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Physicochemical Studies on Some Phenolic Polymer-Transition Metal Complexes in Nonaqueous Media

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ABSTRACT

The formation of complexes between phenolic oligomer/polymer with some transition metal ions has been studied by conductance and emf measurements. Sharp changes in color, conductance, and potential at definite stoichiometric quantities of ligand and metal ions have been attributed to polymer-metal chelation. Interpretations of the results have been sought in terms of the length of the polymer chain and the nature of the transition metal ions.

INTRODUCTION

Polymer-metal complexes formed by the combination of an organic polymer with a metal ion have been studied extensively in recent years [1, 2]. The potential applications of the polymer-metal complexes probably outweigh the limitations of their study. It is well known that phenolic monomers form colored complexes with transition metal ions [3]. Complex formation between metal ions and phenolic oligomers and polymers is expected to be more interesting in view of the presence of intramolecular hydrogen bonding in them

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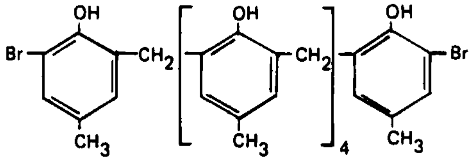
[4-6]. In the present investigation a hexanuclear phenolic oligomer of uniform structure and molecular weight and a p-cresol-HCHO polymer (PCF) have been chosen to study the interactions with some transition metal ions. Comparison of these two systems may show how intrapolymer chelate formation may be influenced by the length of the polymer chain. The reduction of viscosity of the polymer solution with increasing concentration of metal ions show that the intrapolymer chelate takes a very compact form and the metal ions are crowded within the contracted polymer chain [7-9]. It has also been reported that the contracted structure of the polymer chelated with a metal ion differs for various metal ions species [7]. Keeping this fact in view, three transition-metal ions, e.g., Cu^{2+}, Co^{2+}, and Fe^{3+}, have been chosen for interaction with phenolic polymers studies.

EXPERIMENTAL

Synthetic Preparation of Polymers

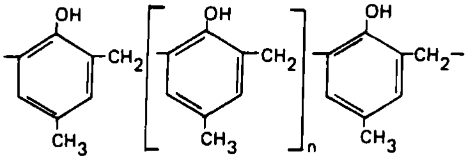
For the preparation of hexanuclear phenolic oligomer (I) of uniform structure and molecular weight, the methods of Kämmerer and coworkers [10, 11] were followed.



I

Compound I (Br-6-Br) was prepared by condensing 0.01 mol of 2,2'-dihydroxy-5,5'-dimethyl-diphenyl methane (H-2-H) with slightly more than 0.02 mol of 3-bromo-3'-hydroxymethyl-2,2'-dihydroxy-5,5'-dimethyl-diphenyl methane ($Br-2-CH_2OH$) in the presence of concentrated HCl as catalyst. The reaction mixture was heated at 130°C for 1 h and then the fused mass was dissolved in dioxane and finally precipitated with methanol.

p-Cresol formaldehyde condensation polymer (PCP) (II) was prepared by refluxing the components in equimolar proportion in the presence of 2 mL of 10 N HCl as catalyst for 2½ h at 130°C. The $\overline{DP}$ of the polymer has been determined by electrometric titration technique in nonaqueous solvent [6].



II

Preparation of Solution and Procedure for Titrations

Acetone solutions of the hexanuclear oligomer and polymer (PCF) were neutralized completely with stoichiometric quantities of sodium methoxide in methanol. Increasing quantities (in millimoles) of chlorides of Cu^{2+}, Co^{2+}, and Fe^{3+} in acetone were added to the neutralized polymer solutions and the variations of their conductance and potential were measured. The reproducibility of each measurement had been checked and found to be within ± 2-3%.

A Leeds and Northrup 4959 conductivity bridge was used for conductance measurement and a Radiometer pH meter (pHM 26C) with glass (G 202B) and a calomel electrode (K 401) as reference was used for EMF measurements. The titration vessel was stirred with a magnetic stirrer which was switched off during each measurement.

