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FLUORESCENCE STUDIES OF COMPLEXATION OF AURAMINE O LABELED POLY(METHACRYLIC ACID) AND RELATED ACRYLIC COPOLYMERS WITH NON-IONIC HOMOPOLYMERS

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ABSTRACT

Fluorescence studies of interpolymer complexation between PMA and non-ionic homopolymers (e.g. PAAm, PVP, PEO) were carried out using auramine O labeled PMA. These studies were extended to multicomponent systems as well as copolymer complexes involving methacrylic acid as one of the comonomer unit [e.g. poly(MA-co-AAm)]. The degree of linkage (q), stability constant (K) and thermodynamic parameters (e.g. $\Delta G°, \Delta H°$, and $\Delta S°$) of copolymer and polyelectrolyte complexes were determined using Osada's method. A reasonable correlation could be obtained from electrochemical, viscometric, and fluorescence studies.

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INTRODUCTION

Interpolymer complexes formed through hydrogen bonding between poly (carboxylic acid) as proton donor and non-ionic homopolymers as proton acceptors have been extensively studied during the last decade. Some excellent reviews by Bekturov and Bimendina [1] and Tsuchida and Abe [2], summarizing the progress, are available. Study of polymer-polymer interactions has assumed considerable importance in the field of polymer science due to the potential applications of their interaction products [1–3]. Several electrochemical and physical methods have been used to study these interactions [1–7]. During the recent years, in addition to conventional methods, fluorescence intensity measurements have been used as a tool to study interpolymer complex formation. Several substances such as 5-dimethyl amino-1-naphthalene sulfonyl group (Dansyl) [8–10], pyrene [11], auramine O [12], ethidium bromide [13], acridine O [14], etc. [15] have been incorporated into poly (carboxylic acids), and thus used as fluorescent probes. In the case of auramine O, the free probe shows very weak fluorescence but on binding with poly(methacrylic acid) (PMA) it shows strong fluorescence. The enhancement of fluorescence intensity has been interpreted as due to local compact structures in the PMA molecules which binds the dye molecule (e.g. auramine O) very strongly. The binding is electrostatic as well as non-electrostatic in nature. Fluorescence arises due to non-electrostatic binding taking place at the local compact structure in the PMA molecules which are stabilized by the hydrophobic interactions of the methyl groups [16, 17]. Keeping this fact in mind, we have used fluorescence intensity measurement as a tool for studying the interaction of Auramine O (AuO) labeled PMA and related acrylic copolymers with some non-ionic homopolymers (e.g. PVP, PEO and PAAm). In this report, effort has been made to correlate fluorescence studies with other conventional methods which are normally used for studying polymer-polymer interactions.

EXPERIMENTAL

Poly(methacrylic Acid) (PMA) [18]

Methacrylic acid, distilled twice in vacuo , was polymerized with benzoyl peroxide in dioxan-methanol mixture at 65 °C for 3 hours. Nitrogen gas was constantly bubbled through to maintain inert atmosphere. The reaction mixture was dissolved in methanol and the polymer was obtained by precipitating with ether and then drying in vacuo . The number average molecular weight $(\overline{M}_n)$ was ob-

tained from viscosity data in methanol at 25 °C using the following equation [18]:

$$[\eta] = 24.2 \times 10^{-4} \ \overline{M}_n^{0.51}. \ \overline{M}_n \text{ was found to be } 2.3 \times 10^5$$

Poly(acrylamide) (PAAm) [19, 20]

PAAm was prepared from acrylamide by free-radical polymerization using 2,2'-azobisisobutyronitrile (AIBN) as initiator [19]. The polymerization was carried out in acetone medium in nitrogen atmosphere at 50 °C for 45 minutes. The polymer was obtained as a white solid that was removed from the reaction mixture. It was washed thoroughly with acetone and dried in vacuo. The number average molecular weight ($\overline{M}_n$) of the polymer was obtained from viscosity measurements in aqueous medium using the following equation [20]:

$$[\eta] = 6.8 \times 10^{-4} \ \overline{M}_n^{0.66} \text{ and found to be } 1.2 \times 10^5$$

Poly(vinyl Pyrrolidone) (PVP) [21]

PVP was supplied by Fluka (U.S.A.) in the form of white crystalline powder readily soluble in water. The weight average molecular weight ($\overline{M}_w$) of the polymer was obtained from viscosity measurements in aqueous medium using the relation $[\eta] = 6.76 \times 10^{-2} \ \overline{M}_w^{0.55}$ and was found to be 2.4×10^4.

Poly(ethylene Oxide) (PEO) [22]

PEO was supplied by Iwai Karu Co. Ltd., Japan in the form of white crystalline flakes readily soluble in water. The weight average molecular weight ($\overline{M}_w$) was determined by viscosity measurements [22] in aqueous medium at 25 °C and was found to be 1.9×10^4.

Poly(ethylene Imine) (PEI) [23]

PEI was supplied by BDH Chemicals Ltd. Poole, England in the form of 50% viscous water solution. The number average molecular weight ($\overline{M}_n$) of PEI was determined from osmotic pressure measurements by using Polderman's method [23] and found to be 1.5×10^5.

Methacrylic Acid-Acrylamide [poly(MA-co-AAm)]
Random Copolymer [24]

Two samples of random copolymer poly(MA-co-AAm) were prepared by free radical polymerization using $K_2S_2O_8$ as initiator. An aqueous solution of methacrylic acid and acrylamide monomers taken in 9:1 (W:W) ratio with 0.2%

$K_2S_2O_8$ was heated in a suitable vessel fitted with a reflux condensor and an inlet for nitrogen gas. Polymerization was carried out in nitrogen atmosphere at 70°C for 50 minutes. As soon as the product precipitated it was separated, dissolved in acetone and reprecipitated with ether. The process was repeated thrice to remove unreacted monomers. The composition was determined by conducto-metric and pH-metric titrations [25], and was found to be 0.78 : 0.22 (i.e. 78% of MA units and 22% of AAm units). The second sample was prepared by taking the monomers ratio to be 8:2 (W:W). The composition was found to be 0.58 : 0.42 (i.e. 58% of MA units and 42% of AAm units).

