

## Selectivity in interpolymer complex formation between phenolic copolymer, polyelectrolyte, non-ionic polymer and metal ions

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### Summary

Multicomponent complexes of the phenolic copolymer with specific coordinating groups with polyethylene imine (PEI), polyvinyl pyrrolidone (PVP),  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions has been studied in dimethyl formamide – methanol solvent mixture by several experimental techniques e.g. by viscometry, potentiometry, conductometry, IR and UV spectrophotometry and selective complexation, and mutual compatibility of the complementary polymers attached to the phenolic copolymer chain have been studied.

### Introduction

Study of polymer - polymer interactions and formation of intermacromolecular complexes has assumed considerable importance in the field of polymer science [1-23].

The interactions take place through secondary binding forces, such as hydrogen bonding, ion -dipole interaction, coulombic forces, hydrophobic interaction etc. Of course, the specific type of interacting forces in a complex depends on the nature of polymer components. Transition metal ions (e.g.  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ) are also known to form stable complexes with polyelectrolyte [23-28]. Another aspect which has attracted considerable attention is selectivity in their intermacromolecular complexation; this is due to close similarity with substitution reactions in biological systems [1,2,24,25,29].

It may also be mentioned that phenolic polymers may provide interesting systems for interpolymer complexation. This is in view of the fact that phenolic polymers are characterized by the presence of intramolecular hydrogen bonding in them [29,30].

Since one of the basic mode of polymer - polymer interactions is through hydrogen bonding, therefore phenolic polymers are likely to form stable complexes with polyelectrolyte and non-ionic polymers. Keeping this fact. In mind, a phenolic copolymer has been prepared by condensing four different phenolic monomers; e.g.

p-chlorophenol (PCIP), p-nitrophenol (PNP), p-hydroxybenzoic acid (PHB) and p-aminobenzoic acid (PAB) with H-CHO in the presence of acid catalyst. The phenolic copolymer has been characterized by electrometric titration techniques [30], and the relative proportion of various comonomer units have been determined. Thus, knowing the amounts of the various co-ordinating groups (e.g. -OH, -COOH, -NH<sub>2</sub> groups) associated with the various comonomer units in the phenolic copolymer chain, one can incorporate appropriate polyelectrolyte (e.g. PAA or PEI), non-ionic polymers (e.g. PVP or PEO), and transition metal ions (e.g. Cu<sup>2+</sup> and Ni<sup>2+</sup>) through these groups. The formation of some of these multicomponents intermacromolecular complexes have been studied with the help of several experimental techniques, such as, viscometry, conductometry, potentiometry, IR and UV spectrophotometry. In this paper an effort has been made to explain the mode of interaction through the structural characteristics of the polymers and the nature of transition metal ions.

## Experimental

### Material

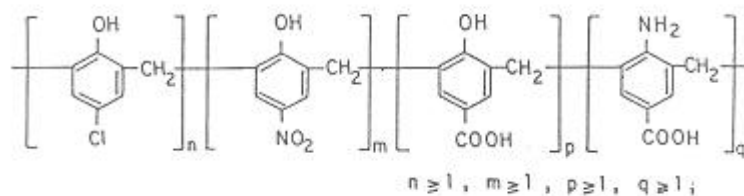
*Poly (vinyl pyrrolidone) (PVP)*: was supplied by Fluka, U.S.A. The  $\overline{M}_w$  of the polymer was calculated from viscosity data [25], and found to be  $2.4 \times 10^4$ .

*Poly (ethylene imine) (PEI)*: was supplied by B.D.H. chemical Ltd., Poole, England in the form of 50% viscous water solution.

*Poly (ethylene oxide) (PEO)*: was supplied by Iwai Kagaru Co. Ltd., Japan. Its weight average molecular weight ( $\overline{M}_w$ ) was  $1.9 \times 10^4$  as calculated from viscosity equation [28].

### Polymer Synthesis

*p-chlorophenol – p-nitrophenol – p-hydroxybenzoic acid – p-aminobenzoic acid – formaldehyde random copolymer (I) [ PCIP-PNP-PHB-PAB ]*, were prepared by refluxing the monomers in definite molecular proportions with 10N HCl ( 2ml ) as the catalyst for 4 hours at 100°C [29].