RESULTS AND DISCUSSION

The presence of intramolecular hydrogen bonding has often been postulated to explain the peculiar behavior of phenolic oligomers and polymers [4, 5, 12]. As a result of the intramolecular hydrogen bonding present in them, the phenolic oligomers and polymers are expected to coordinate with transition metal ions. A hexanuclear phenolic oligomer (I) and p-cresol-HCHO polymer (PCF) (II) have been completely neutralized in acetone solution with sodium methoxide in methanol. Figure 1 shows the change in conductance and potential (in mV) of these solutions with increasing concentration of Cu^{2+} ions. The completely charged oligomer and the polymer PCF molecules are expected to have extended conformations as a result of mutual repulsion of charges within the molecule. However, on addition of Cu^{2+} ions, electron transfer takes place from the ligand, and Cu^{2+} is reduced to Cu^{+}. Thus, at the first stage of interaction in the hexanuclear molecule, a sharp fall in conductance and potential has been observed (e.g., Curves A and B of Fig. 1), whereas with polymer PCF (DP = 16.2) the fall in conductance has been observed up to the addition of three equivalents of Cu^{2+} ions, and the potential fell sharply after this stage (cf. Curves C and D, Fig. 1). The distinct difference in behavior of the two polymers can obviously be attributed to the length of the chain, i.e., the longer the polymer chain, the

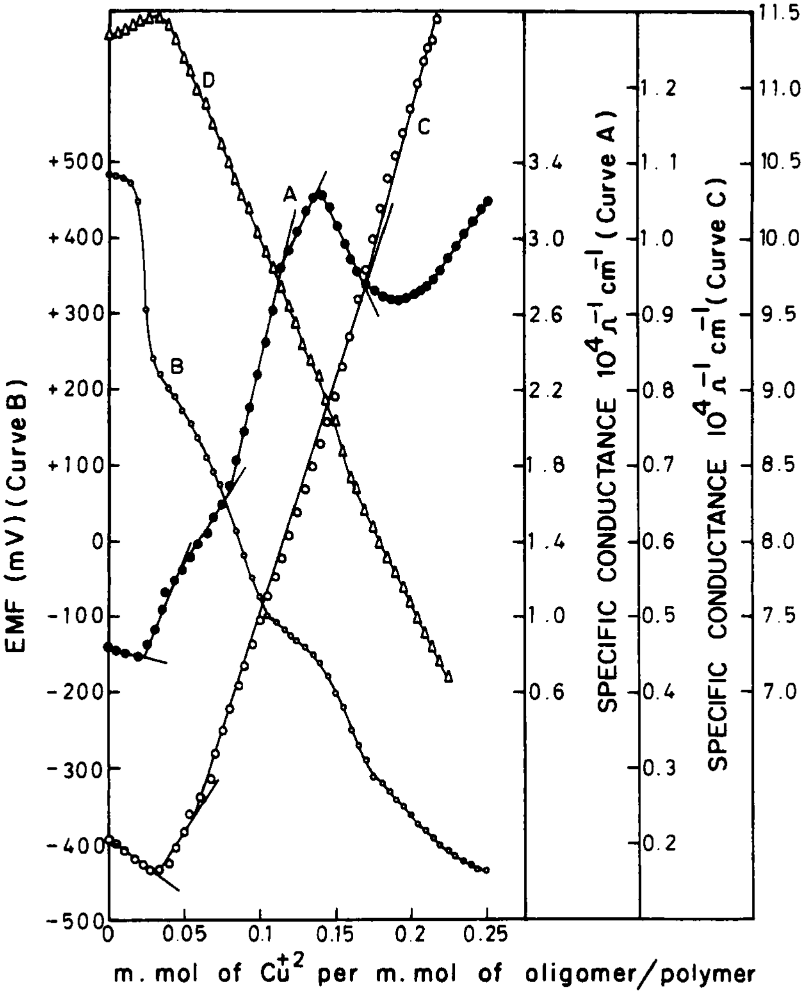


FIG. 1. Variation of conductance and emf of completely neutralized oligomer/polymer solutions in acetone with increasing concentration of Cu^{2+} ions. Oligomer: Conductance (A) and emf (B). Polymer: Conductance (C) and apparent pH (D).

greater is the cooperation in the interaction. In other words, different stages of interactions with metal ions are merged in polymer PCF whereas a distinct stepwise interaction is observed in the case of hexanuclear oligomer. At constant polymer concentration an increase in the amount of metal ions added causes a decrease in

