

Interpolymer association between phenolic copolymers and polyelectrolytes: effects of copolymer structure and hydrophobic interactions on the stability of polycomplexes

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Summary

Phenolic copolymers have been prepared with two different feed compositions from some typical phenolic monomers, such as, p-Chlorophenol, p-Cresol and p-Aminophenol. They have been characterized by known methods. Some interpolymer complexes of the phenolic copolymers have been prepared with polyelectrolytes, such as poly(methacrylic acid) (PMA) and poly(ethylene imine) (PEI). The degree of linkage, stability constant, enthalpy and entropy changes of the systems were determined at several temperatures. Interpretations have been sought in terms of the various interacting forces involved in the complex formation.

Introduction

Interpolymer complexes occupy a unique position in the field of polymer science in view of their potential applications in medicine and industries (1-3). Though considerable amount of work has been reported in the literature during the last decade on polyelectrolyte and hydrogen bonding complexes in aqueous and organic solvents (1-8), but very little information seems to be available on phenolic copolymer-polyelectrolyte interactions, particularly in water-organic solvent mixtures. Phenolic copolymers provide unique systems in view of the presence of intramolecular hydrogen bonding in them (9-11), and also one could incorporate various coordinating groups (e.g. $-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$) in these copolymers which could be complexed with the functional groups of specific polyelectrolytes. Polyelectrolyte complexes of phenolic copolymers may possibly find wider application in industries compared to phenolic resins as such. Keeping this object in mind, we have made an attempt to probe into the mechanisms of interaction of p-Chlorophenol-p-Cresol-p-Aminophenol-formaldehyde (PCIP-PC-PAP) copolymer, with two typical polyelectrolytes, such as poly(methacrylic acid) (PMA), and poly(ethylene imine) (PEI) in DMF- H_2O and DMSO- H_2O mixtures. The two solvents, DMF and DMSO differ in their dielectric constant, hydrogen bonding ability, and in the degree of solvation of the component polymers. All these factors are likely to influence interpolymer complex formation. Unlike in pure organic solvents, presence of water in mixed solvent media is likely to make interpolymer complexes more stable due to hydrophobic interactions. One could predict the relative stability of the interpolymer complexes, on the basis of characteristics of solvent media, as well as on the mode of interaction between the pairs of interacting units. Therefore, determination of stability constant (K), and degree of

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linkage (θ) of these complexes may provide an insight regarding the mode of formation of the complexes (12,13). Electrochemical studies, such as variation of specific conductance during interpolymer complex formation, as well as distinct shifts in characteristic group frequencies in IR spectra of the complexes, are likely to provide authentic evidence regarding the mode of complexation. In this report an attempt has been made to correlate various thermodynamic parameters with the nature of the interpolymer complex and the solvent media.

Experimental

p-Chlorophenol-*p*-Cresol-*p*-Aminophenol-Formaldehyde Copolymer (PCIP-PC-PAP)

The three monomers PAP, PCIP, and PC have been refluxed with formaldehyde in the presence of 2 ml of 10N HCl as catalyst for 3 h at 130°C. The reaction mixture was then poured into ice-cold water and washed several times with distilled water to remove unreacted monomers.

Two samples of the three component random copolymer were prepared by choosing the following feed compositions:

Copolymer I: 0.2m PCIP+0.2m PC + 0.6m PAP + 1.0m HCHO

Copolymer II: 0.33m PCIP + 0.33m PC + 0.33m PAP + 1.0m HCHO.

The copolymer yield in both the cases was 70-75%. The halogen content of each of the two copolymer samples was determined by treating the copolymer with sodium metal and the resultant sodium chloride was estimated by Volhard's method (14). The composition of the copolymer was established by electrometric titration techniques(15).

Poly(methacrylic acid) (PMA) was prepared by known methods (16). The weight average molecular weight (\bar{M}_w) was calculated from viscosity measurements and was found to be 2.5×10^5 g mol⁻¹.

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

Solvent DMF-H₂O and DMSO-H₂O mixtures in the volume ratio of 90% DMF or DMSO + 10% H₂O were used as solvents in all experimental measurements.

