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Electrochemical Studies of the Interaction of Some Transition Metal Ions with a Phenolic Oligomer

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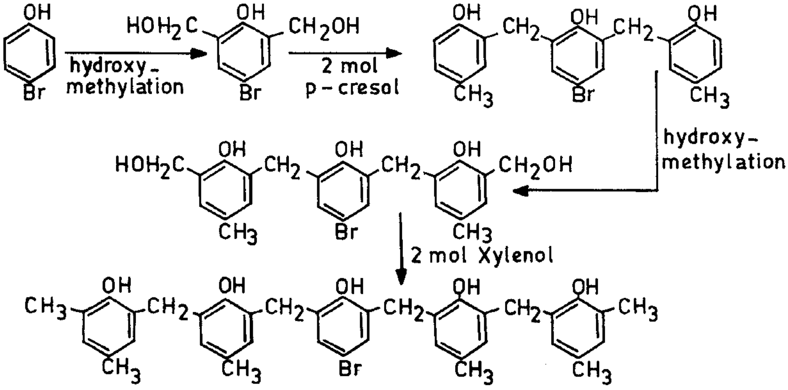
ABSTRACT

A pentanuclear phenolic oligomer of uniform structure and molecular weight has been prepared by a known method of stepwise synthesis. The presence of intramolecular hydrogen bonding in this compound has been well established. Interactions of some transition metal ions (e.g., Fe^{3+}, Cu^{2+}, Co^{2+}) with this chelating oligomer have been studied by conductance, EMF, and optical density measurements in nonaqueous media. Interpretations of the results have been sought in terms of charge on the metal ion as well as charge on the ligand molecule.

Polymers with coordinating groups such as $-NH_2$, $-COOH$, $-OH$, $C=O$, etc. readily interact with transition metal ions to form polymer-metal complexes. In fact, such a synthesis represents an attempt to give an organic polymer inorganic functions. Extensive work has been done on the formation, stability, and catalytic activity of polymer-metal complexes due to their biological importance [1]. Because of the presence of intramolecular hydrogen bonding in phenolic oligomers and polymers [2-5], one can expect that such a system may provide an excellent ligand for coordinating with transition metal ions. Keeping this fact in mind, a phenolic oligomer with uniform structure and molecular weight has been prepared by a known method of synthesis [6]. Since the formation and stability of a polymer metal complex is largely influenced by the initial pH of the ligand solution, interactions of the metal ions have been studied at different stages of neutralization of the polymeric acid. The formation of polymer chelates could be recognized by sharp color changes of the solution at various concentrations of the metal ions. The shift in the absorption maxima indicated a step by step interaction of the metal ion with the polymeric ligand. An excellent correlation could be observed between the change in conductance and EMF of the solution at different stages of interaction with the metal ions. An attempt has been made in this paper to explain these interactions in terms of charge and nature of transition metal ions.

EXPERIMENTAL

The pentanuclear oligomer was prepared according to the method of Hunter and co-workers [6]. p-Bromophenol was hydroxymethylated at room temperature with formaldehyde. 4-Bromo-2,6-dimethylol phenol thus obtained was condensed with p-cresol (with concentrated HCl as catalyst) to get 2,6-bis-2'-hydroxy-5'-methyl benzyl-4-bromophenol. The trinuclear compound was further hydroxymethylated with formaldehyde at room temperature to obtain 2,6-bis-2'-hydroxy-3'-methylol-5'-methylbenzyl-4-bromophenol. The trinuclear dialcohol thus obtained was further condensed with 2,4-xylenol to 2,6-bis-2'-hydroxy-3'-(2''-hydroxy-3'',5''-dimethylbenzyl)-5'-methylbenzyl-4-bromophenol.



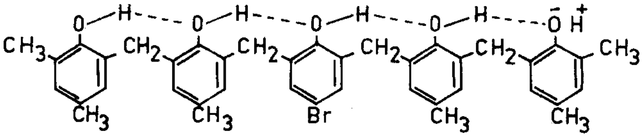
(1)

A Leeds and Northrup 4959 electrolytic conductance bridge was used for conductance measurements, and a Radiometer pH meter (Model PHM 26c) with glass electrode (G202B) and a calomel electrode (K 401) as reference was used for EMF measurements. The vessel was stirred with a magnetic stirrer which was switched off during each measurement. The optical density of the solutions was measured by a Unicam SP 600 spectrophotometer.