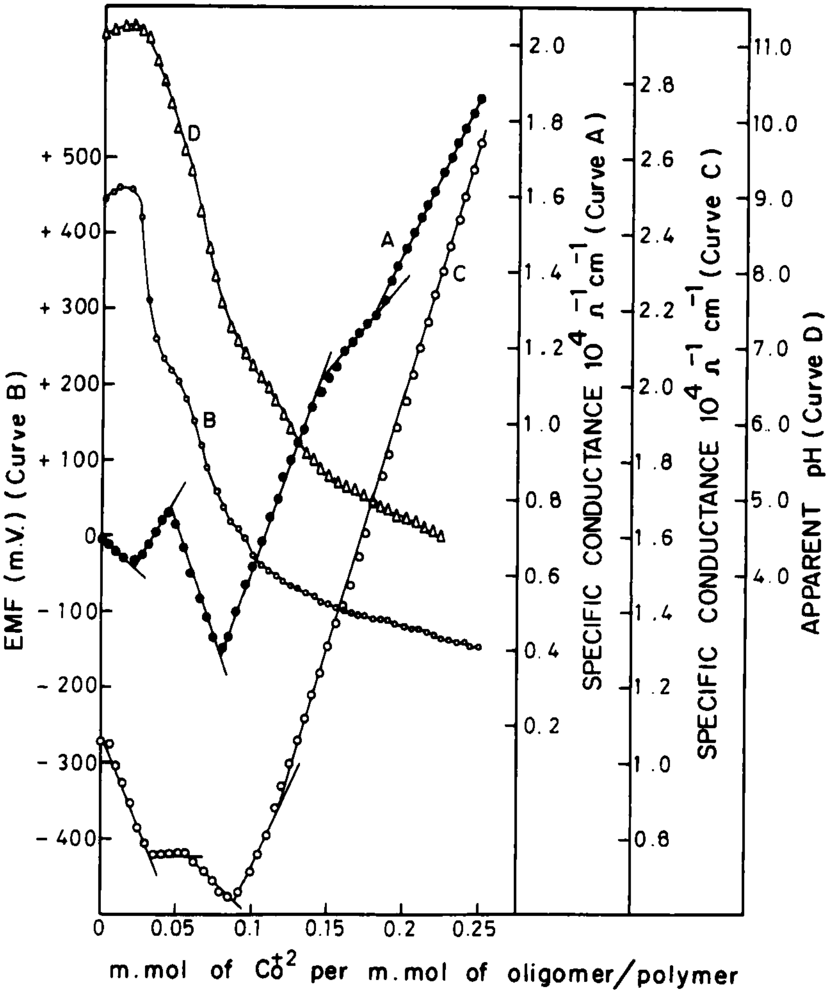


FIG. 2. Variation of conductance and emf of completely neutralized oligomer/polymer solutions in acetone with increasing concentration of Co^{2+} ions. Oligomer: Conductance (A) and emf (B). Polymer: Conductance (C) and apparent pH (D).

conductance up to a certain stage which indicates that as a result of electron transfer, a more conducting species is being replaced by a less conducting one. The subsequent increase in conductance with further addition of metal ions reveals that the polymer-ligand chain is probably markedly contracted due to intrapolymer chelation. An