(I)

The reaction product was poured in ice cold water and washed several times with distilled water to remove unreacted monomers. The random copolymer was characterized and found to contain a composition of 0.0556 mol of PCIP, 0.0694 mol of PNP, 0.111 mol of PHB and 0.7639 mol of PAB units respectively [30-32].

*Poly (acrylic acid) (PAA)*: Purified acrylic acid (distilled twice in vacuo) was polymerized with benzoyl peroxide as an initiator in a moist dioxane methanol

mixture for 2.5 hour in nitrogen atmosphere at 50°C. The reaction mixture was dissolved in methanol and reprecipitated twice with ethyl acetate. The polymer was dried to constant weight in vacuo at 110°C. The molecular weight of the polymer was calculated from viscosity data [33]. The weight average molecular weight was  $\overline{M}_w = 4.0 \times 10^5$ .

#### *Solvent*

For all experimental measurements, analytical grade dimethyl formamide (DMF) and methanol (M) were used for mixed solvent studies.

#### *Characterizations*

*Conductometric titrations* were carried out with a Leeds and Northrup (4959) conductance bridge [31]. The conductance of the mixed solutions was measured at various unit mole ratios (umr) and the reproducibility of the values was found to be within  $\pm 2\%$ .

*pH - titrations* were carried out with an EC digital pH meter (model pH 5651) using a combination electrode [31]. The concentration of the polymer solution was of the same order as in the conductance experiment (e.g.  $5 \times 10^{-3}$  um/l).

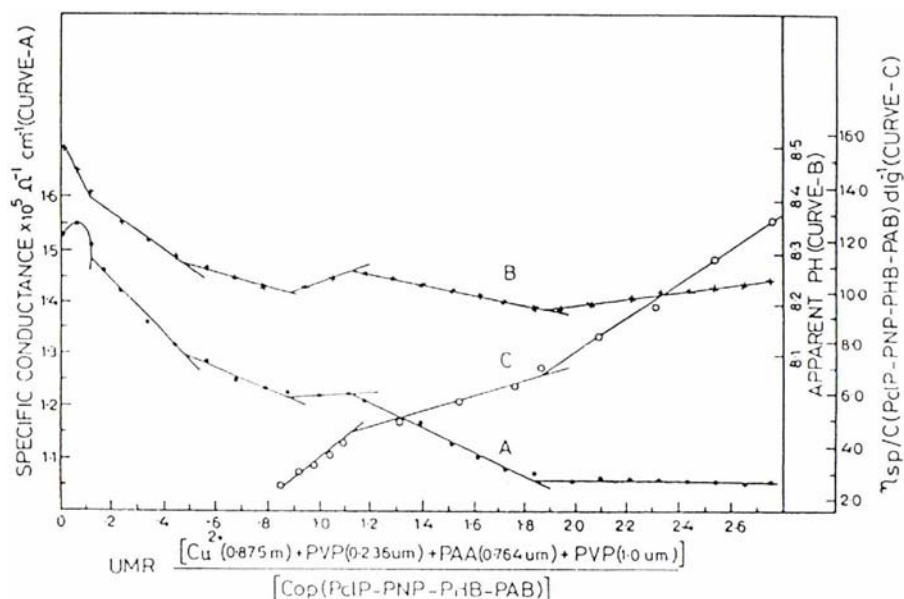
The viscosity of the mixed solution of the various homopolymers (e.g. PVP, PEI, PAA and PEO), metal ions and phenolic copolymer at various unit mole ratios (umr) was determined at  $30^\circ\text{C} \pm 0.05$  by an Ubbelohde viscometer for which the kinetic energy correction was negligible.

The polymer - polymer complexes were isolated at various stoichiometries of the component polymers and their IR spectra were recorded using a Perkin - Elmer model 1710 spectrophotometer.

*The UV spectra of the polymer - metal complexes* were recorded at various stoichiometries in mixed solvents, e.g. DMF and methanol. A Shimadzu UV-260 spectrophotometer was used for recording the spectra.