Conductometric titration: The conductometric titrations were carried out with a Leeds and Northrup conductance bridge (4959).

The pH measurements of the polymers in mixed solvents were carried out in a water-jacketed cell with 'PTA' digital pH meter, using a combination electrode. The temperature of the sample solution was thermostatically controlled within $\pm 0.05^\circ\text{C}$ by circulating water.

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

Infrared spectra of the interpolymer complex (IIA) and the component polymers were recorded on KBr pellet by using Perkin Elmer model 1710 spectrophotometer.

Results and discussion

The two phenolic copolymers (I and II) have been prepared by choosing two different feed compositions, and characterized by known methods (14,15). They have been found to have the following compositions in terms of the three comonomer units:

| Copolymer | p-Chlorophenol | p-Cresol | p-Aminophenol |
|-----------|----------------|----------|---------------|
| I | 0.278m | 0.045m | 0.677m |
| II | 0.373m | 0.135m | 0.492m |

The copolymers (I and II) have both basic and acidic functional groups (e.g. $-\text{NH}_2$ and $-\text{OH}$), and they could be complexed by adding stoichiometric amounts of poly(methacrylic acid) (PMA) and poly(ethylene imine) (PEI), respectively. Such 1:1 umr (unit mole ratio) complexes of copolymer (I and II) have been prepared by adding 0.677 μm (unit mole) of PMA and 1.0 μm of PEI to copolymer (I) (complex IA), and 0.492 μm of PMA and 1.0 μm of PEI to copolymer (II) (complex IIA), respectively. The complexes have been studied in two different solvent mixtures, e.g., in (90% DMF + 10% H_2O), and (90% DMSO + 10% H_2O), respectively. The two organic solvents, DMF and DMSO have been extensively used as a medium in the study of interpolymer complexation (1,2) and they are also miscible with water in all proportions. Unlike in pure organic solvents, the mixing of water with organic solvent, will possibly help in enhancing the stability of the interpolymer complexes due to hydrophobic interactions. Keeping this object in mind, the stability constants (K) of interpolymer complexes (IA and IIA), have been determined in DMF- H_2O and DMSO- H_2O media, at different temperatures, using Osada's method (12,13).

Osada's method is based on the determination of proton concentrations of the copolymer solution in the presence $[\text{H}^+]$ and absence $[\text{H}^+]_0$ of the polyelectrolytes (e.g. PMA and PEI). The degree of linkage (θ), which is defined as the ratio of binding groups to the total number of potentially interacting groups, could be correlated with the respective proton concentrations by the following expression:

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

The stability constant (K), could be determined from θ and C_0 , which is the initial concentration of the copolymer (unit mol l^{-1}) by the expression mentioned below:

$$K = \theta/C_0(1-\theta)^2$$

The plot of $\ln K$ vs. $1/T$ for complexes IA and IIA, both in DMF- H_2O and DMSO- H_2O media, are shown in Fig. 1. The nature of the curve for a particular complex (i.e. either IA or IIA), in the two solvent media, has been found to be different. Moreover, the absolute values of stability constant (K) of a given complex in the two solvent media, have been also found to be different. Interestingly enough, the following trend has been observed for the complexes (IA and IIA) in the two media:

$$\begin{aligned} \text{For complex IA: } & \ln K \left(\begin{array}{c} \text{DMF-}\text{H}_2\text{O} \\ \text{medium} \end{array} \right) > \ln K \left(\begin{array}{c} \text{DMSO-}\text{H}_2\text{O} \\ \text{medium} \end{array} \right) \\ \text{For complex IIA: } & \ln K \left(\begin{array}{c} \text{DMSO-}\text{H}_2\text{O} \\ \text{medium} \end{array} \right) > \ln K \left(\begin{array}{c} \text{DMF-}\text{H}_2\text{O} \\ \text{medium} \end{array} \right) \end{aligned}$$

Another interesting observation which may be pointed out from Fig. 1. is that in DMF- H_2O medium both complexes (IA and IIA), showed maximum value of $\ln K$ at around 30°C . The abrupt fall in $\ln K$ above 30°C , perhaps indicates that some of the interacting pairs in the complexes may not be stable in this medium at higher temperature.

