

Selectivity in Interpolymer Complexation Involving Phenolic Copolymer, Polyelectrolytes, Non-ionic Polymers and Transition Metal Ions

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ABSTRACT

Selectivity in interpolymer complex formation involving a typical four-component phenolic copolymer (*p*-chlorophenol-*p*-aminophenol-*p*-toluidine-*p*-cresol-HCHO copolymer), polyelectrolytes such as polyethylene imine (PEI) and Polyacrylic acid (PAA), a non-ionic homopolymer polyvinyl pyrrolidone (PVP), and some transition metal ions (e.g., Cu (II), Ni (II)) have been studied in dimethylformamide (DMF)-methanol solvents mixture. The coordinating groups of phenolic copolymer form complexes through hydrogen bonding and ion-dipole interactions. The different stages of interactions have been studied by several experimental techniques, e.g., viscometry, potentiometry and conductometry. Some schemes have been suggested to explain the mode of interaction between these components.

Key Words:

selectivity;
phenolic copolymer;
polyelectrolytes;
non-ionic polymer;
metal ion.

INTRODUCTION

Inter-macromolecular complexes have acquired a unique position in the field of polymer science, in view of their potential applications in industry and medical biology [1-6]. Interaction between two different macromolecular species may lead

to the formation of an inter-macromolecular complex which essentially possesses properties entirely different from those of the component polymers. These interactions occur through secondary binding forces such as: H-bonding, van der Waals,

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and electrostatic forces, hydrophobic interactions, etc. [1,2].

Another aspect which, has attracted considerable attention, is selectivity in inter-macromolecular complexation; this is due to its close similarity with substitution reactions in biological systems. Although, it is not clearly understood how the macromolecule chain effectively selects a complementary one, in order to perform specific functions. It was thought by some previous workers that selective complexation between synthetic polymers of known characteristics, may provide an excellent model for simulating biological process [1,2].

Many attempts have been made during recent years to incorporate transition metal ions into a polymer chain. These metal containing polymers have potential applications in many fields [7-11].

Phenolic copolymer with specific co-ordinating groups may provide interesting systems, in view of the presence of intramolecular hydrogen bonding [7,12]. With this in mind, some phenolic copolymers were prepared by condensing formaldehyde (HCHO) with *p*-chlorophenol (PCIP)-*p*-aminophenol (PAP)-*p*-toluidine (PT)-*p*-cresol (PC) in the presence of an acid catalyst, and characterized by conventional methods [13,14]. This system is interesting in view of the fact that each comonomer units of the phenolic copolymer has specific functional groups whose proportions are also known.

From the known composition of the phenolic copolymer one could obtain multicomponent inter-macromolecular complexes by adding polyvinyl pyrrolidone (PVP), polyacrylic acid (PAA) and polyethyleneimine (PEI), and some transition metal ions (e.g. Cu (II) and Ni (II)) in definite sequences.

Since phenolic polymers are mostly insoluble in water, a mixture of dimethylformamide (DMF) and methanol (CH₃OH) was used. In the present investigation several experimental techniques such as: IR and VU spectrophotometry, viscometry, potentiometry, and conductometry have been used to study the interaction between polymers and metal ions. Some plausible schemes are proposed to interpret the mode of interactions through the structural characteristics of the copolymers and the nature of the transition metal ions.

EXPERIMENTAL

Materials

Poly vinyl pyrrolidone (PVP)

PVP Was supplied by Fluka, USA, in the form of white crystalline powder. The polymer was characterized by calculating its viscosity average molecular weight (\bar{M}_v) by using ubbelohde viscometer and from viscosity measurements by using the following relationship [9]:

$$[\eta] = 6.76 \cdot 10^{-2} \bar{M}_v^{0.55} \quad (\text{in aqueous medium at } 25 \text{ C})$$

$[\eta]$ = Intrinsic viscosity

\bar{M}_v = Viscosity average molecular weight,

and \bar{M}_v was found to be:

$$(\bar{M}_v) = 2.4 \cdot 10^4 \text{ g/mol}$$

Polyethylene imine (PEI)

PEI was supplied by BDH Chemical Ltd., Poole, England; in the form of 50% viscous liquid solution.

