December 2009 Volume 5 Issue (1-2)

Trade Science Inc.

Macromolecules

An Indian Journal

Full Paper

MMAIJ, 5(1-2), 2009 [28-33]

Thermodynamic and electrochemical and spectral studies of some multicomponent complexes involving polyelectrolytes and non ionic homopolymers

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Received: 14th July, 2009 ; Accepted: 24th July, 2009

ABSTRACT

Some multi component inter polymer complexes or polymer blends have been prepared by incorporating some polymers (e.g., PVP, PEO, PVA etc.) on the poly (methacrylic acid) (PMA) chains. Stability constants and related thermodynamic parameters (e.g., ΔH^0, ΔS^0) for the systems at different temperatures were determined. Interpretations have been sought in terms of the various proportions of the component polymers and hence the secondary binding forces associated with them. A closed chain mechanism has been proposed on the basis of the experimental findings. further confirmation has been provided by spectral and electrochemical studies.

KEYWORDS

Acrylic polymers;
Nonionic homopolymers;
Stability constants;
Thermodynamic parameters;
Closed chain mechanism;
Molecular recognition;
Polymer blends.

INTRODUCTION

Studies involving polyelectrolyte complexes (PEC) have been of great interest due to their close resemblance to the complicated biological systems[1-6]. Polycomplexes of the given type are used in designing new medicines, as separating membranes, flocculants and other important functional materials. Processes of polymer – polymer interactions between very long (matrices) and relatively short (oligomers) macromolecules are of special interest:

$$P_1 \text{ (matrice)} + n.P_2 \rightarrow \text{inter PC } (P_1 + nP_2)$$

By involving various nonionic homopolymers on the matrice. It is expected that their properties and stabilities could appropriately be modified. Keeping this thing in mind, we have incorporated various homopolymers on the methacrylic acid (PMA) chain in definite order and stoichiometries. Simultaneous interactions between PMA and homopolymers like poly (ethylene imine) PEI, poly (vinyl pyrrolidone) PVP, poly (ethylene oxide) PEO, poly (vinyl alcohol) PVA, lead to the formation of multicomponent complexes. Formation of such of such quaternary and higher ordered complexes can be explained on the basis of open and closed chain mechanisms[7,8] as well as *'all or none'* mechanisms[9]. Different interacting pairs undergo complexation due to different secondary binding forces[1,2,4]. Depending upon the secondary stoichiometric amounts and types of these forces, one could predict the stability of these complexes. Different interacting units are destabilized at different temperatures. This is reflected from their enthalpy and entropy data. Thus, on the basis of the temperature dependence studies of stability constants, an insight to the mechanism of degradation of these complexes can be provided. In this investigation, Osada's method[10,11] to calculate the stability constants and the related thermodynamic parameters (e.g., ΔH^0, ΔS^0). Of various multicomponent complexes has been used.

Excellent correlation was observed between the stability and relative proportions of various interacting units present in the complexes. A closed chain mechanism has been suggested on the basis of these observations.

EXPERIMENTAL

Poly (Methacrylic acid) PMA was prepared by known methods. M_w was calculated from viscosity measurements and was found to be2.5 x 10^5g. mol^{-1}[12].

Poly (Ethylene imine) PEI was supplied by BDH chemicals Ltd. (Poole, U.K.)in the form of 50% viscous aqueous solution.[13]

Poly (Vinyl pyrrolidone) PVP was supplied by Fluka, Switzerland. The polymer was characterized by viscosity measurements and its weight average molecular weight (Mw) was found to be 2.4 x 10^4 g/mol.[14]

Poly (Ethylene oxide) PEO was supplied by Iwai Kagaru Co. Japan. It was characterized by calculating its weight average Molecular weight from viscosity measurements in aqueous medium at 25^{0}C and was found to be 1.9 x 10^4 g/mol.[15]

Poly (Vinyl alcohol) PVA was supplied by Fluka, USA. Mw was calculated from viscosity measurements in aqueous medium at 25^{0}C and was found to be 2.1 x 10^4 g/mol.[16]