### **Result and Discussion**

The four component phenolic copolymer (I), characterized by electrometric titration techniques [30-32], was found to contain 0.764 m (mole ratio) of PAB units, 0.111 m of PHB units, 0.069 m PNP units and 0.055 m of PCIP units. A mixed solvent (e.g. 50% dimethyl formamide (DMF) + 50% methanol (M) (v/v)) has been used as a medium in order to get a better resolution of the different stages of interaction between the component polymers. Fig.1 shows the variation of conductance, apparent pH and reduced viscosity of phenolic copolymer(I) solution addition of stoichiometric amount of transition metal ions and various component polymers, (e.g.  $\text{Cu}^{2+}$  (0.875m), PVP (0.236 um), PAA (0.764 um) and excess of PVP solution). The specific quantities of the different components have been added in order to quantitatively complex the respective co-ordinating groups associated with comonomer units in the phenolic copolymer chain. The various unit mole ratios (umr) at which breaks in the titration curves have been observed and the probable stoichiometries assigned to the different complexes are summarized in Table - 1, on the basis of actual composition of the phenolic copolymer, it can be predicted that carboxylic groups of PHB and PAB interact with Cu (II) in preference to phenolic hydroxyl groups.



**Fig.1.** Variation of conductance (A), apparent pH (B), reduced viscosity (C), with unit mole ratio for phenolic copolymer (I) -  $\text{Cu}^{2+}$  PVP - PAA system

**Table 1.** Observed stoichiometries in interpolymer complex formation of phenolic copolymer (I) with  $\text{Cu}^{2+}$ , PVP, and PAA

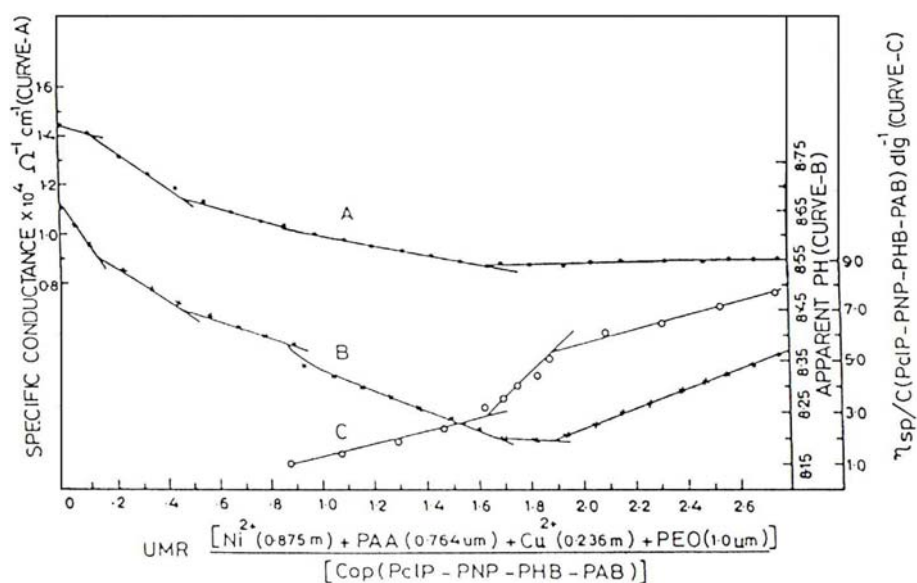
System	Break observed at umr*	Probable stoichiometries
Phenolic copolymer (1.0 um) + $\text{Cu}^{2+}$ (0.875m)	0.11 0.49 0.87	1:1 ( $\text{Cu}^{2+}$ : -COOH of PHB) 1:1 ( $\text{Cu}^{2+}$ : -COOH of PAB) 1:2 ( $\text{Cu}^{2+}$ : -COOH of PAB)
Phenolic copolymer (1.0um)+ $\text{Cu}^{2+}$ (0.875m) +PVP (0.236 um)	1.11	1:1 (PVP: -OH of PHB, PCIP, and PVP)
Phenolic copolymer (1.0 um) + $\text{Cu}^{2+}$ (0.875 m) + PVP (0.236 um) + PAA (0.764um)	1.87	1:1 (PAA: - $\text{NH}_2$ of PAB)

