by studying the variation of pH and
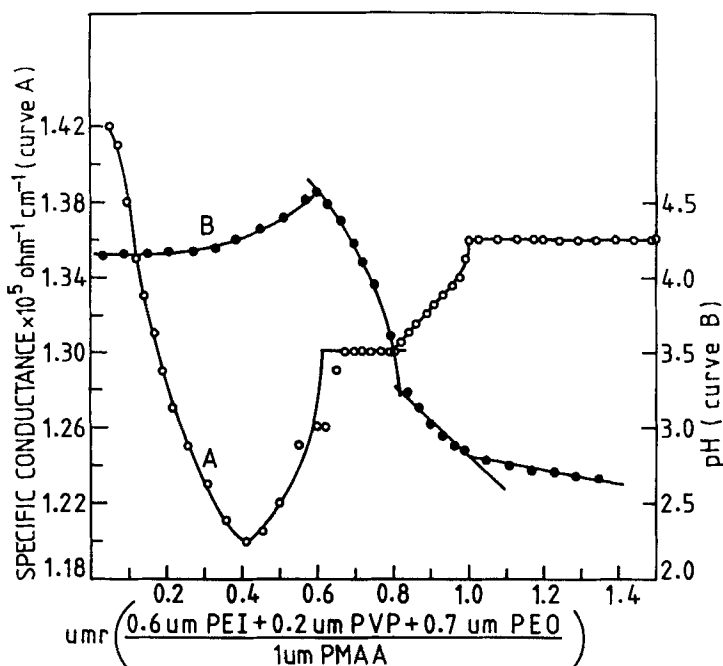

FIG. 4.   Variations of pH and conductance of PMA solution with the addition of PEI, PVP, and PEO in sequence: I.
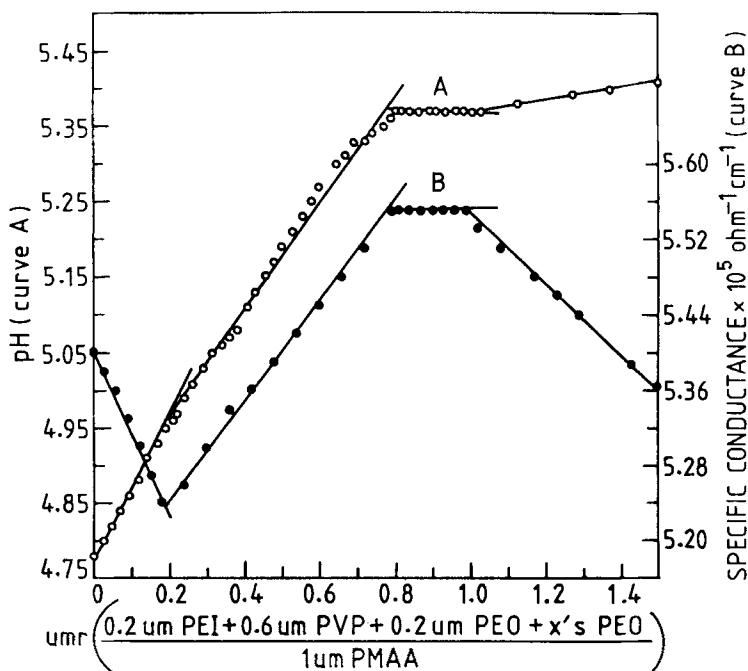
FIG. 5.   Variations of pH and conductance of PMA solution with the addition of PEI, PVP, and PEO in sequence: II.

specific conductance of PMA solution with the addition of complementary polymers (PEI, PVP, and PEO) in small increments. In Figs. 4 to 6, such variations are depicted with the addition of different stoichiometric amounts of complementary polymers. The distinct breaks in the titration curves (cf. Figs. 4 to 6) unequivocally indicate the stepwise interaction of the various complementary polymers with the PMA chain.

A more unequivocal proof of the interaction of PMA with the component polymers (PEI, PVP, and PEO) could be obtained by comparing the characteristic group frequencies in IR spectra of component polymers and the interpolymer complexes. For instance, the carbonyl frequency [$\nu(C=O)$] of pure PMA, which was observed at 1690 cm^{-1}, shifted to 1710 cm^{-1} in the complex. The $\nu(C-O-C)$ frequency of pure PEO, which was observed at 1100 cm^{-1}, shifted to 1150 cm^{-1} in the complex. The $\nu(N-H)$ frequency in pure PEI, which was observed at 1560 cm^{-1}, shifted to 1630 cm^{-1} in the complex. The distinct shifts in the characteristic group frequencies in the IR spectra also provide authentic evidence of the involvement of various functional groups during the complexation process.