A known volume of a standard solution of the pentanuclear compound in acetone was added in a series of glass-stoppered bottles and then a stoichiometric quantity of sodium methoxide was added to each bottle to neutralize only one of its OH groups. Increasing quantities (in millimoles) of chlorides of Cu^{2+}, Co^{2+}, or Fe^{3+} in acetone were added to these bottles, and their optical densities measured. In subsequent experiments the pentanuclear compound was neutralized up to the 2nd, 3rd, 4th, and 5th stages, respectively, and the metal chloride solutions were added in an identical manner. The conductance and EMF measurements were also made by adding increasing concentrations (in millimoles) of the metal ions to the pentanuclear compound, neutralized up to different stages. The reproducibility of each measurement had been checked and found to be within ±2-3%.

RESULTS AND DISCUSSION

The presence of intramolecular hydrogen bonding in the oligomer molecule (1) has been established from electrometric titration studies in nonaqueous media [7]. IR spectra of the oligomer also showed sharp absorbance in the region 3200-3600 cm^{-1}, indicating the probable presence of intramolecular O– –H...O bonding (2).



(2)

Because of the presence of the chelating center, the oligomer molecule is expected to coordinate easily with the transition metal ions. The oligomer, being insoluble in water, was dissolved in acetone for electrochemical studies. Three typical transition metal ions, i.e., Fe(III), Cu(II), and Co(II), have been chosen for this investigation. However, contrary to our expectations, when acetone solutions of these metal ions were added to the oligomer solution, no distinct color change was observed. Therefore, it was thought that coordination with the metal ions may be influenced by changing the pH of the ligand solution. In other words, coordination is likely to be more favorable if the polymeric acid is in the ionized form. With this idea, the oligomer molecule was neutralized up to different stages by adding stoichiometric quantities of sodium methoxide in methanol. Interestingly enough, sharp color changes were observed when increasing concentrations of metal ions were added to the oligomer solutions at different stages of its neutralization.

The variation of conductance, EMF, and optical density of the solution were measured at different metal ion concentrations to a given concentration of the ligand. Figures 1 to 5 present such variations when Cu(II) ions were added to the oligomer solution in which ligand molecule had one, two, three, four, and five negative charges, respectively. In all cases the solution was pale yellow in color in the beginning, changed to reddish brown, and finally to brown when a certain stoichiometric amount of Cu(II) ions were added to the ligand solution. On comparing the conductance curves (i.e., Curve A of Figs. 1 to 5), it is observed that step by step interaction with Cu(II) ions becomes more distinct if the oligomer molecule carries a higher negative charge (e.g., Curve A of Figs. 4 and 5). Similar observations were made in the EMF curves (e.g., Curve B of Figs. 4 and 5), i.e., very sharp potential changes were observed when definite stoichiometric quantities of Cu(II) ions were added to the ligand solution. The distinct color changes of the solutions were also studied by measuring the optical density of the solution at various concentrations of the Cu(II) ions. The step by step interaction of the metal ions with the ligand are indicated more distinctly in the optical density curves. Similar observations have been made during interaction with Co(II) ions except, of course, the color of the solution changed from light yellow to green and finally blue with an increasing concentration of metal ions.

In order to study the influence of charge on the metal ion, the interaction of Fe(III) ions with the polymeric ligand has also been studied. Figures 6 to 10 show the variation of conductance, EMF, and optical density of the solution when increasing stoichiometric quantities of Fe(III) ions are added to the solution of the ligand at the 1st, 2nd, 3rd, 4th, and 5th stages of its neutralization, respectively. Contrary to the observations made with bivalent cations (e.g., Cu^{2+} and Co^{2+}), the step by step interaction with Fe(III) ions takes place more distinctly when the oligomer molecule has a smaller number of negative charges, i.e., when it was neutralized only up to the 1st or 2nd stage. Another factor which differentiates the interaction of Fe(III) from bivalent cations is the sudden increase in potential in the EMF curve (i.e., Curve B of Figs. 6 to 10) when an exact stoichiometric quantity of Fe(III) ions has been added corresponding to the negative charges in the oligomer molecule. The color of the solution changed from yellow to light red and finally to deep red with an increasing concentration of Fe(III) ions in the ligand solution, and the corresponding changes in optical density of the solution are shown in Curve C of Figs. 6 to 10. As in the case of bivalent cations, the step