\* unit mole ratio

Subsequently, these groups (e.g. phenolic OH) are complexed by adding stoichiometric amount of PVP. The unreacted  $\text{NH}_2$  groups (0.764 um) of PAB units have been complexed with the required amount of PAA. The apparent pH curve (cf. curve B of Fig.1), indicated a sharp fall in pH till the addition of  $\text{Cu}$  (II) is completed. This is anticipated in view of the release of protons as a result of interaction with metal ions [26]. However, the conductance curve also showed a fall during this stage of interaction with  $\text{Cu}$  (II). This may be attributed to ion-association in a medium of

low dielectric constant. The corresponding reduced viscosity curve (cf. curve C of Fig.1) also indicated breaks which coincided with some of the breaks of pH and conductance curve. The continues linear increase in viscosity at different stages of interaction may be attributed to bulkiness of the three and four component complexes molecules.

In order to see the role and the nature of transition metal ions and the order of addition of various components during multicomponent complex formation, the variations of conductance, pH, reduced viscosity of phenolic copolymer (I) have been studied by adding of  $\text{Ni}^{2+}$  (0.875 m), PAA (0.764  $\mu\text{m}$ ),  $\text{Cu}^{2+}$  (0.236 m) and excess of PEO in small instalments (cf. Fig. 2).



**Fig.2.** Variation of conductance (A), apparent pH (B), reduced viscosity (C), with unit mole ratio for phenolic copolymer (I) –  $\text{Ni}^{2+}$ -PAA -  $\text{Cu}^{2+}$ - PEO - system

The stoichiometries assigned to different complexes at different stages of interaction of the phenolic copolymer has been summarized in Table-2. It is indicated that irrespective of the nature of transition metal ions, the co-ordinating groups of the phenolic copolymer interact with the various components in the same sequence. This obviously proves the authenticity of some of these observations.

It is known from our earlier work that relative complexation ability of phenolic OH group is greater than carboxyl group with respect to PVP [24]. Keeping this fact in mind we have studied the selective complexation of phenolic OH groups by adding stoichiometric quantities of PVP (0.236  $\mu\text{m}$ ), PAA (0.764  $\mu\text{m}$ ),  $\text{Cu}^{2+}$  (0.875 m) and then excess PVP to the phenolic copolymer. The variation of conductance, apparent pH and reduced viscosity are shown in Fig. 3. The observed breaks and the corresponding stoichiometries assigned to various complexes are shown in Table-3. The probable composition of the various complexes could be accounted on the basis of actual composition of the phenolic copolymer (I).

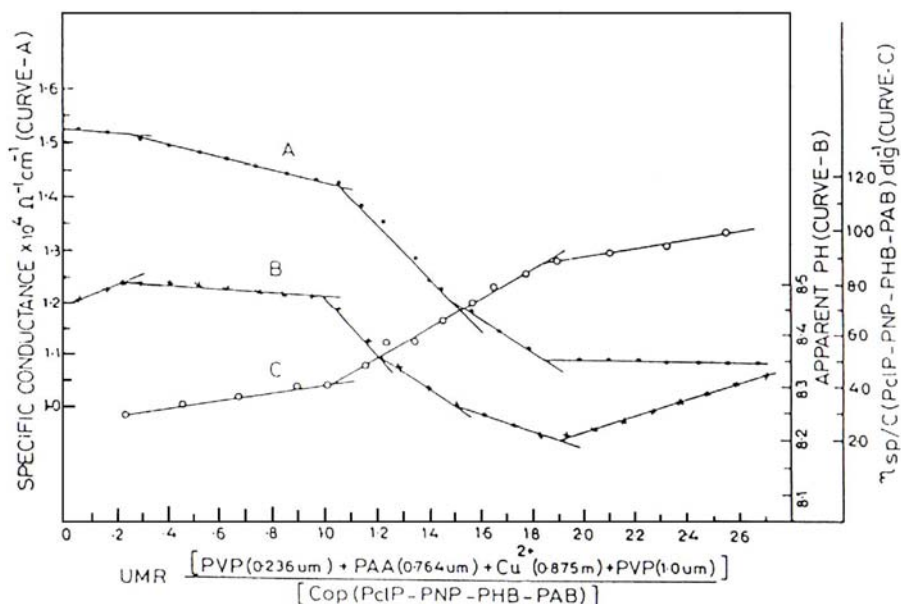
**Table 2.** Observed stoichiometries in interpolymer complex formation of phenolic copolymer (I) with Ni<sup>2+</sup>, PAA, Cu<sup>2+</sup> and PEO