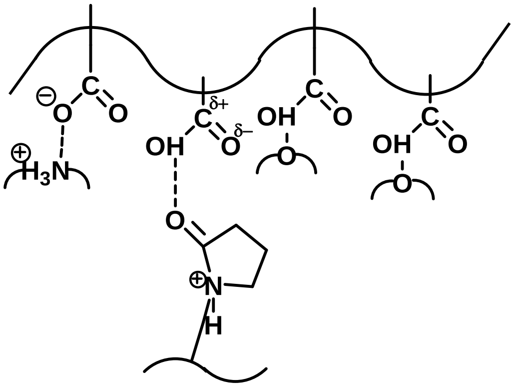
Solvent: Double distilled water was used in the present experiment.

Measurement of pH: the measurement of pH of various solutions of the homopolymers or complexes was carried out in a water jacketed cell using a PTA digital pH meter using a combination electrode. The temperature of the sample was controlled by circulating thermostatically controlled water.

The pH was measured at the homopolymer concentrations of 5 x 10^{-3} (unit mole) umL^{-1} in the absence and presence of stoichiometric concentrations of PEI, PVP, PEO and PVA. Complexes did not precipitate at these concentrations.

RESULTS AND DISCUSSION

PMA interacts with PEI through coulombic interactions[17], with PVP through H – bonding and ion – dipole interactions[18], with PEO and PVA through only H – bonding[19]. Strengths of these forces are widely different from each other. The stability is also influenced by the stoichiometric amounts of different interacting pairs. The probable structure of such a complex may be represented as:



The following four multicomponent complexes containing five different component polymers with different stoichiometries have been prepared. It should be noted here that um refers to the unit moles of the polymers:

Complex 1: 1um PMA + 0.4um PEI + 0.2um PVP + 0.2um PEO + 0.2um PVA

Complex 2: 1um PMA + 0.2um PEI + 0.4um PVP + 0.2um PEO + 0.2um PVA

Complex 3: 1um PMA + 0.2um PEI + 0.2um PVP + 0.4um PEO + 0.2um PVA

Complex 4: 1um PMA + 0.2um PEI + 0.2um PVP + 0.2um PEO + 0.4um PVA

Degree of association (Θ) and stability constants (K) of the complexes (1 to 4) at different temperatures have been calculated using Osada's procedure[10,11] and presented in TABLE 1. Plots of lnK Vs 1/T for the systems are shown in Figure 1. The bond energy ΔE in the polycomplex is the sum of various energies. The multicomponent complex formed, due to various secondary forces is stable even if the energy of formation of each separate bond formed between the units, ΔE_1 is very small. If, $\Delta E_1 \sim -kt$, it can commensurate with the energy of interaction of sections of double chains of polycomplex, or with ΔE_2 the energy of hydrophobic interactions, or ΔE_3, in the formation of polycomplex in water if the later is a solvent for it. Hence,

$$\Delta E = \Sigma_i \Delta E_i$$

All the interactions corresponding to these energies contribute to the stabilization of the polycomplex. Moreover, a relative role of any interaction can change if the reaction conditions are altered[1,20].

TABLE 1 : The degree of linkage (θ) and stability constant (K) of complexes 1 to 4 at various temperatures