Auramine O (AuO, Dimethyl Amino Diphenyl-amine Hydrochloride) [13]

Auramine O was supplied by CDH Pvt. Ltd., India in the form of yellow powder. It was purified by recrystallizing from hot methanol [13].

The probe was soluble in water. A stock solution of 1×10^{-3} M concentration was prepared and stored in dark. It was freshly diluted just before use. The absorption spectra of auramine O in water showed two maxima at 429 nm and 366 nm.

Solvent

For all experimental measurements double distilled water was used as solvent.

Fluorescence Measurements

The emission spectra for fluorescence titration were recorded on Jasco FP-550 spectrofluorimeter at 25°C. The concentration of auramine O in the polymer solution was 5×10^{-5} mol/L. The concentration of PMA in the solution was 5×10^{-3} um/L (um = unit mole i.e., moles of repeat units) while the concentration of poly(MA-co-AAm) copolymer was taken as 1×10^{-3} um/L. The concentration of titrant homopolymer solutions were 1×10^{-2} um/L. A quartz cell of 1 cm optical path was used. The excitation wavelength was 366 nm while the emission maximum occurred between 505 nm-515 nm. The emission intensity for the titration curves was measured at 510 nm. The excitation and emission slit widths were maintained at 3 nm and 20 nm, respectively.

During the titration, 5 mL solution of AuO labeled polymer [e.g., P M A or poly(MA-co-AAm)] was taken and 1×10^{-2} um/L solution of titrant polymer was added in small lots and fluorescence measurements were made after each addition.

pH Measurements

The measurements were carried out with PTA digital pH-meter using combination electrode. For thermodynamic studies the solution was taken in a water jacketed cell and the temperature was controlled by circulating thermo-statically controlled water. The concentration of each polymer solution was 1×10^{-3} um/L (um = unit mole). At these concentrations complexes did not precipitate.

Conductometric Titrations

Conductometric titrations were carried out with Leeds and Northrup (4959) conductivity bridge. The concentration of the polymer solutions in both the conductometric and pH-metric titrations were of the order of 1×10^{-3} um/L.

Viscosity

The viscosity of the mixed solution of copolymer with homopolymers at various unit mole ratios (U M R) was determined at $30 \pm 0.05 \,°C$ using an Ubbelohde viscometer for which the kinetic energy correction was negligible. The concentration of copolymer solution was of the order of $1 \times 10-4$ um/L and the concentration of titrant homopolymer solution was 1×10^{-3} um/L.

Abbreviations

The concentration of polymer solutions have been written in terms of um/L, i.e., unit mole per litre. Unit mole refers to moles of repeat units of titrant homopolymer (e.g. PVP, PAAm, etc.) to the moles of repeat units of polymer in the reaction mixture at any stage during the titration.

For the representation of complexation systems, the polymers have been written in the order of addition of these polymers. The coefficient before the polymer denotes the stoichiometric amount of polymer solutions added.

RESULTS AND DISCUSSION

Fluorescence Studies of Auramine O Labeled PMA with Some Non-ionic Homo-polymers (e.g. PAAm, PVP and PEO)

Poly(methacrylic acid) is known to form 1:1 (UMR) interpolymer complexes with several non-ionic homopolymers such as PAAm, PVP, PEO etc. This has been shown by conventional physical methods by several workers [1, 2]. It would be of interest to see whether fluorescence method could be used as a tool

to study the complex formation in simple binary systems mentioned above. Later on, one could extend these studies to more complicated multicomponent systems. Keeping this object in mind, we have studied the variation of fluorescence intensity of auramine O labeled PMA with the addition of PAAm, PVP and PEO, respectively. AuO does not show fluorescence in the presence of PAAm, PVP and PEO but when these homopolymers are added to a solution of AuO labeled PMA, the fluorescence intensity of the solution changes. The variation of fluorescence intensity is attributed to the changes accompanying polycomplex formation. These changes include changes in the conformation, rigidity and the polarity of the polymeric systems, which are dependent on the nature of interacting units involved [17].

In Figure 1 are presented the variations of fluorescence intensity with unit mole ratio (UMR) of aqueous solution of AuO labeled PMA with the addition of increasing concentration of respective homopolymer solutions (e.g. PAAm, PVP and PEO). The measurements have been done at λem = 510 nm at 25°C. A blank titration (cf. Curve 4 of Figure 1) has been carried out using water instead of homopolymer solution. The linear fall in fluorescence intensity in the blank titration may be attributed to dilution of PMA-AuO on addition of water. Each of the other three titration curves (cf. Curves 1 to 3 of Figure 1) indicated distinct breaks at 1:1 stoichiometry, [Homopolymer]/[PMA] of the complex. However, the nature of the titration curves for the three complexation systems is different. This is expected in view of the fact that the secondary binding forces involved in the interaction of units are different (e.g. MA-AAm, MA-VP, MA-EO) in the respective systems. The interpretations of the nature of various curves have been summarized below.

PAAm vs AuO Labeled PMA Fluorescence Titration Curve (Curve 1 of Figure 1)