System	Break observed at umr*	Probable stoichiometries
Phenolic copolymer (1.0 um) + Ni <sup>2+</sup> (0.875m)	0.11	1:1 (Ni <sup>2+</sup> :-COOH of PHB)
	0.49	1:1 (Ni <sup>2+</sup> :-COOH of PAB)
	0.87	1:2 (Ni <sup>2+</sup> :-COOH of PAB)
Phenolic copolymer (1.0 um) + Ni <sup>2+</sup> (0.875 m)+ PAA (0.764 um)	1.65	1:1 (PAA:-NH <sub>2</sub> of PAB)
Phenolic copolymer (1.0 um) + Ni <sup>2+</sup> (0.875 m) +PAA (0.764 um) + Cu <sup>2+</sup> (0.236 m)	1.87	1:1 (Cu <sup>2+</sup> : -OH of PHB, PCIP, and PNP)

\* Unit mole ratio

Instead of complexing the carboxyl groups of the phenolic copolymer (I) with transition metal ion, it was considered of interest, to prepare selectively polyelectrolyte complexes by interacting the carboxyl groups with polyethylene imine (PEI).

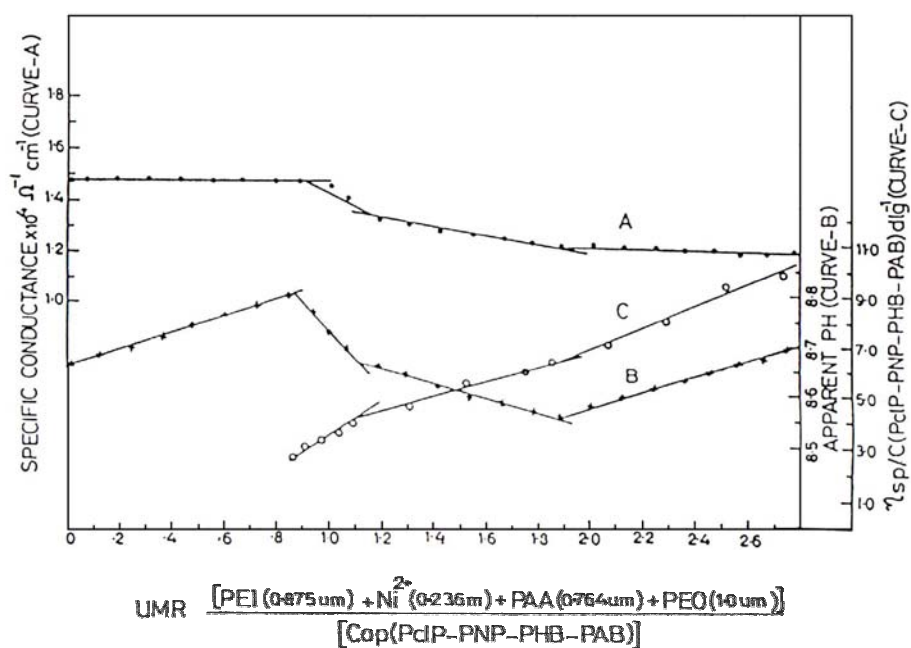
The variations of reduced viscosity, conductance and apparent. pH of the phenolic copolymer have been observed by adding stoichiometric quantities of PEI (0.875 um), Ni<sup>2+</sup> (0.236 m), PAA (0.764 um) and excess of PEO in very small instalments (cf. Fig.4).