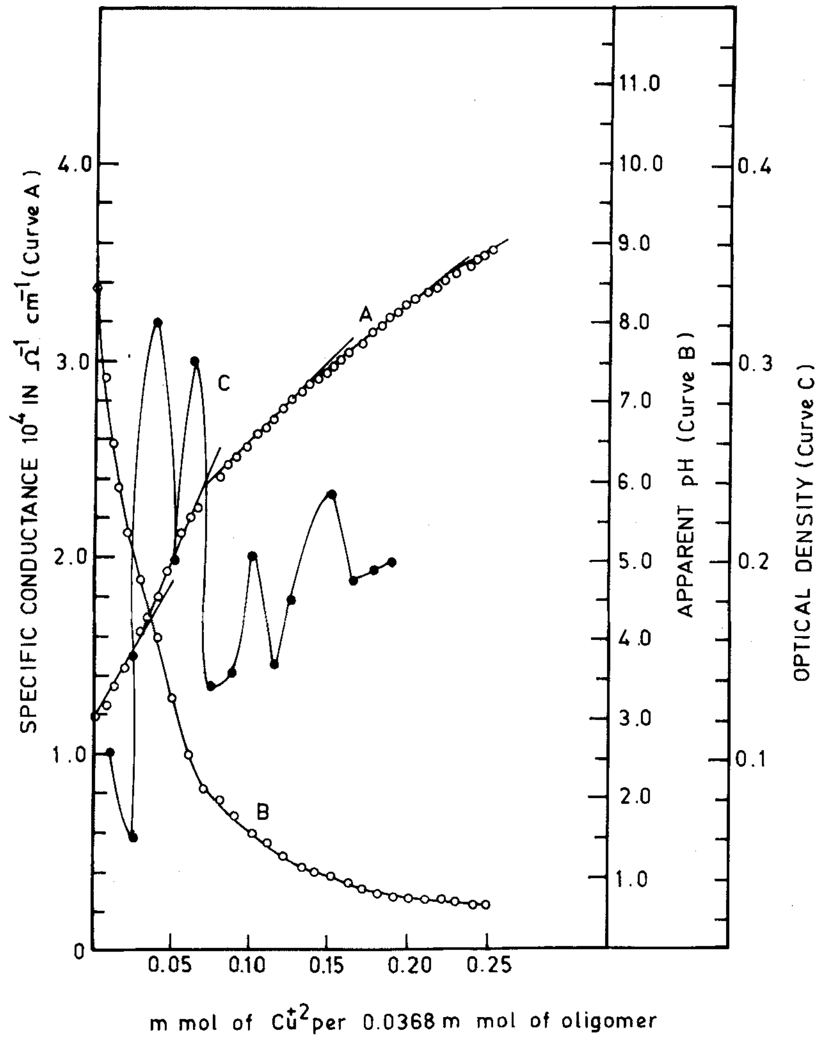


FIG. 1. Variation of conductance (A), apparent pH (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 1st stage) with increasing concentration of Cu^{2+} ions.

