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Metal-containing intermacromolecular complexes: Electrochemical and viscometric studies in DMF-methanol mixture

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SUMMARY :

Multicomponent intermacromolecular complexes have been prepared from some typical phenolic copolymers with a non-ionic polymer (e.g. PVP), and a polyelectrolyte (e.g.PAA). Some transition metal ions (e.g. Cu(II) and Ni(II)) have been incorporated in the complex through its unreacted co-ordinating groups. The formation of these complexes has been studied by several techniques, such as viscometry, conductometry, potentiometry, IR and UV spectrophotometry. A scheme has been presented to explain the mode of interaction of the various components.

INTRODUCTION :

In recent years the study of interactions between two macromolecular species with complementary binding sites has assumed considerable importance (1,2). Intermacromolecular complexes which are formed as a result of such interactions have unique properties and they have already found wide applications in technology and medicine(2). These complexes are formed by the association of different macromolecular chains through secondary binding forces. Phenolic copolymers with specific co-ordinating groups may provide interesting systems, in view of the presence of intramolecular hydrogen bonding (3,4). One could obtain multicomponent intermacromolecular complexes from these phenolic copolymers by adding poly(vinyl pyrrolidone) (PVP) and poly(acrylic acid) (PAA) in a definite sequence. From the known composition of the phenolic copolymer, the amount of unreacted functional groups in the complex can be calculated. Thus one can incorporate some typical transition metal ions (e.g. Cu(II) and Ni(II)) in the complex through these unreacted functional groups. Formation of these complexes have been studied through several techniques, such as viscometry, conductometry, potentiometry, IR and UV spectrophotometry. A mixture of DMF and methanol (50% : 50% V/V) has been used as solvent to get a better resolution of the different stages of interaction. Metal-containing intermacromolecular complexes may prove useful in catalysis, membranes, and other related substances (2).

EXPERIMENTAL :

P-Chlorophenol - p-Cresol - p-Aminophenol (PClP-PC-PAP) Block Copolymer(I)

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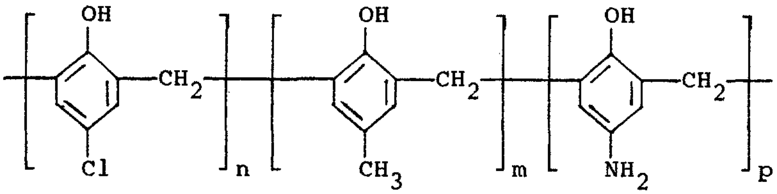
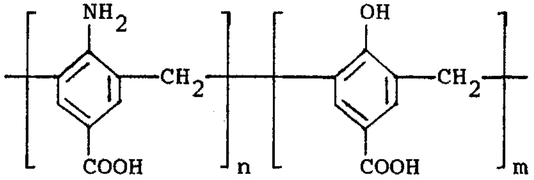


I

$n \geq 1$, $m \geq 1$, $p \geq 1$

Two samples (IA and IB) of the above copolymer were prepared by using known methods(5). Both block copolymers were characterized.

P-Aminobenzoic acid - p-Hydroxybenzoic acid (PAB-PHB) Copolymer (II).



$n \geq 1$, $m \geq 1$ II

The copolymer (II) was prepared by known methods and characterized(6). It contained 0.59 mol. of PHB and 0.41 mol. of PAB units, respectively.

PAA was prepared by known methods(7). The weight average molecular weight ($\bar{M}w$) was found to be approximately 4.5×10^5 g/mol.

PVP used was of commercial origin (Fluka, Switzerland). $\bar{M}w$ was calculated from viscosity measurements and was found to be 2.4×10^4(8).

Analytical grade dimethyl formamide (DMF) and methanol (M) were used for mixed solvent studies.

The viscosity of the mixed solutions of copolymers, PAA, PVP, and metal ions was determined at 30°C ± 0.05°C by an Ubbelohde viscometer for which kinetic energy correction was negligible.

A Leeds and Northrup (4959) electrolytic conductance bridge was used for conductometric titrations and a digital pH meter (Model pH 5651) with a combination electrode was used for pH measurements. The titrations were performed at room temperature and sufficient time was given after each addition of titrant to obtain equilibrium readings.