The slight increase in fluorescence intensity till 0.5 UMR, and subsequent fall up to 1.0 UMR, could be attributed to the following factors. During the process of complexation, the organic character of the microenvironment around AuO increases and at the same time the compact structures in PMA chains open up. It is known that fluorescence intensity increases due to first factor and the decrease in intensity is attributed to the second factor [16]. The nature of the curve depends on the contribution of each of these factors, i.e., increase or decrease in fluorescence intensity during complex formation depends on the relative contributions of the two factors.
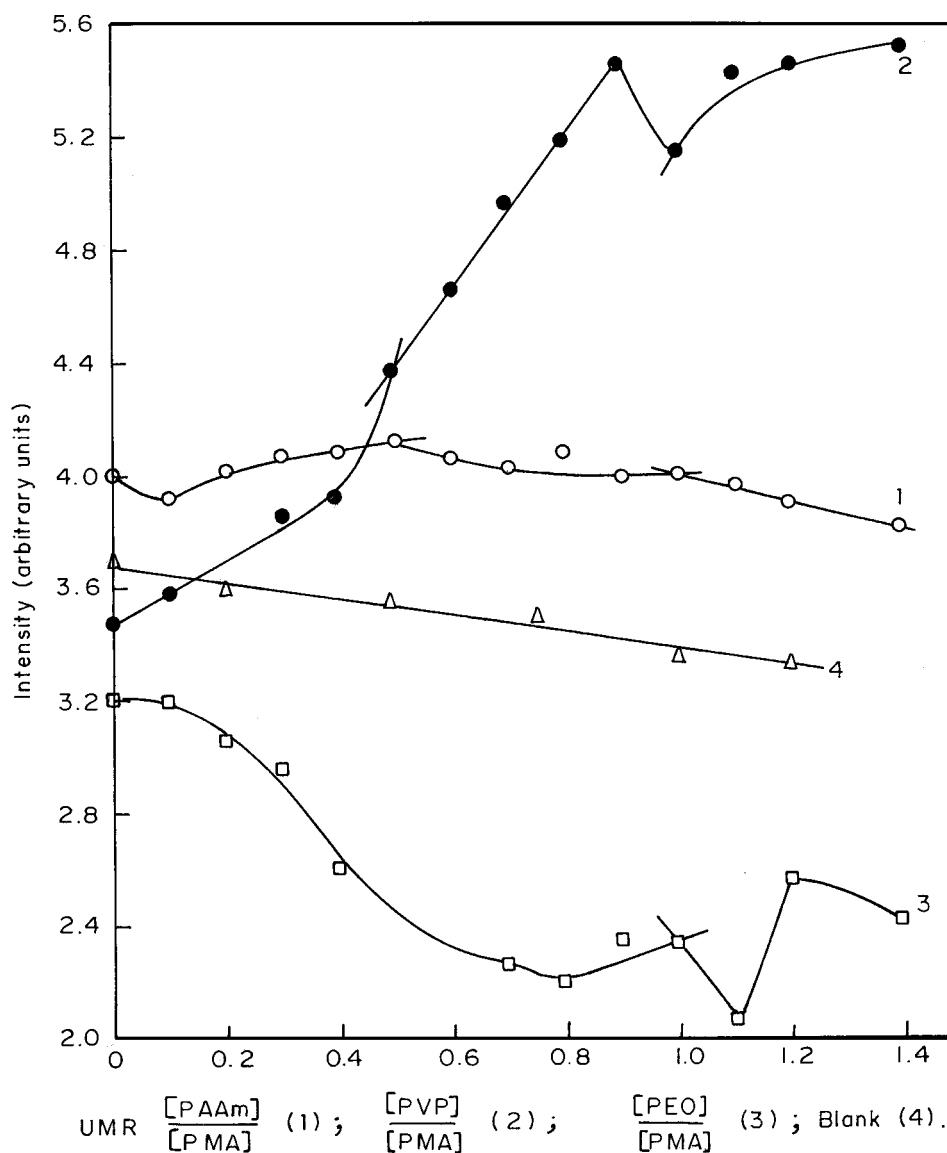
Figure 1.   Variation of fluorescence intensity with unit mole ratio (UMR) of
(a) [PAAm]/[AuO-PMA], Curve 1 (b) [PVP]/[AuO-PMA], Curve 2
(c) [PEO]/[AuO-PMA], Curve 3 (d) Blank, Curve 4.

PVP vs AuO Labeled PMA Fluorescence Titration Curve
(Curve 2 of Figure1)

The fluorescence intensity indicated a sharp increase followed by a slight fall near 1.0 UMR, and subsequent increase beyond 1.0 UMR. Though, it is expected that the local compact structures of PMA will open up during the interaction with PVP, but it is more than compensated by the increased organic character of the medium due to the greater hydrophobicity of PVP. The slight increase in fluorescence intensity beyond 1.0 UMR may be attributed to possible increase in rigidity or organic character of the medium around the probe.

PEO vs AuO Labeled PMA Fluorescence Titration Curve
(Curve 3 of Figure1)

The fall in fluorescence intensity during the addition of PEO may be attributed to increased proportion of non-ionized PMA, which in turn affects the electrostatic binding of AuO with PMA i.e. number of molecules of AuO bonded to PMA decrease. At the same time, local compact structures on PMA are likely to open up. Both these factors contribute to the fall in fluorescence intensity. With excess PEO, the intensity falls due to dilution as no further reaction is expected to take place.