Temp (°C)	Complexation Systems							
	1 um PMA + 0.4 um PEI + .0.2 um PVP + 0.2 um PEO + 0.2 um PVA		1 um PMA + 0.2 um PEI + 0.4 um PVP + 0.2 um PEO + 02 um PVA		1 um PMA + 0.2 um PEI + 0.2 um PVP + 0.4 um PEO + 0.2 um PVA		1 um PMA + 0.2 um PEI + 0.2 um PVP + 0.2 um PEO + 0.4 um PVA	
	θ	ln K	θ	ln K	θ	ln K	θ	ln K
10°	0.826	8.61	0.475	5.84	0.450	5.69	0.450	5.69
15°	0.818	8.51	0.521	6.12	0.499	5.98	0.475	5.84
20°	0.834	8.71	0.602	6.63	0.563	6.38	0.521	6.12
25°	0.834	8.71	0.602	6.63	0.583	6.51	0.563	6.38
30°	0.826	8.61	0.619	6.75	0.602	6.63	0.602	6.63
35°	0.826	8.61	0.637	6.87	0.619	6.75	0.919	6.75
40°	0.841	8.81	0.653	6.99	0.637	6.87	0.637	6.87
45°	0.834	8.71	0.669	7.10	0.653	6.99	0.653	6.99
50°	0.826	8.61	0.684	7.22	0.669	7.10	0.669	7.10
55°	0.818	8.51	0.667	7.10	0.653	6.99	0.653	6.99
60°	0.809	8.40	0.637	6.87	0.637	6.87	0.637	6.87

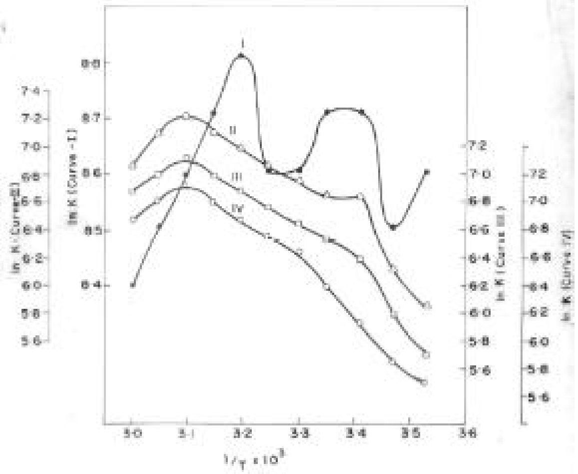


Figure 1 : Variation of lnK with 1/T for complexation systems 1-4.

Keeping in view the above objective, the systems studied here provide an excellent correlation. The nature of the curves for the complexes 2 to 4 is more or less identical whereas, the curve for the complex 1 is distinctly different (cf. Figure 1 and TABLE 1). The difference may be attributed to the presence of relatively higher proportion of PEI present in this complex, which involves comparatively stronger coulombic interactions[21-23]. The related thermodynamic parameters ((e.g., ΔH^0, ΔS^0) of the complexes 1 to 4 have also been calculated using the following equations:

$$d\ln K / d(1/T) = -\Delta H^0/R$$

$$\Delta F^0 = -RT \ln K$$

$$\Delta S^0 = -(\Delta F^0 - \Delta H^0)/T$$

The corresponding plots for ΔH^0 Vs T and ΔS^0 Vs T of the systems are given in Figures 2 and 3 respectively. Both of these Figures. show a sharp and distinct peak at around 17.5^{0}C. these peaks correspond to the breaking of MA-VP, MA-EO and MA-VA interactions. The values of ΔH^0 obtained from the graph at the first peak are given in TABLE 2. The total amount of