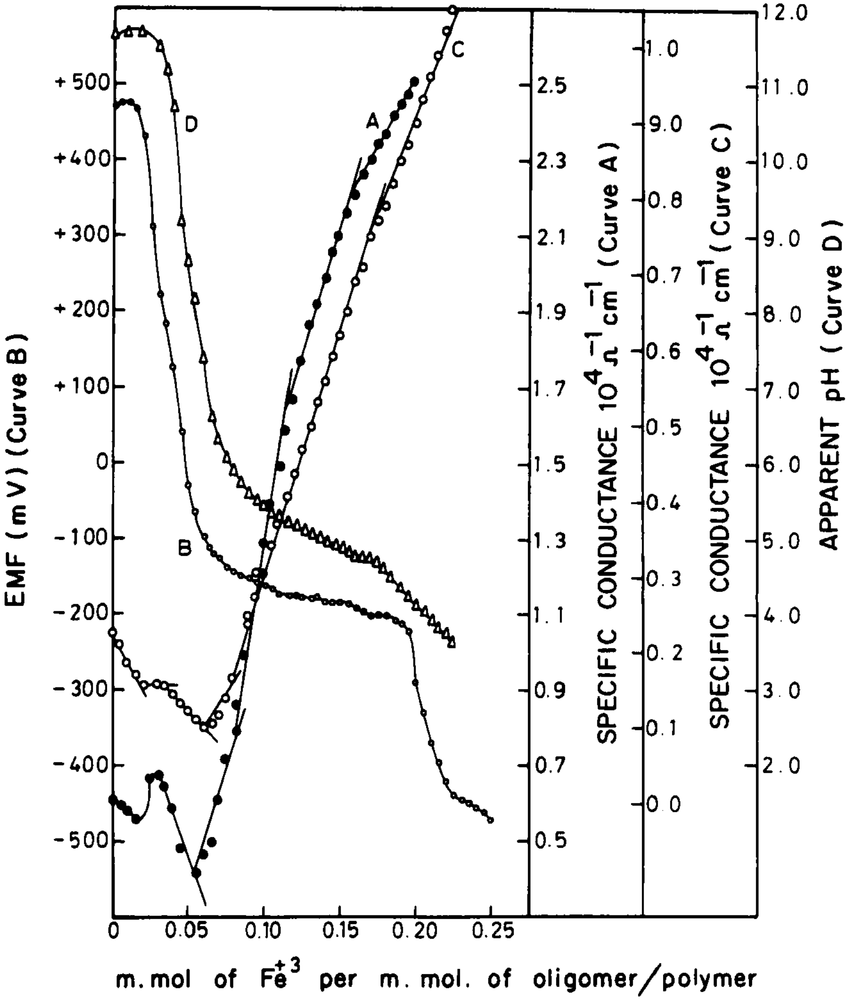


FIG. 3. Variation of conductance and EMF of completely neutralized oligomer/polymer solutions in acetone with increasing concentration of Fe^{3+} ions. Oligomer: Conductance (A) and emf (B). Polymer: Conductance (C) and apparent pH (D).

intrapolymer chelate takes a very compact form wherein metal ions are crowded within the contracted polymer chain. Such a contracted shape of an intrapolymer chelate has been reported for polyacrylic acid (PAA) [8], and polyvinylamine (PVAm) [9]. Many of the distinct breaks in the conductance curve coincided with sharp color changes, and a steep fall in the potential indicates the formation of polymer-metal complexes.

It has been reported from viscometric studies that the contracted structure of polyvinyl pyrrolidone (PVP) chelated with a metal ion is different for various metal ion species [7]. It was considered to be an important finding that the structure of an intrapolymer chelate depends on the metal ion species. Keeping this fact in view, it was considered of interest to study the interactions of phenolic polymers with other metal ion species (e.g., Co^{2+} and Fe^{3+}).

Figures 2 and 3, show the variation of conductance and potential of completely neutralized hexanuclear oligomer (I) and polymer PCF (II) solutions with increasing concentrations of Co^{2+} and Fe^{3+} ions, respectively. The stability of transition metal complexes depends not only on the electron affinity or ionization potential of the metals but also on such factors as the availability of empty d orbitals for π-bonding, stereochemistry, and electron pairing energy [13]. However, all these factors may be summarized by saying that stability, and of course interaction, depend significantly upon the particular number of d electrons in the transition metal ions or atoms [13]. Since Fe, Co, and Cu have $3d^6$, $3d^7$, and $3d^{10}$ electronic configurations, respectively, therefore, as expected, the nature of the conductance curve was found to be different for Fe^{3+} and Co^{2+} compared to Cu^{2+} (cf. Curves A of Figs. 1-3). Another factor which may be attributed to the difference in behavior during interaction with the various metal ions is the difference in electronegativity of Fe, Co, and Cu (e.g., Fe = 1.64, Co = 1.70, Cu = 1.75). As pointed out in the case of interactions with Cu^{2+}, hexanuclear oligomer (I) and polymer PCF (II) also behave differently during interaction with Co^{2+} and Fe^{3+} (compare Curves A and C of both Figs. 2 and 3). This may be explained by the high local concentration of ligands in the polymer domain, i.e., once a metal ion is attached to one ligand group of the polymer chain, the other ligands coordinate more readily [2]. This is precisely the reason for the merging of metal ions at distinct steps of the conductance curve, whereas sharp stepwise interactions with metal ions have been observed in the case of the hexanuclear oligomer.

Thus one can conclude that intrapolymer chelate formation depends to a large extent on the particular number of d electrons in the transition metal ion or atom, their electronegativity, and the length of the polymer chain. Sharp changes in color, conductance, and potential at definite stoichiometric quantities of ligand and metal ions can be attributed to polymer-metal chelation.

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