Fluorescence Titration of Three Component Complexation Systems

Since the nature of fluorescence titration curves of AuO labeled PMA with different non-ionic homopolymers, could be reasonably interpreted, therefore, it was considered of interest to study the variation of fluorescence intensity of AuO labeled PMA with the addition of two different homopolymers in different sequences. The sequences referred to the order of addition of PVP and PAAm to the AuO labeled PMA solutions. For instance, in the first titration, 0.5 um PVP solution was added in small lots to 1 um solution of AuO labeled PMA to complex half of MA units, and subsequently, 0.5 um PAAm solution was added in small installments to complex the remaining MA units and, after 1:1 (UMR) complex is formed, excess of PVP solution was added. In the second titration, the order of addition of PAAm and PVP to Auo labeled PMA has been reversed e.g. firstly 0.5 um PAAm solution was added and subsequently followed by the addition of 0.8 um of PVP (i.e. including 0.3 um of excess PVP) to the AuO labeled PMA solution. All additions of component polymers have been made in small instalments. The following two systems have been studied :
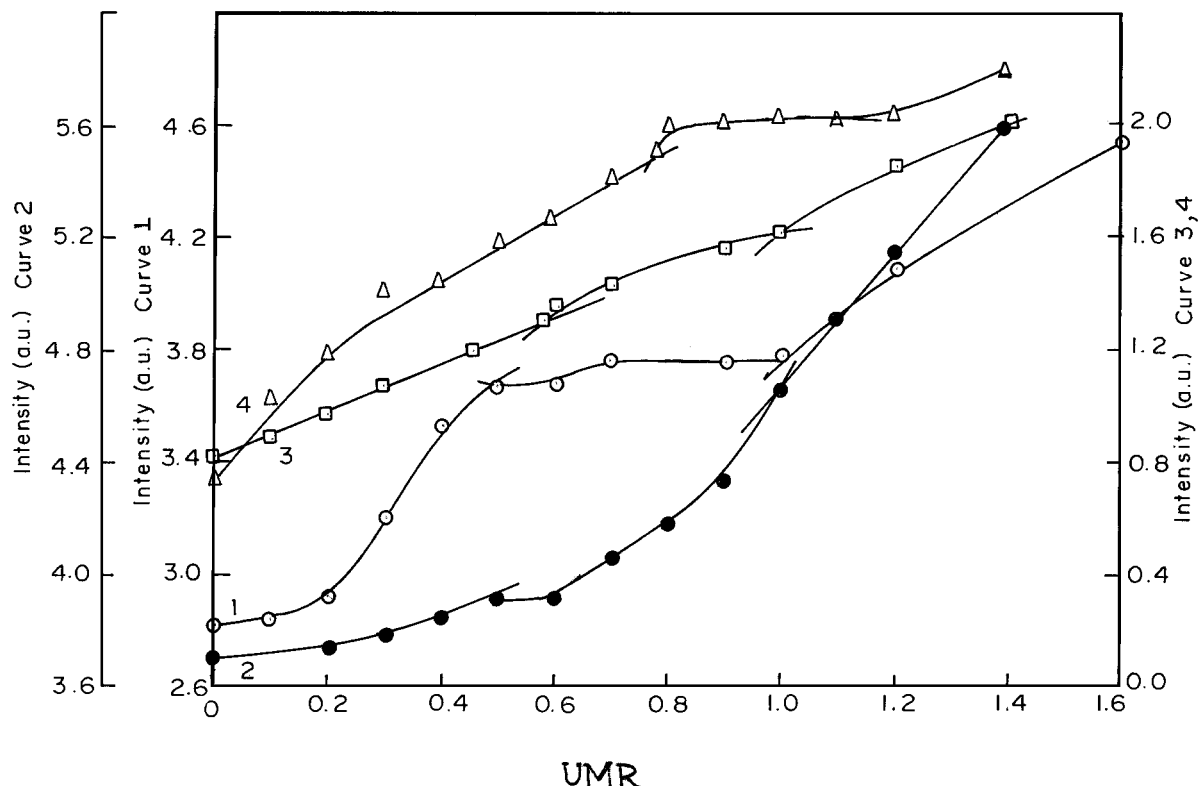
Figure 2. Variation of fluorescence intensity with unit mole ratio (UMR) of

(a) [0.5 um PVP + 0.5 um PAAm + X's PVP]/[AuO-PMA], Curve 1

(b) [0.5 um PAAm + 0.5 um PVP + X's PVP]/[AuO-PMA], Curve 2

(c) [0.58 um PVP + (0.42 um +X's) PMA)]/[AuO-MA-co-AAm] Curve 3

(d) [0.78 um PVP + (0.22 um +X's) PMA)]/[AuO-MA-co-AAm], Curve 4.

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(i) 1 um AuO labeled PMA + 0.5 um PVP + 0.5 um PAAm + X's PVP
     (Cf. Curve 1 of Figure 2)

(ii) 1um AuO labeled PMA + 0.5 um PAAm + 0.5 um PVP + X's PVP
     (Cf. Curve 2 of Figure 2)

As can be seen from curves 1 and 2 of Figure 2, the nature of the initial portion (i.e. up to 0.5 UMR) of curve 1 and final portion (from 0.5 to 1.0 UMR) of curve 2 coincide with the nature of PVP–PMA titration curve (cf. curve 2, Figure 1), while the final portion of curve 1 and initial portion of curve 2 coincide with the nature of PAAm–PMA titration curve (cf. curve 1, Figure 1). This indicates that the nature of changes in fluorescence titration is virtually not affected by the order of addition of PVP and PAAm and also nature of curves is independent of the presence of second interacting unit. Thus, the interaction of PVP and PAAm with AuO labeled PMA could be observed by distinct breaks in the titration curves.

Fluorescence Titration Curves of AuO Labeled poly(MA-co-AAm) Copolymer with PVP and PMA

Since it is reasonably well established that fluorescence intensity of P M A could be enhanced considerably by labeling with a dye such as AuO [14], therefore, it was thought that any PMA containing copolymer, such as methacrylic acid–acrylamide random copolymer [poly(MA–co–AAm)], could also be labeled with AuO to enhance its fluorescence intensity. Keeping this object in mind, the following two complexation systems with copolymers of different compositions have been studied:

(i) 1um poly (MA–co–AAm) (0.58 : 0.42) + 0.58 um PVP + 0.42 um
     P M A + X's PMA   (Curve 3 of Figure 2)

(ii) 1 um poly (MA–co–AAm) (0.78 : 0.22) + 0.78 um PVP + 0.22 um
     P M A + X's PMA   (Curve 4 of Figure 2)

The variation of fluorescence intensity of the two AuO labeled copolymers with the addition of stoichiometric quantities of PVP and PMA are depicted in Figure 2, Curves 3 and 4. The stoichiometric amounts of PVP and PMA were added in accordance with the respective compositions of the two copolymers. As expected, the nature of the two curves also coincided with the fluorescence curves of individual homopolymers with AuO labeled PMA (cf. compare curve 1 and 2 of Figure 1 with curves 3 and 4 of Figure 2).

Thermodynamic Studies of Copolymer and Polyelectrolyte Complexes

Thermodynamic studies of complexes involving copolymers and poly-electrolytes have been carried out in order to have a possible correlation of results obtained from fluorescence and other electrochemical methods. The following systems involving copolymer poly (MA-co-AAm) and polyelectrolyte (PMA) have been studied :

(I) 1 um poly (MA-co-AAm) (0.58 : 0.42) + 0.58 um PEI + 0.92 um P M A + 0.25 um PVP and 0.25 um PEO

(II) 1 um PMA + 0.25 um PEI + 0.25 um PAAm + 0.25 um PVP + 0.25 um PEO

The basic difference between the above two systems is that in system (I) an acrylic copolymer is involved whereas in system (II) a polyelectrolyte is involved. However, the pairs of interacting units in the two systems are identical which are shown below:

(a)   M A   (b)   M A   (c)   M A   (d)   M A
       EI   A A m   V P   E O

Since the nature of secondary binding forces involved in these pairs of interacting units are different, therefore, one would expect them to get destabilized at different temperatures. Keeping this fact in mind, we have determined the stability constant (K), degree of linkage (θ) and related thermodynamic parameters (e.g. $\Delta G^\circ, \Delta H^\circ$, and ΔS°) using Osada's method [4, 26, 27]. The different parameters have been calculated on the basis of the following equations:

$$\theta = 1 - ([H^+]/[H^+]_o)^2$$

$$K = \theta/C_o(1-\theta)^2$$

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

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

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

Where C_o is the initial concentration of copolymer or polyelectrolyte, and $[H^+]$ and $[H^+]_o$ are the proton concentrations in the copolymer or polyelectrolyte solution in the presence and absence of complementary polymers (e.g. PVP, PEI, PAAm and PEO), respectively.