Solvents

Double distilled water was used as solvent when the system was studied in aqueous medium, and for mixed organic solvents studies, Merck analytical grade solvents were used.

Polymer Synthesis

Preparation of Four-component Phenolic Copolymer I (PCIP-PAP-PT-PC)

p-Chlorophenol (PCIP)-*p*-amino phenol (PAP)-*p*-toluidine(PT)-*p*-cresol(PC)-formaldehyde random copolymer I, was prepared by refluxing the monomers in definite molecular proportions with 10 N HCl (2mL) as catalyst for 4 h, at 100°C.

The reaction mixture then, was poured into ice-cold water and washed several times with distilled water to remove any unreacted monomers. The polymer yield was around 75%. Three samples of the above copolymer were prepared by changing the feed compositions.

Phenolic -OH groups have been estimated by titrating against sodium methoxide with pyridine as the medium of titration, whereas, amino groups have been titrated in a glacial acetic acid medium with perchloric acid as the titrant acid. The composition of copolymers could be derived from the titration curves. The halogen content of the copolymer was estimated

by treating it with sodium metal, and the resultant sodium chloride was titrated by Volhard's method [13,14].

Preparation of Polyacrylic Acid (PAA)

Homopolymer polyacrylic acid (PAA) was prepared by polymerizing purified acrylic acid monomer (distilled twice in vacuo) in moist dioxane-methanol mixture using benzoyl peroxide as an initiator [11].

The polymerization was conducted for about 2 h, at 50-60°C and throughout this period, nitrogen gas was continuously passed to maintain oxygen free atmosphere.

At the end of reaction the polymer was separated as white solid mass. The polymer was dissolved in methanol and reprecipitated with ethyl acetate. This process was repeated twice in order to ensure the complete removal of unreacted monomer and initiator. Polymer was dried to constant weight in vacuo at a pot temperature below 110°C.

The polymer was characterized by calculating its weight average molecular weight by the following viscosity equation [15].

$$[\eta] = 4.22 \cdot 10^4 \bar{M}_v^{-0.604} \text{ (in 2 M aqueous NaOH solution at 25°C)}$$

where:

$$[\eta] = \text{intrinsic viscosity,}$$

and:

$$\bar{M}_v = \text{viscosity average molecular weight.}$$

The viscosity average molecular weight was found to be:

$$(\bar{M}_v) = 4.5 \cdot 10^5 \text{ g/mol}$$

Viscometric Measurements

The viscosity of solutions was measured at 30–0.05°C by an Ubbelohde viscometer for which, kinetic energy correction was negligible.

Conductometric and Potentiometric Titrations

The conductometric titrations were carried out with Leeds and Northrup 4959 electrolytic conductance bridge. The limit of error in conductance measurement was 0.15% of reading at the low end.

pH of the solution was measured by ECIL digital pH meter (model pH 5651) using a combination electrode. The limit of the error in the pH measurement was 0.01.

The titrations were performed at room temperature and sufficient time was given after each addition of titrant to obtain equilibrium readings.

For both of the measurements (pH and conductance), concentrations of various homopolymers and copolymers used in aqueous as well as in mixed solvents during titrations were either $1 \cdot 10^{-3}$ unit mol/L or $5 \cdot 10^{-3}$ unit mol/L.

Infrared Spectrophotometry

The copolymer-homopolymer-metal complexes were isolated at various stoichiometries of the component polymer and metal, and their IR spectra were recorded on a KBr pellet, using a Shimadzu spectrophotometer.

Ultraviolet Spectrophotometry

UV Spectra of complexes were recorded at various stoichiometries in aqueous medium, and a UV 260 Shimadzu spectrophotometer was used.