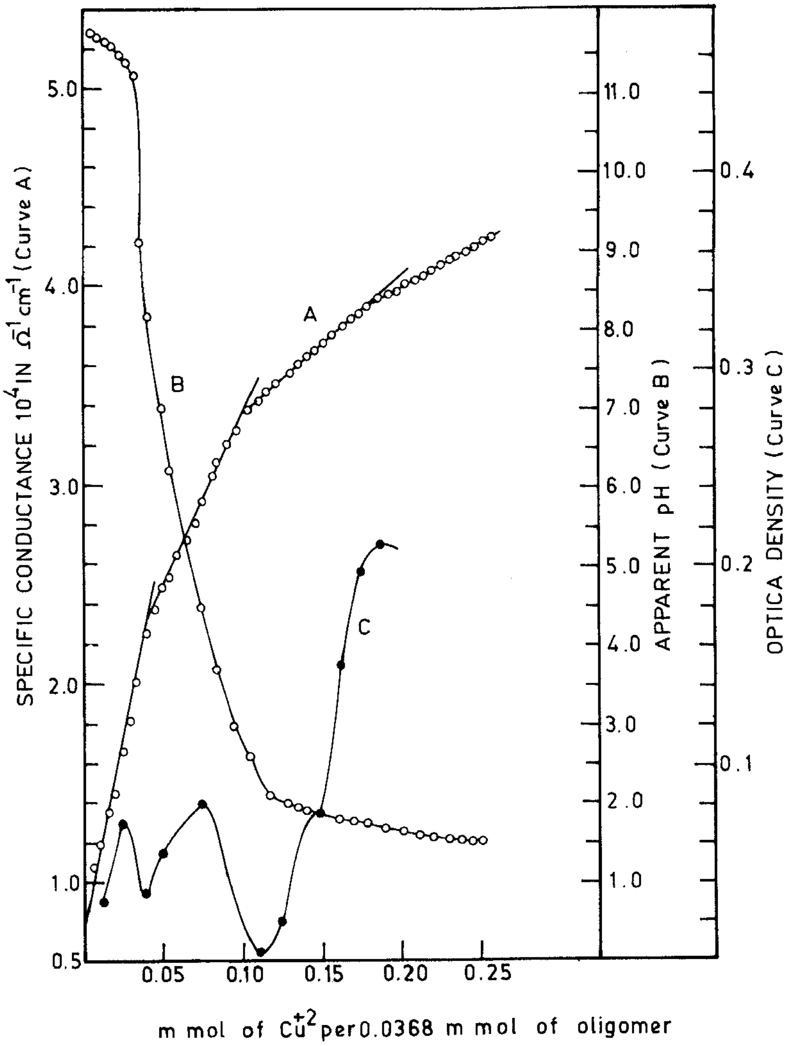


FIG. 2. Variation of conductance (A), apparent pH (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 2nd stage) with increasing concentration of Cu^{2+} ions.

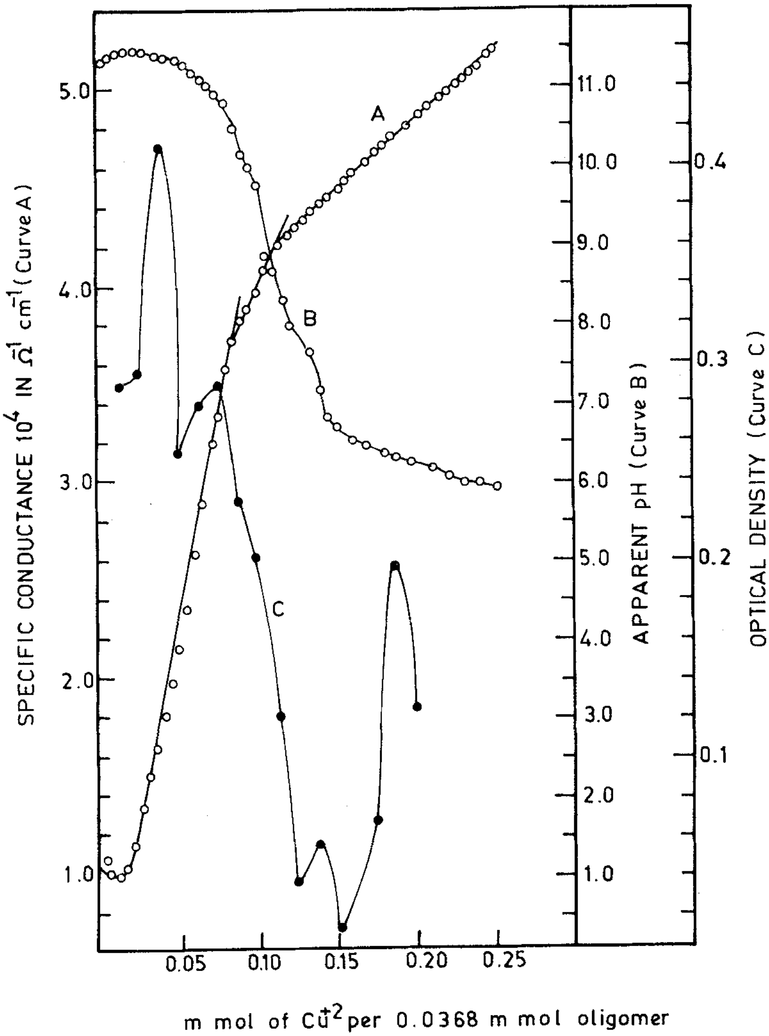


FIG. 3. Variation of conductance (A), apparent pH (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 3rd stage) with increasing concentration of Cu^{2+} ions.