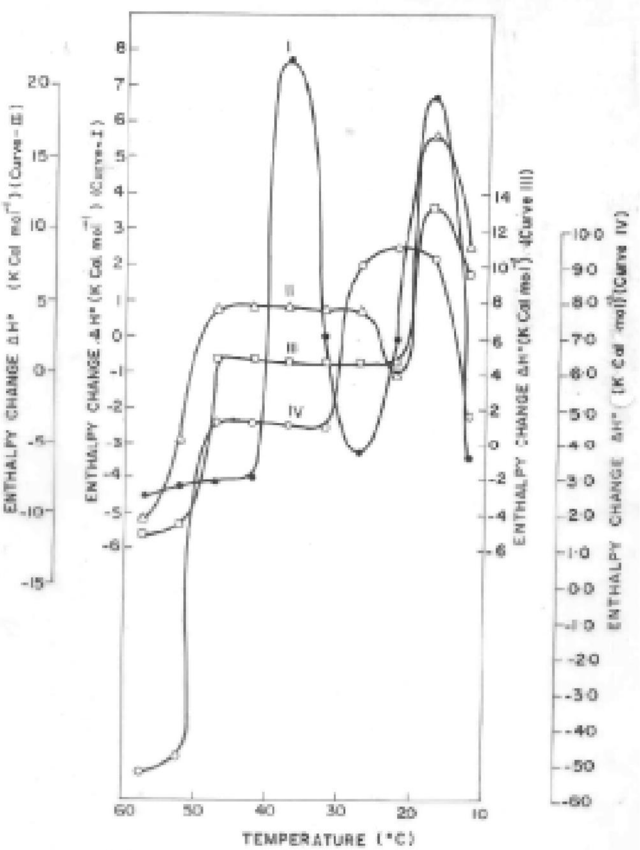


Figure 2 : Temperature dependence of standard enthalpy change (ΔH^0) for the complexation systems 1-4.

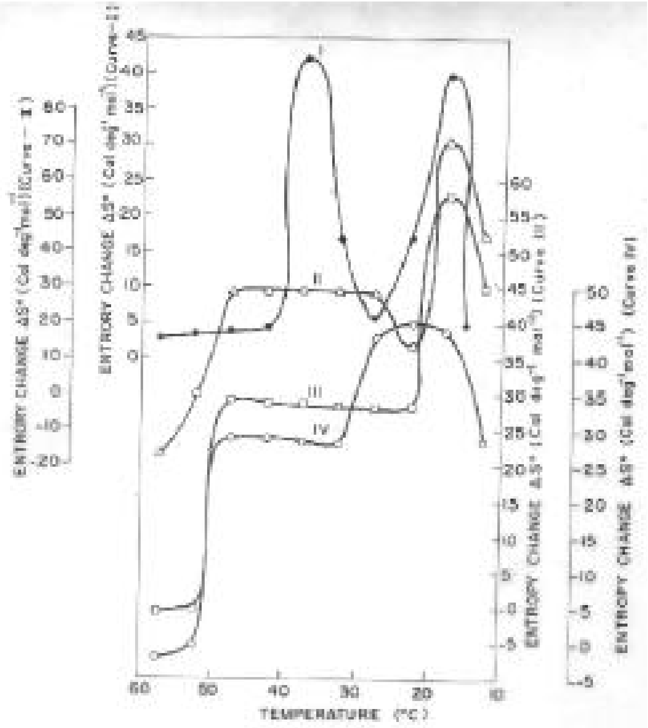


Figure 3 : Temperature dependence of standard entropy change (ΔS^0) for the complexation systems 1-4.

TABLE 2 : Values of maxima of ΔH° corresponding to first peak for systems 1 to 4

Complex	ΔH° value at 17.5°C (Kcal mol^{-1})
1	6.7
2	16.9
3	13.18
4	9.17

nonionic units (e.g., MA,EO, and VA) in complexes 2 to 4 are identical i.e., 0.8 um while in complex 1 this amount is just 0.6 um. The relative difference in the values of ΔH^0 at the first peak may be attributed to the total amount of these units present and their relative proportion[7,8]. As in complex 2, the proportion of PVP is 0.4 um, while PEO is 0.4 um in complex 3 and PVA is 0.4 um in complex 4. The order of the relative strengths of the involved interacting pairs is MA-VP > MA-EO > MA-VA and hence, the trend observed for the first peak is justified. The second peak for complex 1 is very distinct and sharp where as there is a broad halt for each of the systems numbering 2 to 4. The value of ΔH^0 obtained from the graphs (cf. Figure 2 and 3) at the sharp peak (for complex 1) and center of broad peak for complexes 2 to 4 are given in TABLE 3. The higher value of ΔH^0 at the second peak for complex 1 may be attributed to the relatively larger proportion of PEI here. The almost identical value of ΔH^0 for the complexes 2 to 4 may be due to the fact that equal amount of PEI is present in each of these complexes.