IR spectra were recorded on a KBr pellet, using a Perkin -Elmer model 1710 spectrophotometer. A Shimadzu UV-260 spectrophotometer was used for recording the UV spectra.

RESULT AND DISCUSSION:

The three component phenolic copolymer (IA) has been prepared and characterized(3). The copolymer was found to have the comonomer units in the ratio of 0.26 : 0.2 : 0.54 (PClP : PC : PAP). A mixed solvent (e.g. 50% dimethyl formamide (DMF) + 50% methanol (M) (V/V)) has been used in order to get a better resolution of the different stages of interaction between the phenolic copolymer, component polymers and transition metal ions. Fig.1 depicts the variation of conductance, apparent pH and reduced viscosity (η_{sp}/C) of 1 unit mole (um) of the phenolic copolymer (IA) solution on the successive additions of PAA (0.54 um), Cu(II) (0.26m), PVP (0.2 um), Ni(II)(0.54 m) and excess of PVP respectively. The specific quantities of component polymers and transition metal ions have been added to the phenolic copolymer (IA) in a definite sequence in order to complex its co-ordinating groups quantitatively. Both the apparent pH and conductance curves (cf. Curve A and B of Fig.1) showed distinct stages of interaction of phenolic copolymer. During the addition of PAA (e.g. 0.54 um), both the curves showed a slight fall in the conductance and apparent pH. Obviously the break observed at 0.54 umr may be assigned to the formation of 1:1 complex between -COOH groups of PAA and $-NH_2$ groups of PAP units.

However the apprent pH and conductance fell abruptly during the subsequent addition of 0.26 mol. of Cu(II) ions, which can be attributed to the formation of the 1:1 complex between Cu(II) and -OH group of PClP. The higher electronegativity of Cl and the entanglement of PAP units due to complex formation, may perhaps be responsible for the preferential interaction of -OH groups of PClP units. The sharp fall in apparent pH may be due to release of protons during interaction of phenolic -OH groups with transition metal ions(9,10). However, the corresponding fall in conductance may probably be due to association of charged species in the medium of low dielectric constant(11). Subsequent addition of PVP(0.2 um) may lead to the formation of 1:1 complex of PVP with the phenolic -OH groups of PC units. The -OH groups of PAP units finally interact with Ni(II) to form 1:1 complex.

The reduced viscosity curve (cf. Curve C of Fig.1) also indicated breaks which coincided with those observed in the apparent pH and conductance curves. The continuous linear increase in viscosity at different stages of interaction may be attributed to bulkiness of the multicomponent complex molecule in non-aqueous media. The excellent correlation

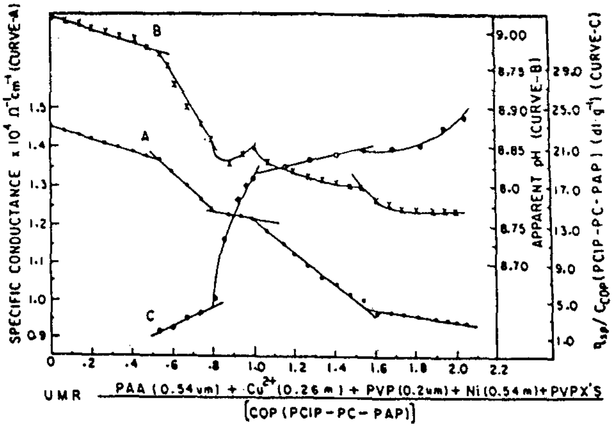


FIG.1. Variation of conductance (A), apparent pH (B), and reduced viscosity (C), with unit mole ratio for phenolic copolymer (IA)- PAA - Cu(II) - PVP - Ni(II) system.