RESULTS AND DISCUSSION

Since synthetic polymers have simpler structure than biopolymers, study of interactions between synthetic polymer chains may lead to the understanding of complex reaction in biological system, therefore we have studied selective complexation involving a four-component phenolic copolymer I, polyelectrolytes such as PAA and PEI, a non-ionic homopolymer e.g., PVP, and some transition metal ions e.g., Cu (II) or Ni (II). The four-component phenolic copolymer, has been prepared by condensing *p*-chlorophenol (PCIP), *p*-aminophenol (PAP), *p*-toluidine (PT) and *p*-cresol (PC) with HCHO in the presence of an acid catalyst.

Three samples of phenolic copolymer I have been prepared by choosing three different feed compositions. These samples have been characterized by conventional methods and as expected, the composition of them have been found to be different [13,14]. The compositions of the three samples of the phenolic copolymer, i.e. IA, IB, IC are summarized in Table 1.

Since the phenolic copolymer I, contains both the acidic (e.g., phenolic -OH) and basic functional groups (e.g., -NH₂), it could be complexed with transition metal ions (e.g., Cu (II)), as well as, with a

Table 1. Composition of three samples of phenolic copolymer (I) obtained from three different feed compositions.

Copolymer	Feed composition (mol)				Copolymer composition (mol)				
	PCIP	PAP	PT	PC	HCHO	PCIP	PAP	PT	PC
IA	0.1	0.4	0.1	0.4	1.0	0.24	0.46	0.06	0.24
IB	0.25	0.25	0.25	0.25	1.0	0.31	0.1	0.31	0.27
IC	0.1	0.2	0.1	0.6	1.0	0.15	0.46	0.1	0.28

polyelectrolyte (e.g., PAA). Figure 1 shows the variation of conductance, apparent pH, and reduced viscosity (η_{sp}/c) of 1.0 μm solution of copolymer IA with the addition of 0.936 m of Cu (II), 0.8 μm of PAA and subsequently, 0.5 m of Cu (II) solution. A mixture of DMF-methanol (50/50, v/v%) has been chosen as the medium for all these studies. The specific amount of transition metal ions has been added, to make complex with phenolic -OH groups, stoichiometrically. PAA has been added in slight excess of the amount of basic -NH₂ groups, so that the unreacted PAA unit can be subsequently complexed with Cu (II) ions.

The distinct breaks were observed by the various measurements at specific unit moles ratios (umr), and their probable assigned stoichiometries, are summarized in Table 2. During the first and second stages of interaction, a sharp fall in pH and a corresponding increase in conductance have been observed. This may be attributed to the release of protons [9-10].

Similar behaviour has been observed during the interaction of Cu (II) with excess of PAA. The reduced viscosity curve (cf. curve C of Figure 1) showed a very

slight increase during interaction of PAA with -NH₂ groups of comonomer units. The addition of excess of PAA is indicated by a very sharp increase in viscosity. This is understandable in view of the extended conformation of dissociated PAA chains. However, the rate of increase in viscosity is less during interaction with Cu (II) ions. An excellent coincidence is observed among different stages of interaction by all three independent measurements of physical properties.

It was considered interesting to study the influence of the nature of transition metal ions on their interactions with phenolic -OH groups associated with various comonomer units (e.g., PCIP, PAP, and PC) in the phenolic copolymer chain. Therefore, by changing Cu (II) with Ni (II) ions, and keeping the same sequence of addition of components to phenolic copolymer IA the observed variations in conductance, apparent pH, and reduced viscosity have been recorded and shown in Figure 2. Obviously, the nature of the curves are identical (cf. Figures 2 and 3), except that with Ni (II) it was possible to differentiate the interaction with -OH groups of PCIP, PAP, and PC. The -OH groups of these

Table 2. Observed breaks and probable stoichiometries in phenolic copolymer IA-Cu (II)-PAA complexation system.