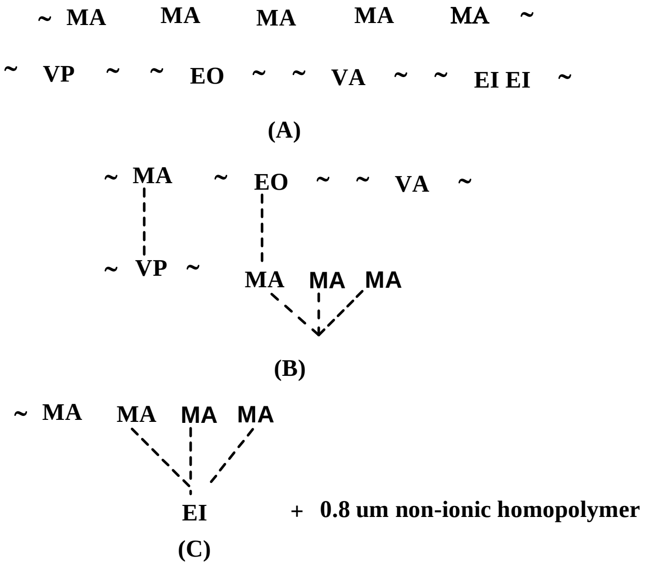


TABLE 3 : Values of maxima of ΔH° corresponding to center of second broad peak for systems 1 to 4

Complex	ΔH° value at 37.5°C (Kcal mol^{-1})
1	7.76
2	4.62
3	4.50
4	4.50

An interesting observation for the complex 2 to 4 was noticed. All of these complexes show an abrupt fall in ΔH^0 value beyond 47^0C, whereas, in case of the complex 1, the fall was at relatively lower temperature, i.e., at 37^0C. in case of complexes 2 to 4 (structure A), the proposed mechanism suggests that the weak H-bonding involved between MA-VP, MA-EO and MA-VA gets destabilized at around 17.5^0C (structure B) resulting in the release of free MA units which might get complexed with already complexed 0.2 um PEI, resulting in the formation of 1:5 PEI-PVP complex (structure C). The abrupt fall ΔH^0 of at 47^0C might be attributed to the breaking down of this complex in case of complexes 2 to 4. Tsuchida and coworkers explained such phenomenon in selective complexation reactions On the basis of a closed chain mechanism. The following mechanism has been proposed[7,8,24,25].

Straight lines indicate covalent bonds between units; curved lines indicate continuity of the polymer while dotted lines indicate secondary binding forces. Further evidence has been provided by the IR studies. In TABLE 4 the stretching frequencies of various bonds in the component polymers and inter polymer complexes are presented.

TABLE 4 : IR studies of component and inter polymer complexes

Component/ interpolymer complex	ν_{N-H} (in PEI)	$\nu_{C=O}$ (in PMA)	$\nu_{C=O}$ (in PVP)	ν_{C-O-C} (in PEO)	ν_{C-O-C} (in PVA)
PEI	1570				
PVP			1625		
PEO				1100	1100
PVA					
PMA		1690			
COMPLEX 1	1619	1718	1637	1180	1180
COMPLEX 2	1618	1718	1637	1179	1179
COMPLEX 3	1618	1716	1638	1180	1180
COMPLEX 4	1690	1718	1637	1181	1181

Some authentic evidence about the interactions of various component polymers (PEI, PVP, PEO and PVA) with the PMA chain could be obtained from electrochemical studies. Figures 4 to 7 present the variation of specific conductance and pH of 1 um aqueous solution of various component polymers in small installments. Both, the conductance and pH curves, show sharp and distinct breaks at various stoichiometries, indicating distinct interactions of the component polymers with the PMA chain. These observations provide an additional evidence for the formation of multicomponent complexes.