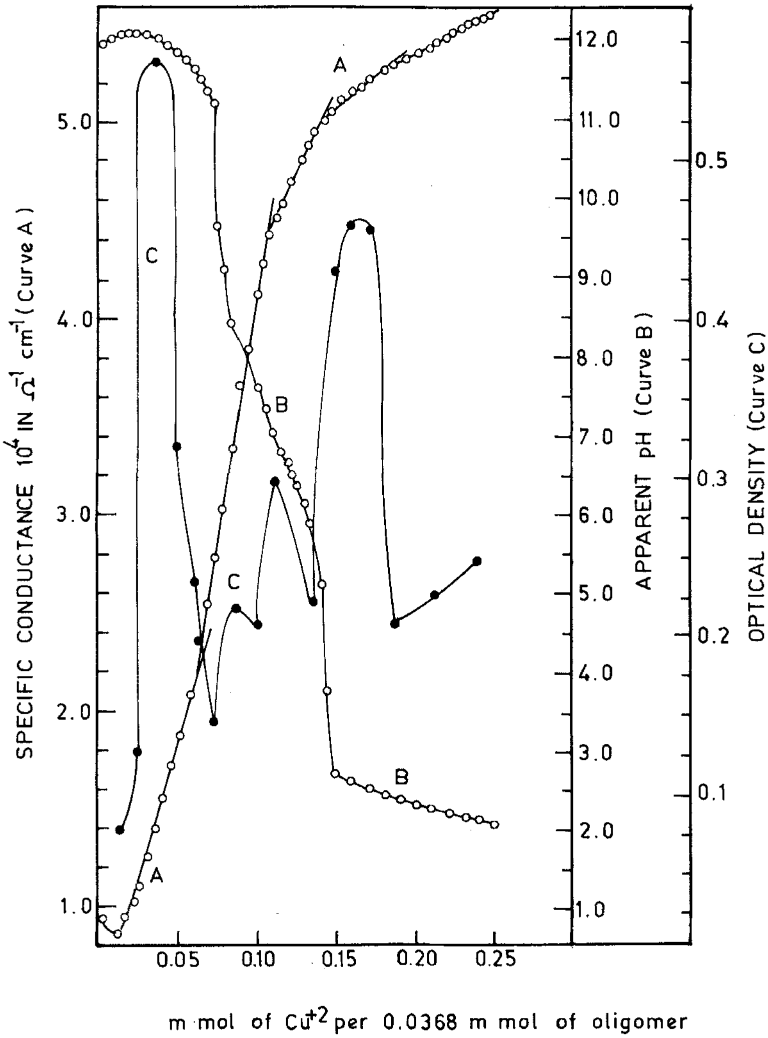


FIG. 4. Variation of conductance (A), apparent pH (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 4th stage) with increasing concentration of Cu^{2+} ions.