**Fig.3.** Variation of conductance (A), apparent pH (B), reduced viscosity (C), with unit mole ratio for phenolic copolymer (I) - PVP - PAA - Cu<sup>2+</sup> system

**Table 3.** Observed in interpolymer complex formation of phenolic copolymer (I) with PVP, PAA and Cu<sup>2+</sup>

System	Break observed at umr*	Probable stoichiometries
Phenolic copolymer (1.0 um) + PVP (0.236 um)	0.23	1:1 (PVP:-OH of PHB, PNP and PCIP)
Phenolic copolymer (1.0 um) + PVP (0.236 um) + PAA (0.764 um)	1.00	1:1 (PAA:-NH <sub>2</sub> of PAB)
Phenolic copolymer (1.0 um) + PVP(0.236 um) + PAA (0.764 um) + Cu <sup>2+</sup> (0.075m)	1.49 1.85-1.90	1:2 (Cu <sup>2+</sup> : -COOH of PAB, and PHB) 1:1 (Cu <sup>2+</sup> : -COOH of PAB, and PHB)

\*Unit mole ratio

**Fig.4.** Variation of conductance (A), apparent pH (B), reduced viscosity(C), with unit mole ratio f or phenolic copolymer (I) - PEI - Ni<sup>2+</sup> - PAA - PEO system

It may be mentioned that specific amount of the respective components have been added in order to complex stoichiometrically the co-ordinating groups associated with the comonomer units in the phenolic copolymer chain. The conductance of the phenolic copolymer solution throughout remains constant during the addition of PEI, whereas apparent pH indicated a linear increase during this stage. The bulkiness of

polyelectrolyte complex formed perhaps compensates the effect of addition of basic polyelectrolyte (e.g. PEI), whereas the addition of PEI is reflected by the linear increase in apparent pH. The subsequent nature of the curves during addition of Ni (II) and PAA is more or less identical with those observed earlier.

On the basis of these arguments, the probable mode of interaction of the various components with the phenolic copolymer (I) can possibly be explained by the Scheme. 1.

The IR spectra of the complexes were recorded in KBr and compared with those of the pure components (i.e. PVP, phenolic copolymer (I) and PAA). Some of the spectra data are given in Table. 4. The distinct shifts in carbonyl ( $\nu_{C=O}$ ) and hydroxyl ( $\nu_{O-H}$ ) frequencies in the interpolymer complexes obviously indicate the involvement of carbonyl and OH groups of the component polymers during interpolymer complex formation. In the complexes, broad bands, were also observed between 1600-1700 $\text{cm}^{-1}$  and an appreciable shift of  $\nu_{C=O}$  band from 1125  $\text{cm}^{-1}$  to 1270 $\text{cm}^{-1}$  probably indicated the simultaneous involvement of carboxylic groups of PVP and OH groups of phenolic copolymer (I). The UV spectra of phenolic copolymer (I) showed  $\Lambda_{\text{max}}$  at 300 nm, and it shifted between the range 310 to 315 nm for most of the Cu-polymer complexes. It seems likely that this new absorption band arises from the formation of charge transfer complexes between the phenolic copolymer and the metal ions [34].