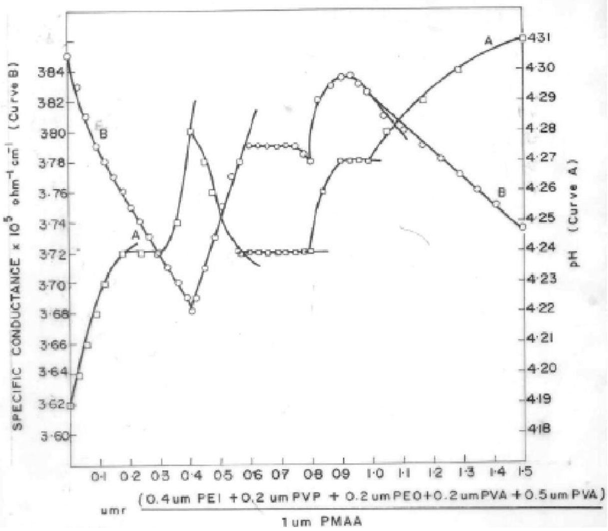


Figure 4 : Variation of pH and specific conductance of PMA solution with the addition of PEI, PVP, PEO and PVA in the sequence for the complexation system 1

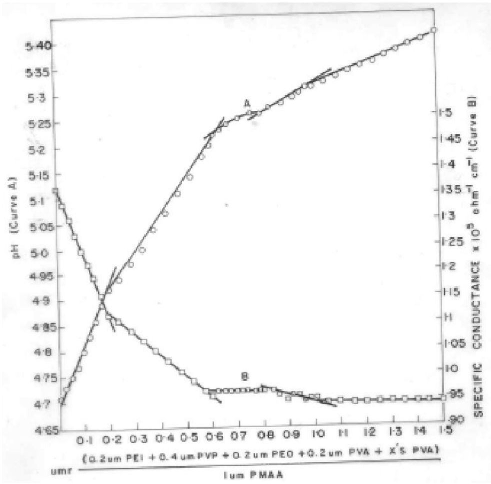


Figure 5 : Variation of pH and specific conductance of PMA solution with the addition of PEI, PVP, PEO and PVA in the sequence for the complexation system 2

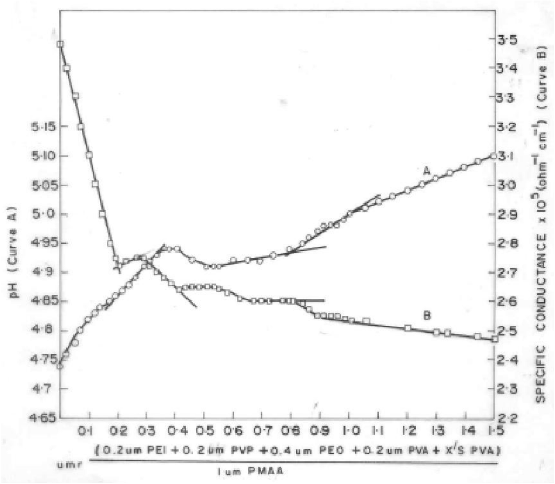


Figure 6 : Variation of pH and specific conductance of PMA solution with the addition of PEI, PVP, PEO and PVA in the sequence for the complexation system 3

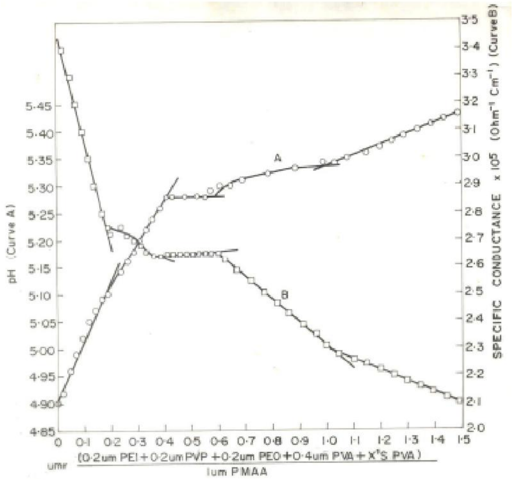


Figure 7 : Variation of pH and specific conductance of PMA solution with the addition of PEI, PVP, PEO and PVA in the sequence for the complexation system 4

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