Although Osada's method was developed for hydrogen-bonding complexes involving polyacid and non-ionic homopolymers, this method could be
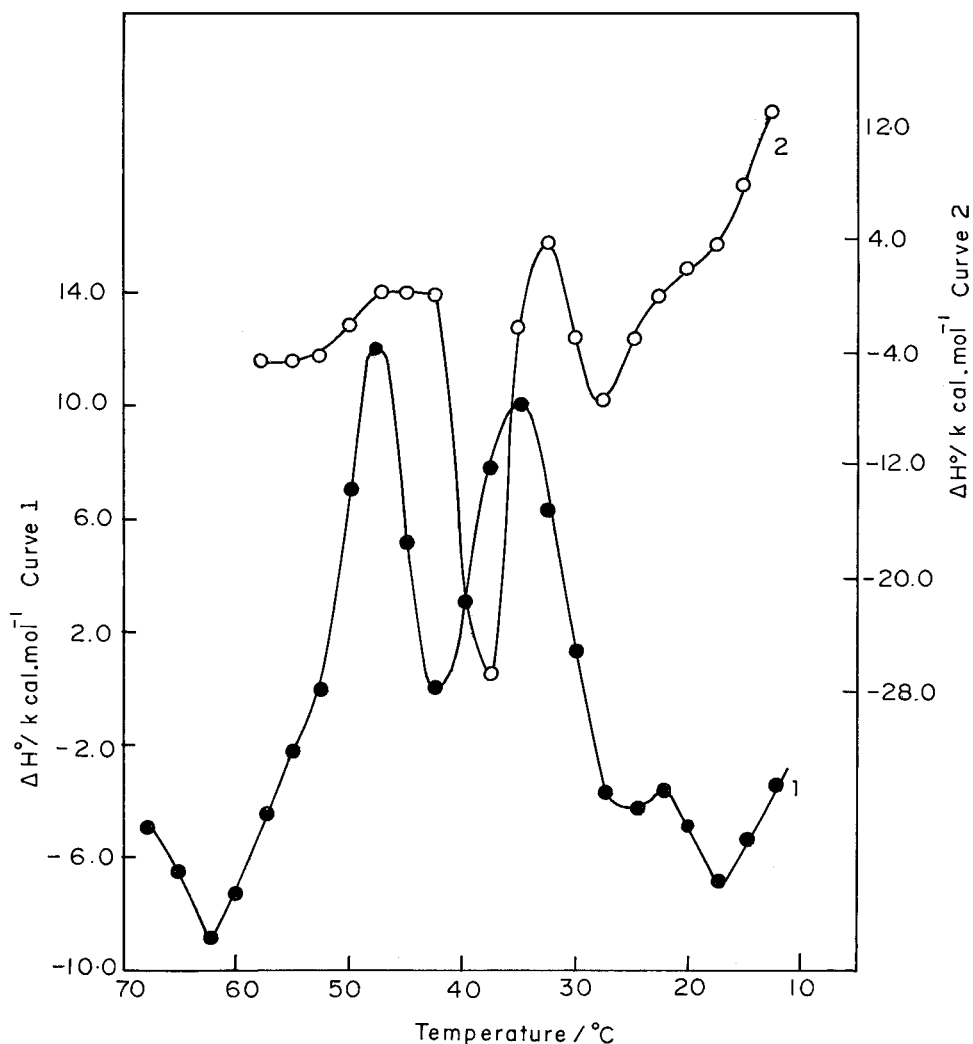
Figure 3.   Variation of standard enthalpy change ($\Delta H°$) with temperature
             for complexation systems (a) I, Curve 1 and (b) II, Curve 2.

extended to two systems under investigation. In these two systems, four pairs of
interacting units are involved, and out of these, three pairs of interacting units
(e.g. MA-AAm, MA-VP, MA-EO) involve hydrogen bonding. The fourth pair
of interacting units (e.g. MA-EI) involves proton transfer as well as electrostatic
interactions. The calculation of degree of linkage (θ) for PMA-PEI complexa-
tion is similar to the hydrogen bonded polycomplexes as electrostatic interac-
tions do not seem to affect the calculation of θ. Since Osada's method is applic-
able to the simple binary complexation systems involving a single pair of inter-
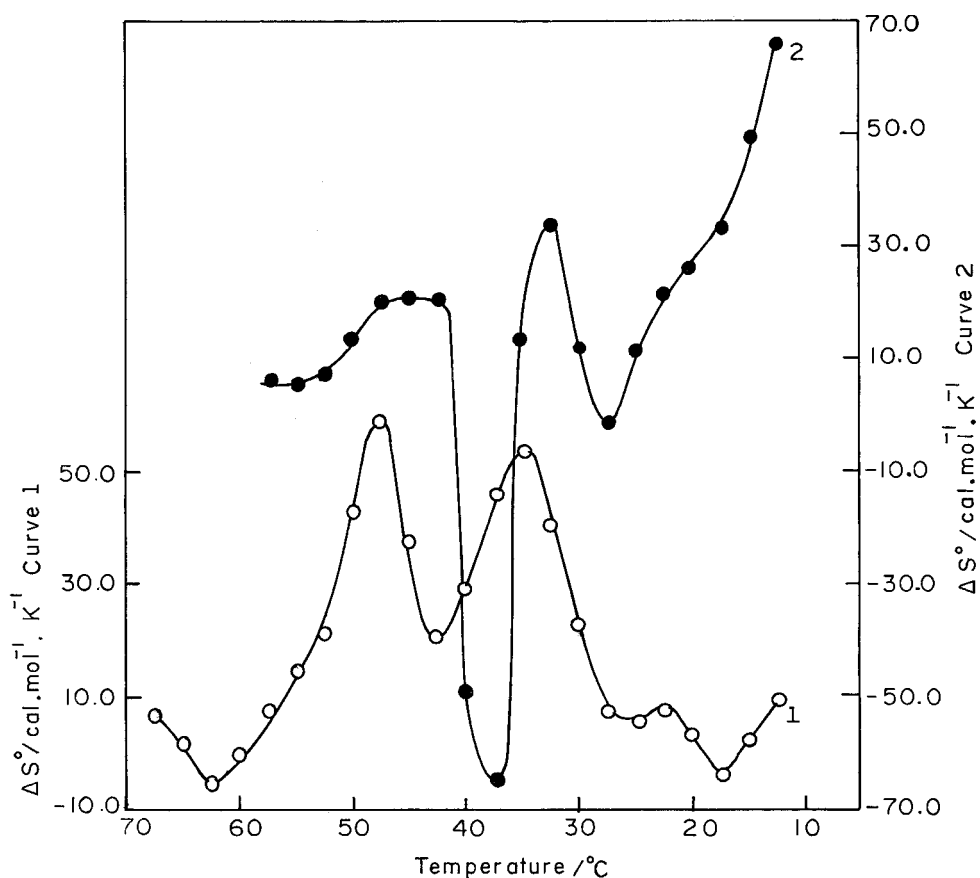
Figure 4.   Variation of standard entropy change ($\Delta S°$) with temperature for complexation systems (a) I, Curve 1 and (b) II, Curve 2.