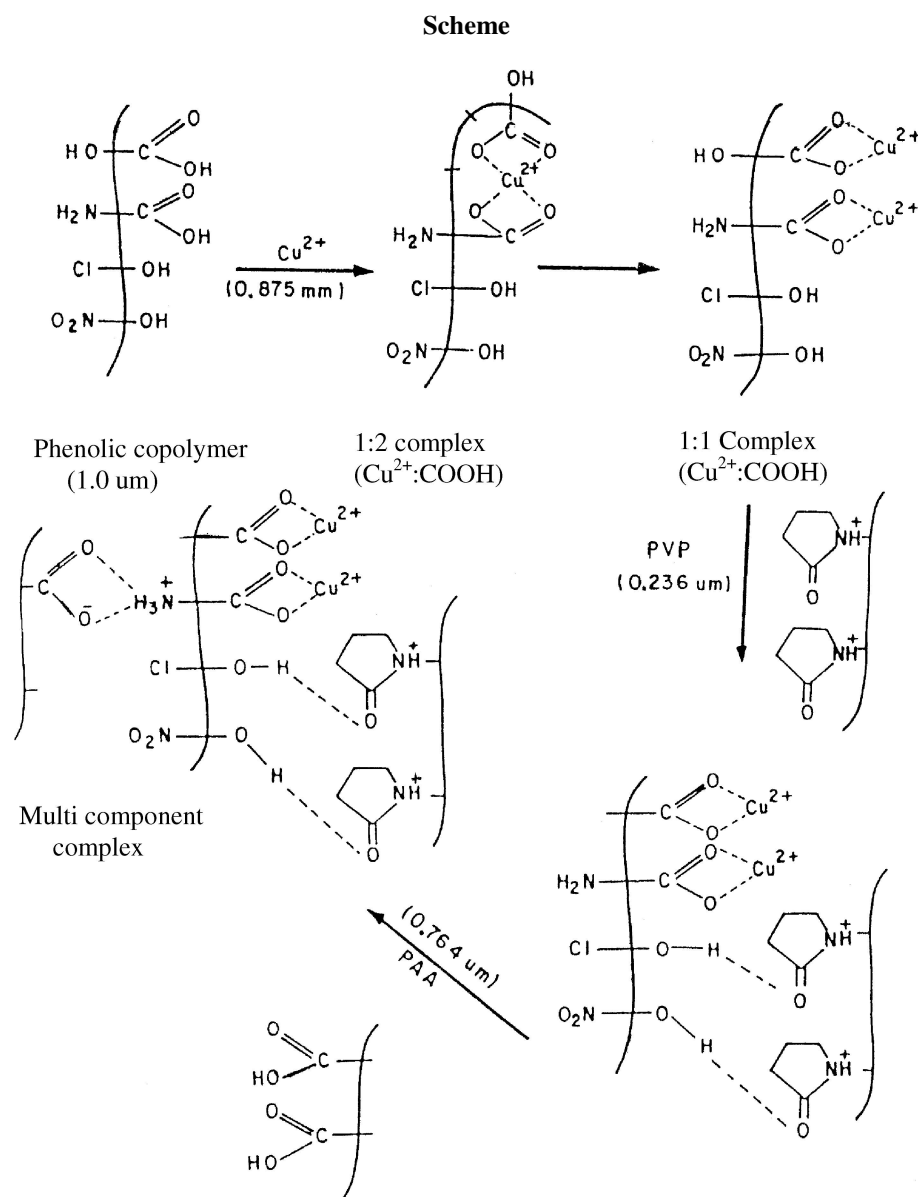
**Table 4.** IR spectra of pure components and the interpolymer complexes between them

Component / multicomponent complex	$\nu_{C=O}$ str. ( $\text{cm}^{-1}$ )	$\nu_{O-H}$ str. ( $\text{cm}^{-1}$ )
PVP	1625	—
PAA	1690	2970
Phenolic copolymer	1670	2760
Phenolic copolymer(1.0 $\mu\text{m}$ ) + $\text{Cu}^{2+}$ (0.875m)	1685	—
Phenolic copolymer(1.0 $\mu\text{m}$ ) + $\text{Cu}^{2+}$ (0.875m) +PVP(0.236 $\mu\text{m}$ )	1695	—
Phenolic copolymer(1.0 $\mu\text{m}$ ) + $\text{Cu}^{2+}$ (0.875m) + PVP(0.236 $\mu\text{m}$ ) + PAA(0.764 $\mu\text{m}$ )	1695-1680	—
Phenolic copolymer(1.0 $\mu\text{m}$ ) + PVP(0.236 $\mu\text{m}$ )	1670-1700	2820
Phenolic copolymer(1.0 $\mu\text{m}$ ) + PVP(0.236 $\mu\text{m}$ ) + PAA(0.764 $\mu\text{m}$ )	1670-1700	2836
Phenolic copolymer(1.0 $\mu\text{m}$ ) + $\text{Ni}^{2+}$ (0.875)	1678	—
Phenolic copolymer(1.0 $\mu\text{m}$ ) + $\text{Ni}^{2+}$ (0.875) + PAA(0.764 $\mu\text{m}$ )	1680	—
Phenolic copolymer(1.0 $\mu\text{m}$ ) + $\text{Ni}^{2+}$ (0.875) + PAA(0.764 $\mu\text{m}$ ) + $\text{Cu}^{2+}$ (0.136m)	1685	—



### Conclusion

In conclusion, it can be said that the phenolic copolymer with specific co-ordinating groups associated with its various comonomer units can enter into interpolymer complex formation with stoichiometric quantities of polyelectrolyte, non-ionic polymers, and transition metal ions through hydrogen bonding and ion dipole interaction. Such multicomponent complexes containing metal ions may prove useful for the development of catalyst and membrane with selective permeability.



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