It may be concluded that quaternary interpolymer complexes can be formed by incorporating various complementary polymers, such as PEI, PVP, and PEO, on a PMA chain. Since the nature and relative strengths of the interacting forces between the reacting pairs (e.g., MA-EI, MA-VP, and MA-EO) are all different, the presence of the actual amount of specific interacting pairs in the complexes will be reflected in their stability constants (K) and related thermodynamic parameters
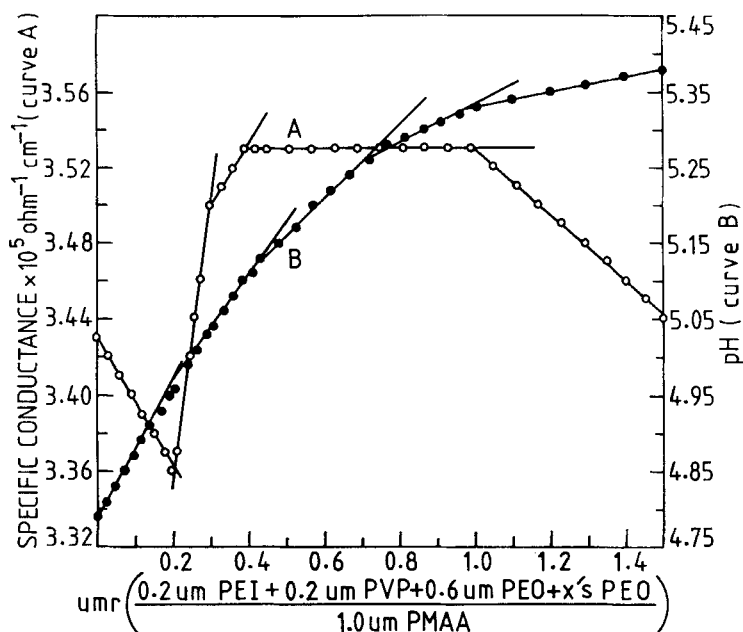
FIG. 6. Variations of pH and conductance of PMA solution with the addition of PEI, PVP, and PEO in sequence: III.

(e.g., $\Delta H°$ and $\Delta S°$). A distinct stepwise destabilization of these forces has been observed at specific temperatures.

REFERENCES

[1] E. Tsuchida and K. Abe, *Adv. Polym. Sci.*, *45*, 1 (1982).

[2] E. A. Bekturov and E. A. Bimendina, *Ibid.*, *41*, 99 (1981).

[3] K. Abe, M. Koide, and E. Tsuchida, *Macromolecules, 10*, 1259 (1977).

[4] I. M. Papisov, V. Yu. Baranovskii, and V. A. Kabanov, *Vysokomol. Soedin, Ser. A, 17*, 2104 (1975).

[5] A. Katchalsky and H. Eisenberg, *J. Polym. Sci.*, *6*, 145 (1951).

[6] S. K. Chatterjee and A. Malhotra, *Angew. Makromol. Chem.*, *126*, 153 (1984).

[7] G. B. Levy and H. P. Frank, *J. Polym. Sci.*, *17*, 247 (1955).

[8] W. Ring, J. Contow, and H. Holtrup, *Eur. Polym. J.*, *3*(2), 151 (1966).

[9] S. K. Chatterjee, D. Yadav, S. Ghosh, and A. M. Khan, *J. Polym. Sci., Polym. Chem. Ed., 27*, 3855 (1989).

[10] L. A. Bimendina, V. V. Roganov, and E. A. Bekturov, *Ibid.*, *12*, 65 (1974).

[11] T. Ikawa, K. Abe, K. Honda, and E. Tsuchida, *Ibid.*, *13*, 1505 (1975).

[12] Y. Osada, *Ibid., 17*, 3485 (1979).
[13] Y. Osada and M. Sato, *J. Polym. Sci., Polym. Lett. Ed., 14*, 129 (1976).
[14] Y. Osada, *J. Polym. Sci., Polym. Chem. Ed., 15*, 255 (1977).