between the actual composition of the phenolic copolymer and stepwise interaction observed from three independent methods certainly indicates the validity of some of these arguments.
In order to substantiate some of the conclusions made earlier, it was considered of interest to find the relative complexation ability of the three -OH groups associated with the three comonomer units (e.g. PClP, PC and PAP) with respect to Cu(II) ions. The variations of apparent pH and conductance were recorded on addition of 1 mol. of Cu(II) in small instalments to 1 um of phenolic copolymer (IA), (cf.Fig.2). Subsequently, PAA(0.54 um) and PVP (0.5 um) were added in small instalments. Both the apparent pH and conductance curves (cf. curve A and B of Fig.2) indicated a distinct break at 0.26 (umr) which incidently coincides with the proportion of PClP units. It is obvious from this observation that the substituent at the para position of the comonomer unit plays a significant role on the complexation ability of -OH groups with respect to Cu(II) ions. However, the complexation of the -OH groups associated with the remaining comonomer units (e.g. PC and PAP) takes place in a single step. The unreacted $-NH_2$ groups of PAP units

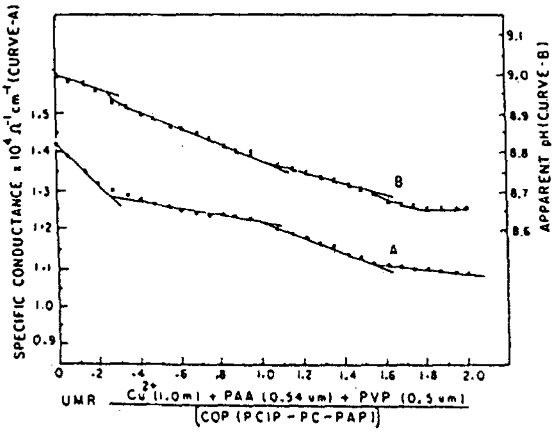


FIG.2. Variation of conductance (A), and apparent pH (B) with unit mole ratio for phenolic copolymer(IA)-Cu(II) - PAA - PVP system.

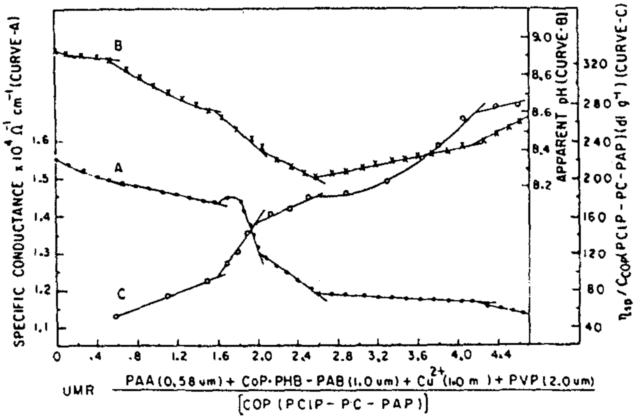


FIG.3. Variation of conductance (A), apparent pH (B), and reduced viscosity (C), with unit mole ratio for phenolic copolymer(IB)- PAA - phenolic copolymer (II) - Cu(II) - PVP system.

were then subsequently complexed by adding stoichiometric amount of PAA(e.g. 0.54 um). Finally, addition of excess of PVP to this complexed system showed almost no change in conductance or apparent pH. This obviously indicates that the relative complexation ability of the transition metal ions is much greater than PVP with respect to -OH groups of the phenolic copolymer.