Complexation system	Observed break at umr*	Probable stoichiometry/unreacted units
Phenolic copolymer IA (1.0 μm)+Cu(II) (0.936m)	0.24 0.94	1/1 (Cu ²⁺ / -OH of PCIP) 1/1 (Cu ²⁺ / -OH of PAP and PC)
Phenolic copolymer IA (1.0 μm)+Cu(II) (0.936m) + PAA (0.8 μm)	1.47 1.75	1/1 (PAA/ -NH ₂ of PAP and PT) (Above complex + 0.276 μm unreacted PAA)
Phenolic copolymer IA (1.0 μm)+Cu(II) (0.936m) + PAA (0.8 μm)+Cu(II) (0.5m)	2.0	1/1 (Cu ²⁺ / unreacted PAA)

*unit mole ratio

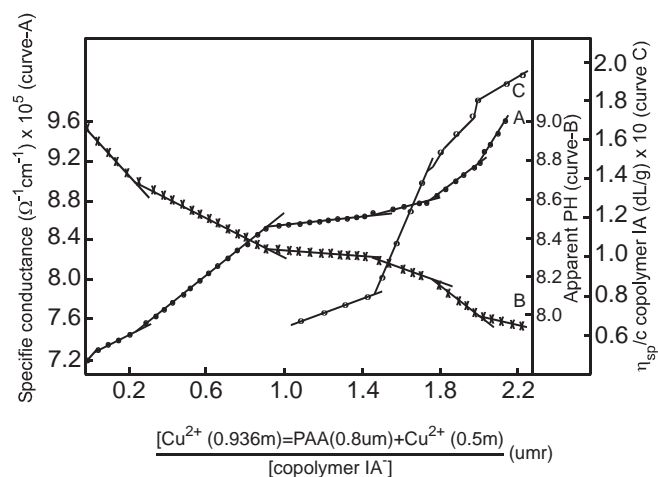


Figure 1. Variation of (A) conductance, (B) apparent pH, (C) reduced viscosity, with unit mole ratio of phenolic copolymer IA-Cu²⁺-PAA-Cu²⁺.

three comonomer units interacted with Ni (II) in three distinct steps possibly due to the inductive influence of the *p*-substituents (e.g. -Cl, -NH₂ and -CH₃) of these three comonomer units.

The work has been extended by choosing the second sample of phenolic copolymer (e.g., IB). As mentioned before, its composition was found to be different from that of IA (cf. table 1).

Phenolic copolymer IB and PAA were mixed in 1/1 (umr), and Cu(II) ions (1.6 m) were added in very small portions to this mixture. The variation of apparent pH and conductance on addition of Cu (II) to 1/1 (umr) mixture of two polymers are shown in Figure 3. From

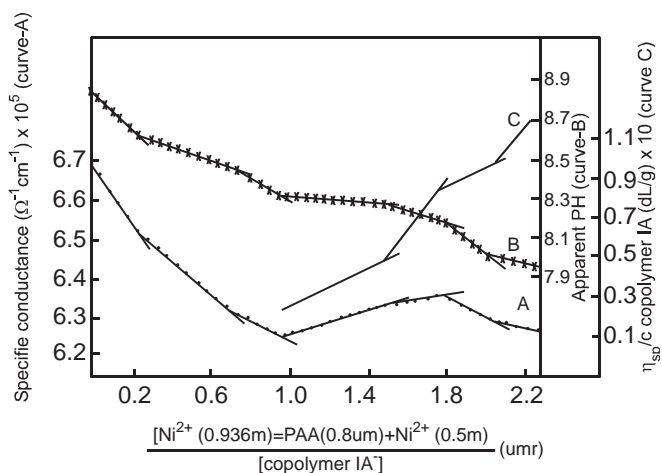


Figure 2. Variation of (A) conductance, (B) apparent pH, (C) reduced viscosity, with unit mole ratio of phenolic copolymer IA-Ni²⁺-PAA-Ni²⁺.