The reversal of order in $\ln K$ value for complex IIA could possibly be interpreted on the

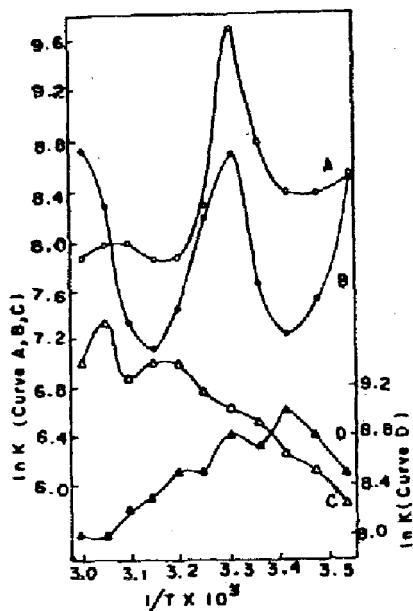


Fig.1: Variation of $\ln K$ vs. $1/T$: (A and B) Complexes IA and II A in DMF- H_2O ; (C and D) Complexes IA and IIA in DMSO- H_2O

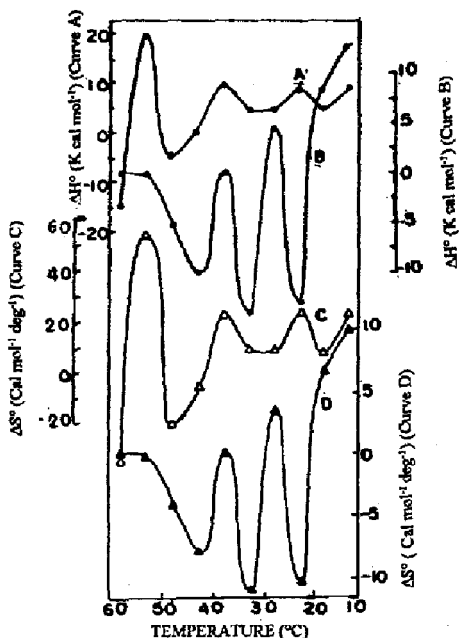


Fig.2: Temperature dependence of standard enthalpy and entropy changes in DMSO- H_2O medium : (A and B) ΔH° vs T for complexes IA and IIA : (C and D) ΔS° vs T for complexes IA and IIA

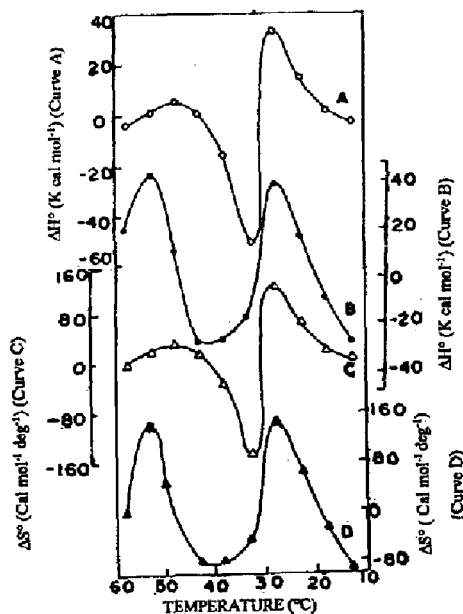


Fig.3: Temperature dependence of standard enthalpy and entropy changes in DMF- H_2O medium : (A and B) ΔH° vs T for complexes IA and IIA : (C and D) ΔS° vs T for complexes IA and IIA.