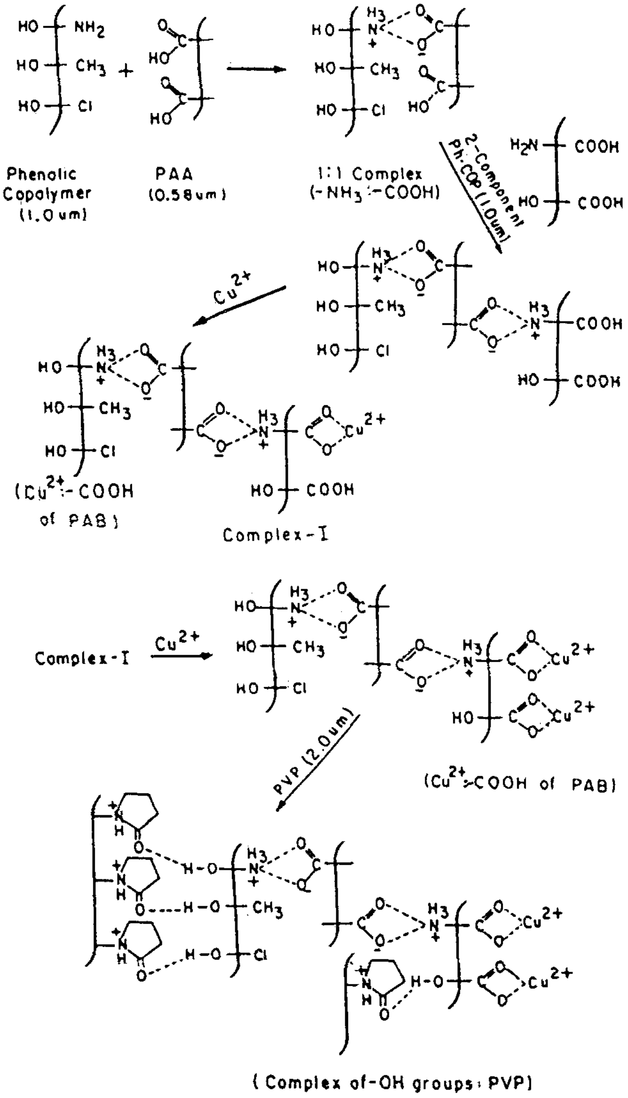
The validity of some of these arguments can possibly be confirmed by studying the interaction of another phenolic copolymer (IB) with a different composition. The phenolic copolymer (IB) was prepared from the same comonomers, but with a different feed composition. The copolymer (IB) was found to contain 0.42 m of PClP, 0.41 m of PC and 0.17 m of PAP. Another two component phenolic copolymer (II) was also prepared and characterized in order to study copolymer--copolymer interactions. The copolymer (II) found to have 0.41 m of PAB and 0.59 m of PHB units. Fig. 3 shows the variation of conductance, apparent pH and reduced viscosity of phenolic copolymer (IB) solution on adding stoichiometric amounts of PAA (0.58 um), 2 component phenolic copolymer (II) (1.0 um), Cu(II) ions (1.0 m), and PVP (2.0 um) in the same solvent, respectively. Both the apparent pH and conductance curves (cf. curve A and B of Fig.3) showed distinct steps of interaction with the various components.

Since 0.58 um of PAA was added, 0.41 um remained unreacted after complexation with $-NH_2$ groups of PAP units (0.17um). The unreacted PAA units were then stoichiometrically complexed with 1 um of two component phenolic copolymer (II). One could calculate the amount of unreacted -COOH and phenolic -OH groups associated with the various comonomer units in the three component complex. Therefore, on adding 1 mol. of Cu(II) ions to this complex, two distinct stages of interaction have been observed. It is known that complexation ability of -COOH groups is much greater than phenolic -OH groups with respect to Cu(II) (12). On the basis of relative proportion of PAB and PHB units in the multicomponent complex, the break at 2.0 (umr), may be assigned to the formation of 1:1 complex between -COOH of PAB units and Cu(II), whereas the break at 2.59 (umr) is likely to be due to 1:1 complex of -COOH of PHB units and Cu(II). A linear change in conductance and apparent pH (cf. curve A and B of Fig.3) was observed on adding PVP which culminated into a distinct break at 4.19 umr. This incidently coincided with the calculated amount of phenolic -OH groups of copolymers (IB and II). Thus a 1:1 complex of phenolic -OH and PVP is predicted.

On comparing the $\nu_{C=O}$ stretching, ν_{N-H} stretching, ν_{O-H} stretching, and ν_{C-N} stretching, frequencies of the component polymers and those of the intermacromolecular complexes, distinct shifts have been observed, which obviously indicate the involvement of various functional groups during intermacromolecular complex formation. The UV spectra of the phenolic copolymer (IA and IB), showed λ_{max} at 301 nm which shifted to about 310 nm for the metal-intermacromolecular complex. It seems likely that the new absorption band arises from the formation of charge transfer complexes between intermacromolecular complex and metal ions(12).

On the basis of spectral data and the distinct steps observed in the measurements of various physical properties, the following scheme has been suggested to explain the mode of interaction between the phenolic copolymers and other components.

SCHEME



In conclusion, it can be said that phenolic copolymers can enter into distinct complex formation with polyelectrolyte, non-ionic polymers, and transition metal ions to form multicomponent complexes. Fundamental studies of this nature may perhaps give some insight regarding the formation of specific metal-containing intermacromolecular complex.

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