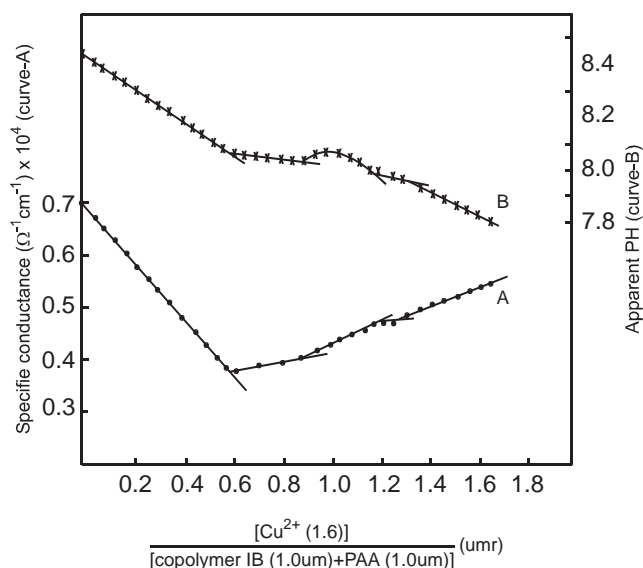


Figure 3. Variation of (A) conductance, (B) apparent pH, with unit mole ratio of phenolic copolymer IB-PAA-Cu²⁺.

the known composition of phenolic copolymer IB, one could calculate the amount of unreacted PAA in 1/1 (umr) mixture of the two polymers. Interestingly enough, the first break at 0.59 (umr) coincided with the amount of unreacted PAA units resulting in the formation of 1/1 (Cu²⁺ / unreacted PAA) complex. The subsequent breaks at 0.9, 1.16, and 1.27 (umr) may be assigned to the formation of 1/1 complex between Cu(II) and -OH groups of PCIP, PC, and PAP units, respectively. The interaction of -OH groups of PC units is more favoured because of the entanglement of PAP