acting units, therefore one could expect it to be applicable to multicomponent complexation systems, involving more than one pair of interacting units. Study of a large number of multicomponent complexation systems [28] on the basis of Osada's method from this laboratory, seem to indicate the validity of the above arguments.

The stability constant (K) of the two complexes have been found to be in the following order :

lnK [poly (MA-co-AAm)-homopolymer] > lnK [PMA-homopolymer]

This may be attributed to the greater neighbouring group influence and cooperativity in the copolymer chains as compared to the polyelectrolyte chains (e.g. PMA). The plot of $\Delta H°$ vs T and $\Delta S°$ vs T for the two complexation sys-

TABLE 1.   The Maximum   Values of ΔH° and ΔS° Observed and Probable Assignment of Destabili-zation of Interacting Units for Complexation Systems I and II

Complexation System	Maxima Observed in		Temperature at which maxima observed	Probable destabilization of interacting units
	ΔH^o (kcal. mol^{-1})	ΔS^o (cal.mol^{-1} K^{-1})		
(I) 1um Poly(MA-co-AAm) (0.58 :0.42) + 0.58um PEI + 0.92um PMA + 0.25 um PVP + 0.25um PEO	-3.6 (ΔH_1) 10.3 (ΔH_2) 12.2 (ΔH_3)	7.9 (ΔS_1) 53.6 (ΔS_2) 59.0 (ΔS_3)	22.5 ^{o}C 35.0 ^{o}C 47.5 ^{o}C	EO : MA VP : MA MA : AAm + MA : EI
(II) 1um PMA + 025um PEI + 0.25um PAAm + 0.25 um PVP + 0.25 um PEO	1.71 (hump) 3.7 (ΔH_2) 0.0 (ΔH_3)	31.2 (hump) 33.7 (ΔS_2) 20.3 (ΔS_3)	20.0 ^{o}C 32.5 ^{o}C 45.0 ^{o}C	EO : MA VP : MA MA : AAm + MA : EI

1 cal = 4.18 J

tems (e.g. I and II) are depicted in Figures 3 and 4, respectively.The copolymer complexation system (e.g. I) showed three maxima in both $\Delta H°$ and $\Delta S°$ vs T curves, at distinct temperatures. Whereas, the polyelectrolyte complexation system (e.g. II), indicated two such maxima and a hump at 20°C. The absolute values of $\Delta H°$/or $\Delta S°$ at the respective maxima in the two systems are summarized in Table 1.

Although, both the complexation systems have identical pairs of interacting units (cf. p. 11), but destabilization of some of the pairs of interacting units, seems to be merged up. The destabilization of different interacting units takes place at different temperatures in view of the different secondary binding forces involved in each pair. The weaker interacting units destabilize at lower temperatures while comparatively stronger interacting units destabilize at higher temperature. The order of stability of the four interacting units has been found to be EO : MA < VP : MA < MA :AAm < MA : EI. On the basis of this argument, one can assign the destabilization of different pairs as indicated in Table 2.

However, it may be mentioned here that the variations of $DH°$ or $DS°$ with temperature are considerably large as compared to calculated experimental errors in these measurements.

In order to substantiate some of the observations made earlier with various systems, it was considered of interest to carry out electrochemcial, viscometric and fluorescence studies with random copolymer [poly(MA-co-AAm)] and polyelectrolyte (PMA), during their interaction with various non-ionic homopolymers (e.g. PAAm, PVP and PEO) and polyelectrolyte (PEI). In Figure 5, are presented the variations of pH, specific conductance, reduced viscosity (η_{sp}/c) and in Figure 6 fluorescence intensity of 1 um AuO labeled random copolymer [poly(MA-co-AAm)] solution on the addition of stoichio-metric quantities (cf. Table 3) of polyelectrolytes and non-ionic homopolymers. The distinct breaks observed in various titration curves and the probable stoichi-ometries assigned to them are summarized in Table 3.

The variation of fluorescence intensity of 1 um of AuO labeled PMA solution with the addition of stoichiometric quantities of polyelectrolyte (e.g. PEI) and various non-ionic homopolymers (e.g. PAAm, PVP and PEO) is depicted in Figure 6 (Curve 2). The distinct breaks observed at various unit mole ratios (UMR) and the probable stoichiometries assigned to them are also summarized in Table 3.

As can be seen from the above table, the various units interact in distinct stages and an excellent correlation could be observed from independent physical methods regarding the coincidence of various breaks in the titration curves.