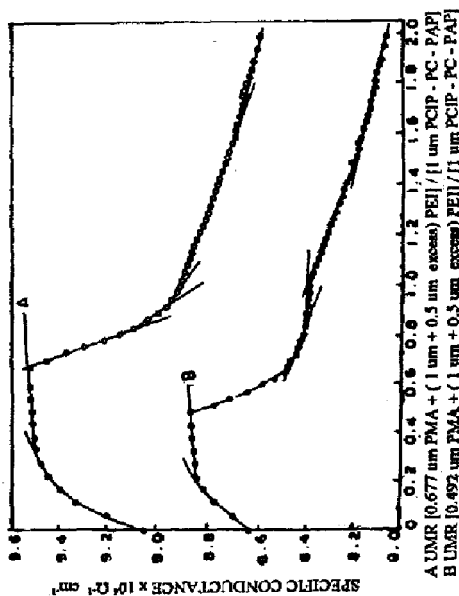
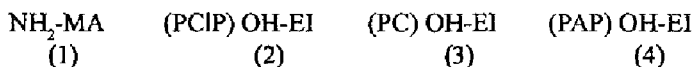


Fig.4: Variation of specific conductance with unit mole ratio in DMF- H_2O medium for complexes IA and IIA.

following lines: The influence of solvent on the two specific interacting pairs (e.g. OH-EI and NH₂-MA) in the two complexes IA and IIA, could possibly be different. DMSO-H₂O medium is perhaps more favourable for the interaction in OH-EI pair, whereas DMF-H₂O medium, which is having a relatively lower dielectric constant, favours the interaction in NH₂-MA pair. Obviously, the stability constant (K) of a given complex will depend on the relative contribution of each interacting pair in a particular medium. Since, the relative proportion of NH₂-MA pair is more in complex IA compared to IIA, therefore, a higher value of $\ln k$ could be anticipated for this complex (e.g. IA) in DMF-H₂O medium. However the relatively lower proportion of NH₂-MA pair in complex IIA, is perhaps not able to compensate the stronger interaction of OH-EI pair in DMSO-H₂O medium. This in fact is reflected in the reversal of trend in $\ln K$ values for the complexes in the two media. The thermodynamic parameters (e.g. ΔH° and ΔS°) could be calculated from the temperature dependence of stability constant (K) of the complexes, by using the following equations:

$$\begin{aligned}\Delta G^\circ &= -RT \ln K \\ d(\ln K) / d(1/T) &= -\Delta H^\circ / R \\ \Delta S^\circ &= -(\Delta G^\circ - \Delta H^\circ) / T\end{aligned}$$

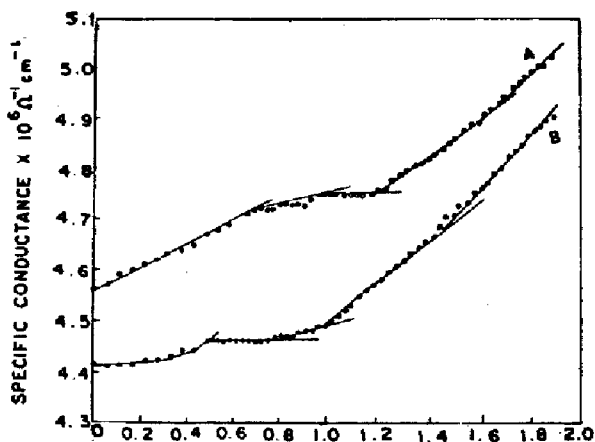
The ΔH° and ΔS° for the complexes IA and IIA have been calculated on the basis of the above equations and their variations with temperature in two different media (e.g. DMSO-H₂O and DMF-H₂O) are shown in Fig. 2 and 3, respectively. The phenolic copolymers I and II have a -OH group and a different p-substituent in each of its comonomer units. Due to inductive effect of the respective p-substituent, it is likely that the phenolic -OH groups of different comonomer units may have different acid character (17,18). This may have a possible influence on their complexation with PEI. On the basis of these arguments, the following four pairs of interacting units in complexes IA and IIA could be anticipated.