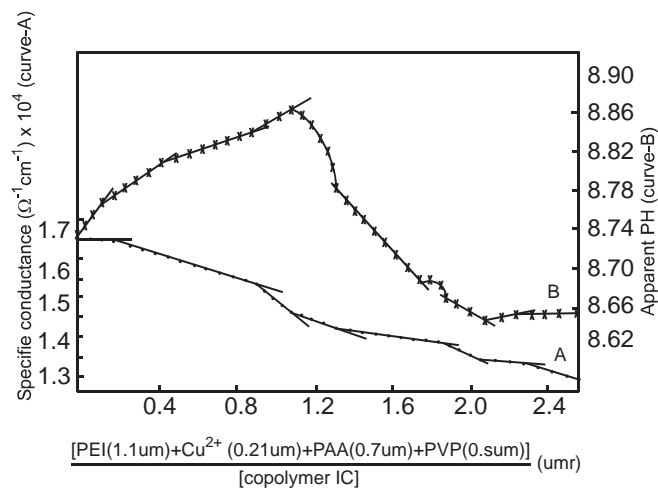
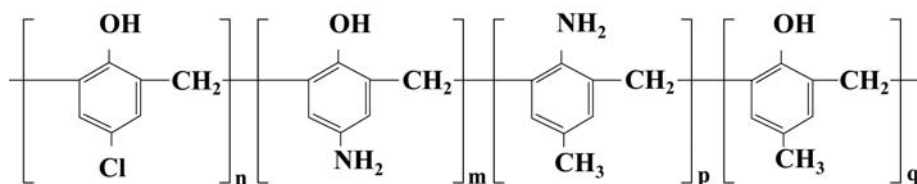
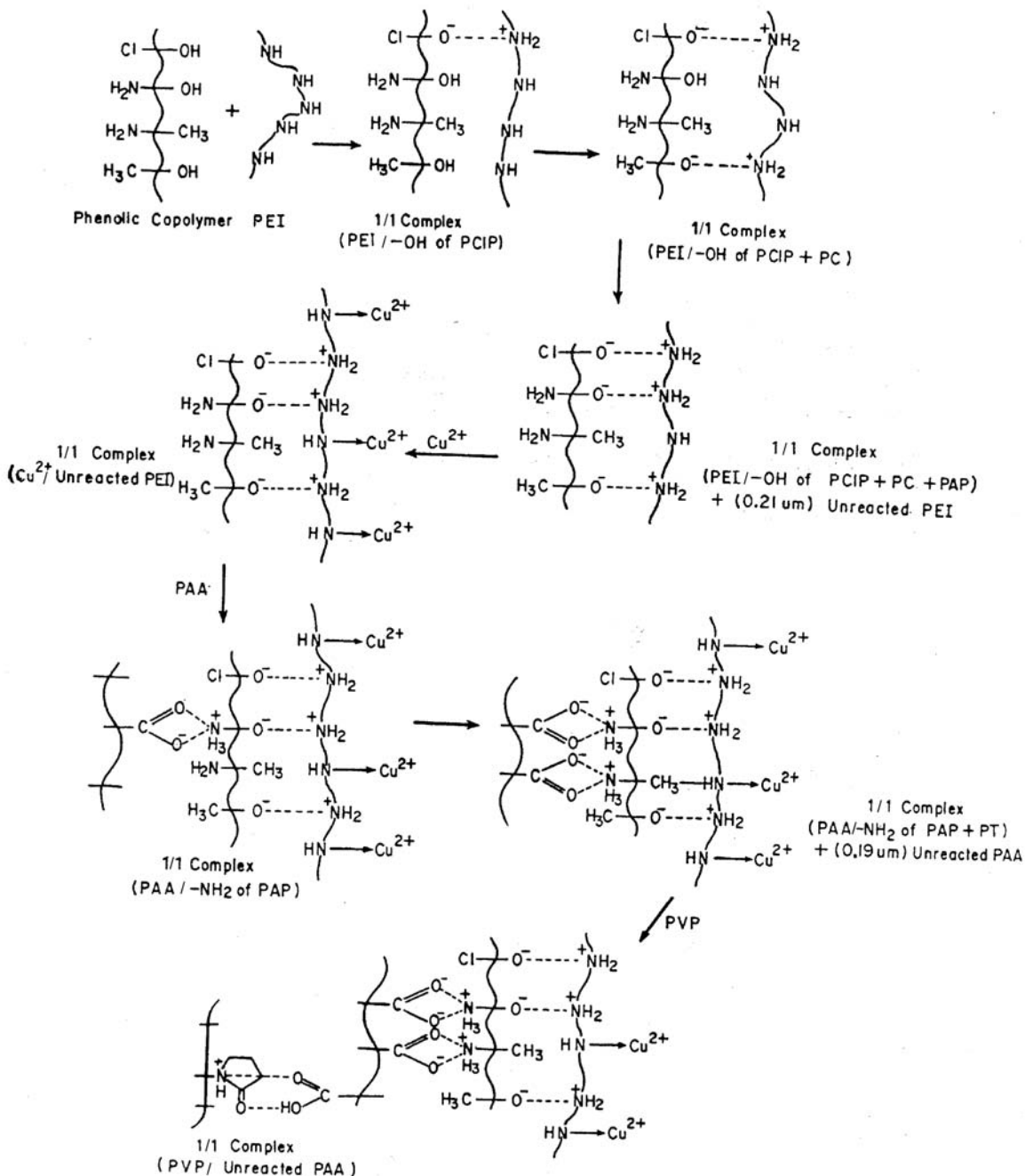


Figure 4. Variation of (A) conductance, (B) apparent pH, with unit mole ratio of phenolic copolymer IC-PEI-Cu²⁺-PAA-PVP.