TABLE 2.   Breaks Observed and Probable Stoichiometries Assigned to Complexes (I) and (II)

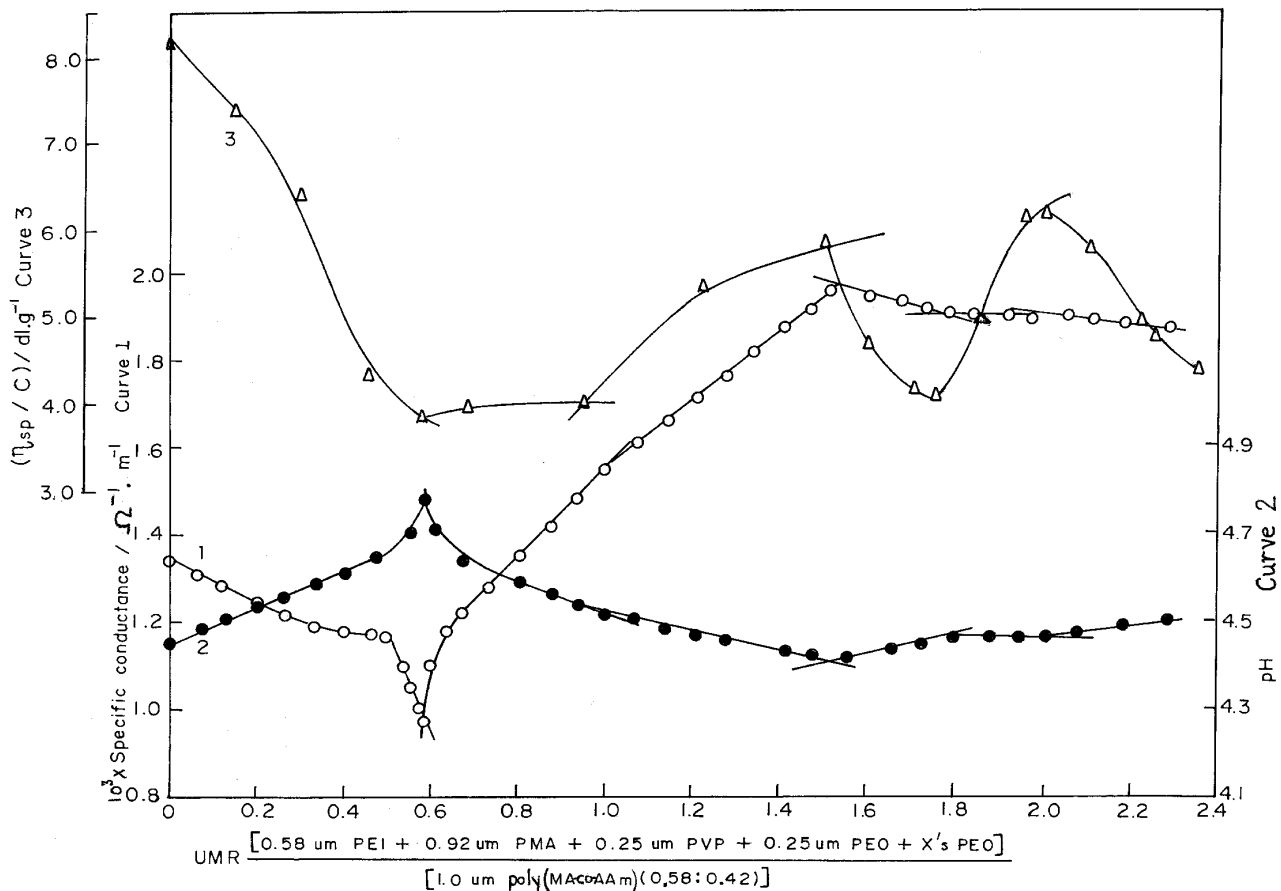| Complexation System	Breaks Observed (UMR)				Probable Stoichiometries
	pH	Specific Conductance	Viscosity	Fluorescence	
(I) 1um poly(MA-co-AAm)	0.58	0.58	0.58	0.58	MA : EI (1:1)
(0.58 : 0.42) + 0.58um PEI	1.0	1.0	0.95	1.0	MA : AAm (1:1)
+ 0.92um PMA	1.5	1.5	1.5	1.5	Excess PMA
+ 0.25um PVP + 0.25um PEO	1.75	1.75	1.75	1.75	MA : VP (1:1)
+ X's PEO	2.0	2.0	2.0	2.0	MA : EO (1:1)
(II) 1um PMA + 0.25um PEI +				0.25	MA : EI (1:1)
0.25um PAAm + 0.25um PVP +				0.50	MA : AAm (1:1)
0.25um PEO + X's PEO				0.75	MA : VP (1:1)
				1.0	MA : EO (1:1)

Figure 5. Variation of specific conductance, Curve 1; pH, Curve 2 and reduced viscosity (η_{sp}/C), Curve 3 for complexation system I.

Curve 1   UMR   [0.58 um PEI + 0.92 um PMA + 0.25 um PVP + (0.25 um + X's) PEO]
                ───
                        [1.0 um poly (MA-co-A Am)(0.58 : 0.42)]