However, it may or may not be possible to differentiate the different phenolic -OH groups on the basis of inductive influence of their p-substituents. In Fig. 2, both the complexes IA and IIA, indicate three distinct peaks in DMSO-H₂O medium. Though, these peaks are experimentally reproducible, but in the absence of additional data from other experimental measurements, one cannot say definitely, whether these peaks are absolutely authentic. However, the error limits of such measurements have been calculated, and also some additional evidences have been found in the conductance measurements, which are given in the later part of this discussion. Considering these facts, one can possibly assign the two peaks at higher temperature to destabilization of relatively stronger interacting pairs (e.g. 1 and 2), whereas the peak observed at lower temperature to interacting pairs 3 and 4. However, the number of peaks observed for the same complexes in DMF-H₂O medium is only two (cf. Fig. 3), which may possibly be assigned to destabilization of interacting pair (e.g. 1) at high temperature and the remaining three pairs (e.g. 2, 3 and 4) perhaps get destabilized together at the second peak observed at the lower temperature. Of course one must admit that though these interpretations look reasonable, but still some uncertainty does exist. The overall value of ΔH° depends on the contributions of several factors, such as (a) desolvation, (b) complex formation by hydrogen bonding, electrostatic interaction etc., and (c) conformational changes of the complex etc. (19,20) Obviously, the solvent

media is likely to influence all these processes during complex formation.

We thought that these rather interesting observations of complexes IA and IIA, could be further substantiated by some electrochemical studies during the complexation process. In Figs. 4 and 5, are presented the variations of specific conductance of 1 μm of copolymer (I) and (II) with the addition of stoichiometric amounts of PMA and PEI in very small installments, in DMF-H₂O and DMSO-H₂O media, respectively. The nature of the curves in the two media are found to be entirely different (cf. compare curves A and B of Figs. 4 and 5). The distinct breaks observed at various stages of interaction and the probable stoichiometries assigned to them are summarized in Table 1.

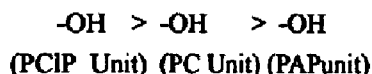


(Curve A) UMR [0.677 μm PMA + (1 μm + 0.5 μm excess) PEI] / [1 μm PCIP - PC - PAP]

(Curve B) UMR [0.492 μm PMA + (1 μm + 0.5 μm excess) PEI] / [1 μm PCIP - PC - PAP]

Fig.5: Variation of specific conductance with unit mole ratio in DMSO-H₂O medium for complexes IA and IIA.

It can be seen from the table 1, that compared to DMSO-H₂O medium, conductance curves in DMF-H₂O medium showed additional stoichiometries. This is expected in view of the fact that DMF has a lower dielectric constant ($\epsilon=36$) compared to DMSO ($\epsilon=49$). In a medium of lower dielectric constant, one would expect ion-association, which may be responsible for the additional steps observed in this medium. In fact, evidence of ion-association in DMF-H₂O medium could be seen by the abrupt fall in conductance during addition of PEI (cf. curves A and B of Fig. 4). Whereas, in DMSO-H₂O medium, no such fall in conductance could be seen at any stage of interaction (cf. curves A and B of Fig. 5). However, as predicted earlier, the electrochemical studies in these two media clearly indicate that the relative interacting ability of phenolic -OH groups present in different comonomer units of the copolymer, depends on the nature of p-substituents. The following trend in reactivity of OH groups has been observed for the different comonomer units.



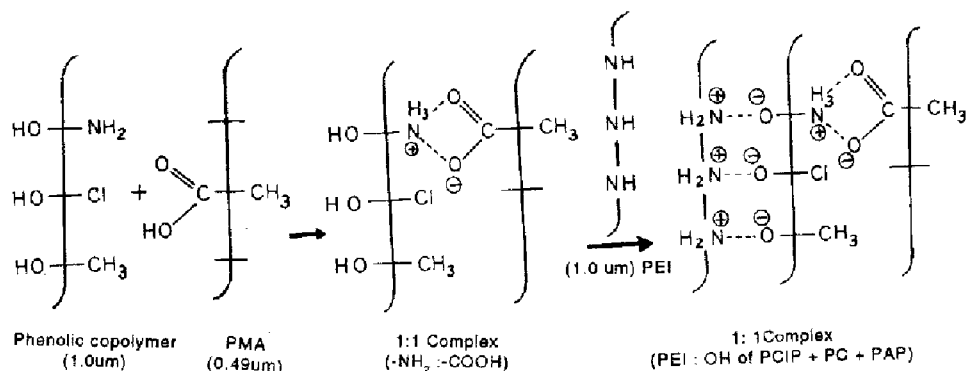
The lowest reactivity of -OH groups in PAP units may also be due to already entangled PMA chains with these units. This will obviously, reduce the accessibility of these -OH to the reacting chains (e. g. PEI).