Copolymer I ($n \geq 1, m \geq 1, p \geq 1, q \geq 1$)



Scheme I

Table 3. Observed breaks and probable stoichiometries in phenolic copolymer (IC)-PEI-Cu(II)-PAA-PVP complexation system.

Complexation system	Observed break at umr*	Probable stoichiometry/unreacted units
Phenolic copolymer IC	0.15	1/1 (PEI/ -OH of PCIP)
(1.0 um)+PEI (1.1um)	0.43	1/1 (PEI/ -OH of PC)
Phenolic copolymer IC	0.89	1/1 (PEI/-OH of PAP)
(1.0 um) + PEI (1.1um) + + Cu(II) (0.21 m)	1.1	(Above complex + 0.21 um unreacted PEI)
Phenolic copolymer IC	1.31-1.35	1/1 (Cu ²⁺ /unreacted PEI)
(1.0 um) + PEI (II) (1.1 um) + Cu(II) (0.21 m)		
Phenolic copolymer IC	1.77	1/1 (PAA/ -NH ₂ of PAP)
(1.0 um) + PEI (1.1 um) + Cu(II)	1.87	1/1 (PAA/ -NH ₂ of PT)
(0.21 m)	2.06	(Above complex + 0.19 um unreacted PEI)
+ PAA (0.75 um) + PVP (0.5 um)	2.25	1/1 (PVP/ unreacted PAA)

(*) unit mole ratio

units with PAA chains.

It is more or less established that, in these observations, transition metal ions (e.g., Cu (II)) interact with -OH groups of the comonomer units according to the following sequence: PCIP, PC, and PAP. This trend could be confirmed further by interacting the -OH groups with a typical basic polyelectrolyte, such as PEI, instead of Cu (II). Figure 4 shows the variation of conductance and apparent pH of 1.0 um solution of phenolic copolymer IC on the addition of various components in the following sequence: PEI (1.1 um), Cu (II) (0.21 m), PAA (0.75 um), and PVP (0.5 um). The observed breaks at various unit mole ratios (umr) and their assigned stoichiometries are summarized in Table 3.

These observations also confirm the predicted sequence of interaction of the various -OH groups associated with the three phenolic comonomer units (e.g., PCIP, PC, and PAP).

On the basis of these arguments Scheme I has been suggested to explain the mode of interaction between the four-component phenolic copolymer and other components .

The IR spectra of some of these complexes were recorded in KBr and compared with those of pure components (i.e., PVP, phenolic copolymer I, and PAA). The

$\nu_{C=O}$ frequency of PVP, phenolic copolymer I and PAA were observed through sharp bands at 1625 cm⁻¹, 1670 cm⁻¹, and 1690 cm⁻¹, respectively. In these complexes, broad bands were observed between 1600-1700 cm⁻¹ and an appreciable shift of $\nu_{C=O}$ band from 1125 cm⁻¹ to 1270 cm⁻¹ probably indicates the simultaneous involvement of carbonyl group of PAA, carboxyl groups of PVP and -OH groups of phenolic copolymer I.

The UV spectra of phenolic copolymer I at 300 nm, is shifted between range 310-315 nm due to formation of Cu-polymer complexes. It seems likely that this new absorption band arises from the charge transfer between phenolic copolymer and metal ion [12].

Table 4. Abbreviation for polymers.

Abbreviation	Full name
PEI	Poly(ethylene imine)
PVP	Poly(vinyl pyrrolidone)
PAA	Poly(acrylic acid)
(PCIP-PAP-PT-PC)	(<i>p</i> -Chlorophenol- <i>p</i> -aminophenol- <i>p</i> -toluidine- <i>p</i> -cresol-formaldehyde copolymer)

CONCLUSION

Since selective complexation between synthetic polymers of known characteristics may provide an excellent model to simulate biological process, therefore, we conclude that phenolic copolymers can enter into distinct complex formation with a polyelectrolyte, a few non-ionic polymers and transition metal ions form multicomponent complexes. The component polymers enter into complex formation through coordinating group of the phenolic copolymer.

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