Curve 2   UMR   [0.25 um PEI + 0.25 um PAAm + 0.25 um PVP + (0.25 um + X's) PEO]
                ──
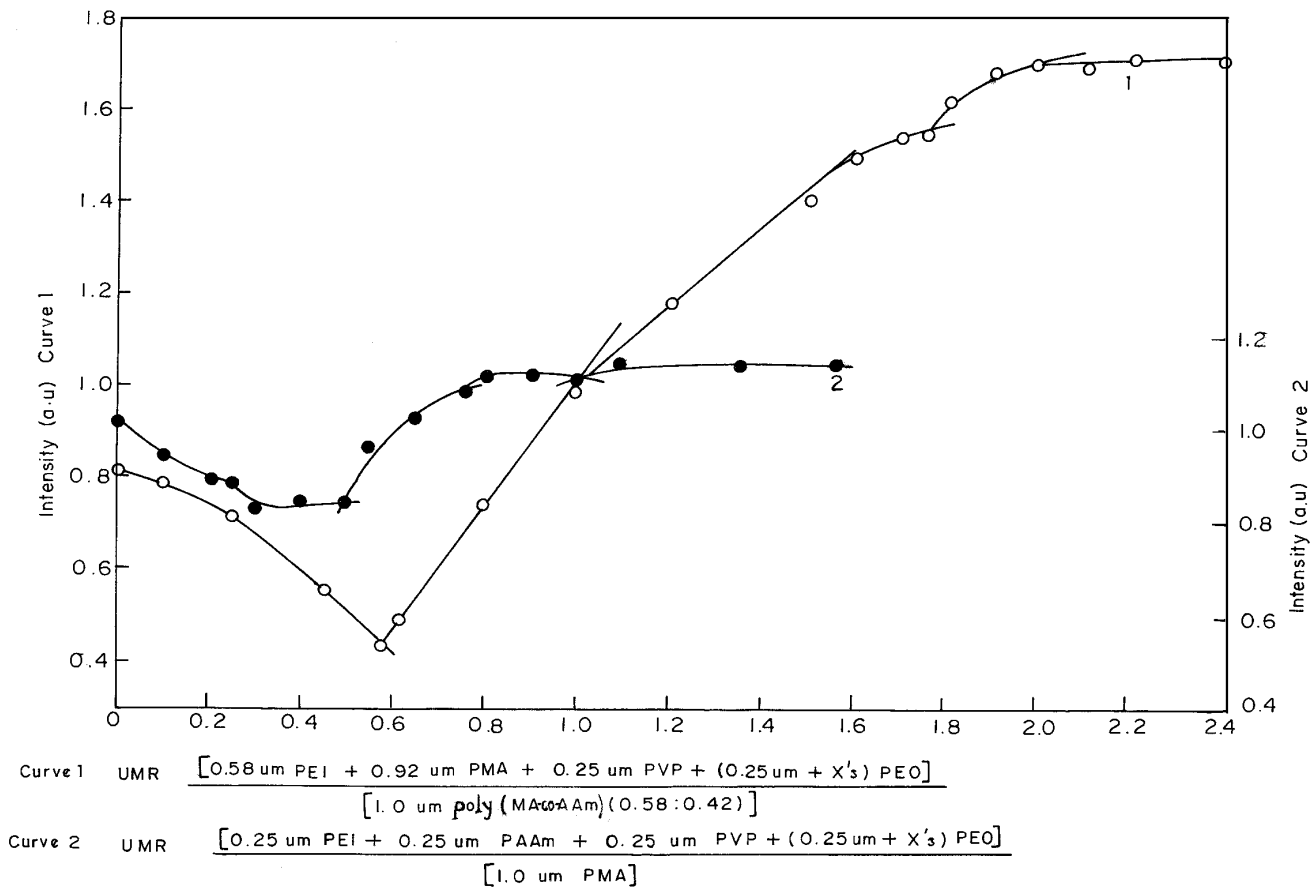   [1.0 um PMA]

Figure 6. Variation of fluorescence intensity with unit mole ratio (UMR) of complexation systems (a) I,
        Curve 1 and (b) II, Curve 2.

In conclusion, it can be said that fluorescence intensity measurements on dyes bound to polyanions provide an excellent additional method of studying polymer-polymer interactions. Moreover, this method could be correlated with other physico-chemical methods, which are normally used to study such interactions. Fluorescence studies can also be extended to copolymers containing polyanions [e.g. poly(MA-co-AAm)].

ACKNOWLEDGEMENT

REFERENCES

[1]   E. A. Bekturov and L. A. Bimendina, Adv. Polym. Sci., 41, 99 (1981).

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

[3]   I. M. Papisov and A. A. Litmanovich, Adv. Polym. Sci., 90, 139 (1989).

[4]   Y. Osada, J. Polym. Sci., Polym. Chem. Ed., 17, 3485 (1979).

[5]   L. A. Bimendina, G. S. Tleubaeva, and E. A. Bekturov, Vysokomol Soedin, Ser.A19, 71, (1977).

[6]   I. Biros, L. Masa, and J. Pouchly, Eur. Polym. J., 10, 629 (1974).

[7]   L. Webster, M. B. Huglin, and I. D. Robb, Polymer, 38(6), 1373 (1997).

[8]   H. L. Chen and H. Morawetz, Eur. Polym. J., 19, 923 (1983).

[9]   B. Bednar, Z. Li, Y. Huang, Li-C.P. Chang, and H. Morawetz, Macromolecules, 18, 1829 (1985).

[10]   Y. Wang and H. Morawetz, Macromolecules, 22, 164 (1989).

[11]   D. J. Hemker, V. Garza, and C. W. Frank, Macromolecules, 23, 4411 (1990).

[12]   J. C. Fenyo, C. Braud, J. Beaumais, and G. Muller, J. Polym. Sci., Polym. Lett. Ed., 13, 669 (1975).

[13]   J. C. Fenyo and L. Mognol, J. Polym. Sci., Polym. Chem. Ed. 17, 4069 (1979).

[14]   E. V. Anufrieva, T. M. Birshtein, T. N. Nekrasova, O. B. Ptitsyn, and T. V. Sheveleva, J. Polym. Sci., Part C, 16, 3519 (1968).

[15]   J. J. Heyward and K. P. Ghiggino, Macromolecules, 22, 1159 (1989).

[16] (a) B. Erny and G. Müller, J. Polym. Sci., Polym. Chem. Ed., 17, 4011 (1979); (b) M. Mandel and W. H. Stork, J. Biophys. Chem., 2, 137 (1974).

[17] Y. Wang and H. Morawetz, Macromolecules, 19, 1925 (1986).

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

[19] S. K. Chatterjee, E. Prokopova, and M. Bohdanecky, Eur. Polym. J. 14, 665 (1978).

[20] E. Collinson, F. S. Daniton, and G. S. McNaughton, Trans. Faraday Soc., 53, 489 (1957).

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

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

[23] A. Polderman, Biopolymer, 14, 2181 (1975).

[24] S. H. Pinner, J. Polym. Sci., 10, 379 (1953).

[25] S. K. Chatterjee, R. L. Pandith, and L. S. Pachauri, Polymer, 23, 1659 (1982)

[26] Y. Osada and J. Sato, J. Polym. Sci., Polym. Chem. Ed., 17, 3485 (1979).

[27] Y. Osada, J. Polym. Sci., Polym. Chem. Ed., 15, 255 (1977).

[28] S. K. Chatterjee, S. Nigam, and V. Kapoor, Polymer Bulletin, 35, 489 (1995).

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