Table I : Breaks observed and probable stoichiometries assigned to various complexes.

| Medium | System | Breaks (μm^*) | Probable stoichiometries |
|---|---------------------------|-------------------------------|---|
| DMF-H ₂ O (90 % + 10%) (Curve A of Fig. 4) | 1 μm Cop. (I) | 0.33 | 2:1 (-NH ₂ of Cop. (I) : PMA) |
| | +0.677 μm PMA | 0.67 | 1:1 (-NH ₂ of Cop. (I) : PMA) |
| | + 1.5 μm PEI | 0.82 | 2:1 (-OH of PCIP : PEI) |
| | | 0.94 | 1:1 (-OH of PCIP : PEI) |
| | | 1.00 | 1:1 (-OH of PC : PEI) |
| | | 1.67 | 1:1 (-OH of PAP : PEI) |
| DMF-H ₂ O (90 % + 10%) (Curve B of Fig. 4) | 1 μm Cop. (II) | 0.24 | 2:1 (-NH ₂ of Cop. (II) : PMA) |
| | +0.492 μm PMA | 0.49 | 1:1 (-NH ₂ of Cop. (II) : PMA) |
| | +1.5 μm PEI | 0.67 | 2:1 (-OH of PCIP : PEI) |
| | | 0.86 | 1:1 (-OH of PCIP : PEI) |
| | | 1.00 | 1:1 (-OH of PC:PEI) |
| | | 1.49 | 1:1 (-OH of PAP:PEI) |
| DMSO-H ₂ O (90% + 10%) (Curve A of Fig. 5) | 1 μm Cop. (I) | 0.68 | 1:1 (-NH ₂ of Cop. (I):PMA) |
| | + 0.677 μm PMA | 1.00 | 1:1 (-OH of PCIP + PC:PEI) |
| | + 1.5 μm PEI | 1.22 | 3:1 (-OH of PAP : PEI) |
| | | 1.67 | 1:1 (-OH of PAP:PEI) |
| DMSO-H ₂ O (90% + 10%) (Curve B of Fig. 5) | 1 μm Cop.(II) | 0.49 | 1:1 (-NH ₂ of Cop.(II):PMA) |
| | + 0.492 μm PMA | 0.86 | 1:1 (-OH of PCIP:PEI) |
| | + 1.5 μm PEI | 1.00 | 1:1 (-OH of PC:PEI) |
| | | 1.48 | 1:1 (-OH of PAP:PEI) |

*Unit mole ratio; p-Chlorophenol (PCIP); p-Cresol (PC); p-aminophenol (PAP).

The IR spectra of the interpolymer complexes provide additional evidence regarding the involvement of various functional groups during complexation. The IR spectra were recorded on KBr pellet and compared with those of the pure components (phenolic copolymer, PMA and PEI). The $\nu_{\text{O-H}}$ frequency observed at 3200 cm^{-1} in the phenolic copolymer shifted to 3350 cm^{-1} in the interpolymer complex. The $\nu_{\text{C=O}}$ frequency observed at 1690 cm^{-1} for pure PMA, shifted to 1650 cm^{-1} for the complex. The $\nu_{\text{N-H}}$ bending frequency observed at 1560 cm^{-1} for pure PEI, shifted to 1525 cm^{-1} in the complex. On the basis of various experimental evidences, the following scheme may be suggested for the mode of interaction of the phenolic copolymer with the polyelectrolytes.



In conclusion, it can be said that phenolic copolymers enter into complex formation with polyelectrolytes such as PMA and PEI. The relative complexation ability of different phenolic-OH groups associated with the various comonomer units, depends on the inductive effect of respective *p*-substituents as is evident from electrochemical studies. The solvent dielectric constant and reduced hydrophobic interaction also affect the stability of the polycomplexes.

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