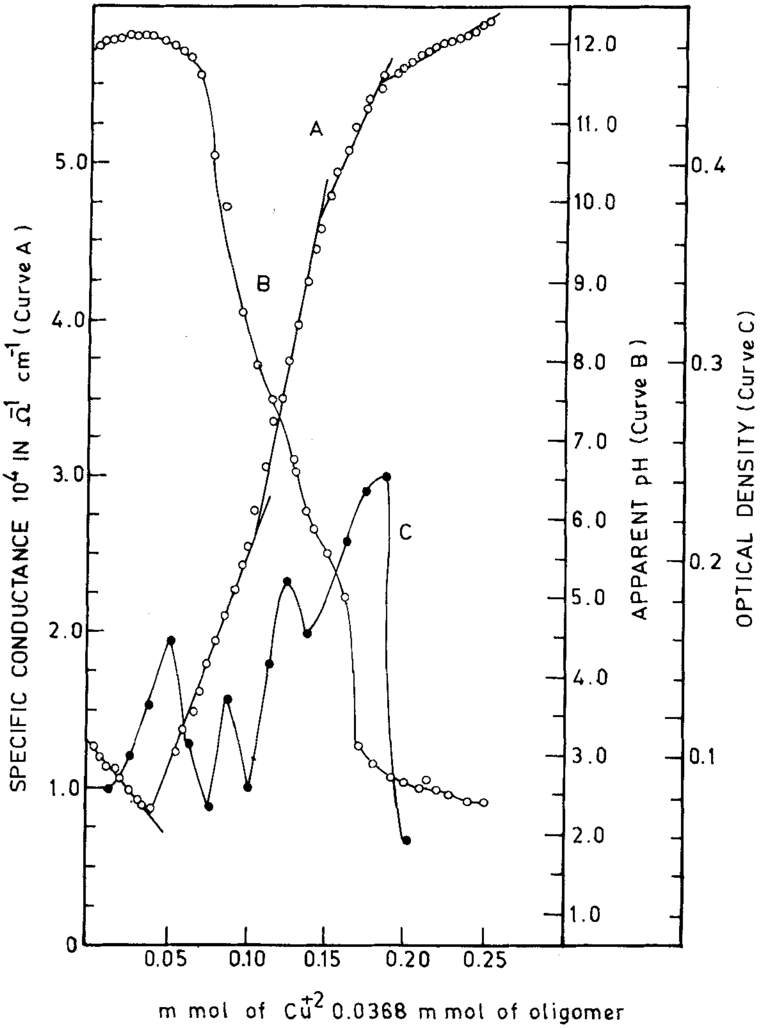


FIG. 5. Variation of conductance (A), apparent pH (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 5th stage) with increasing concentration of Cu^{2+} ions.

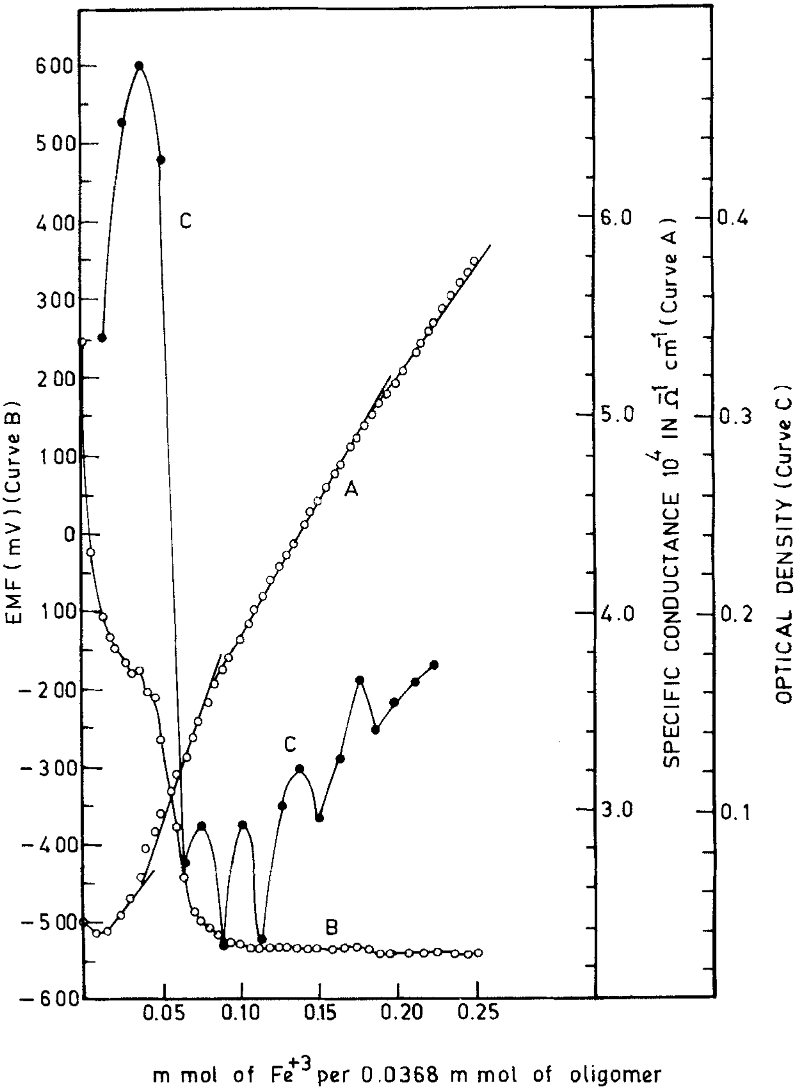


FIG. 6. Variation of conductance (A), EMF (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 1st stage) with increasing concentration of Fe^{3+} ions.

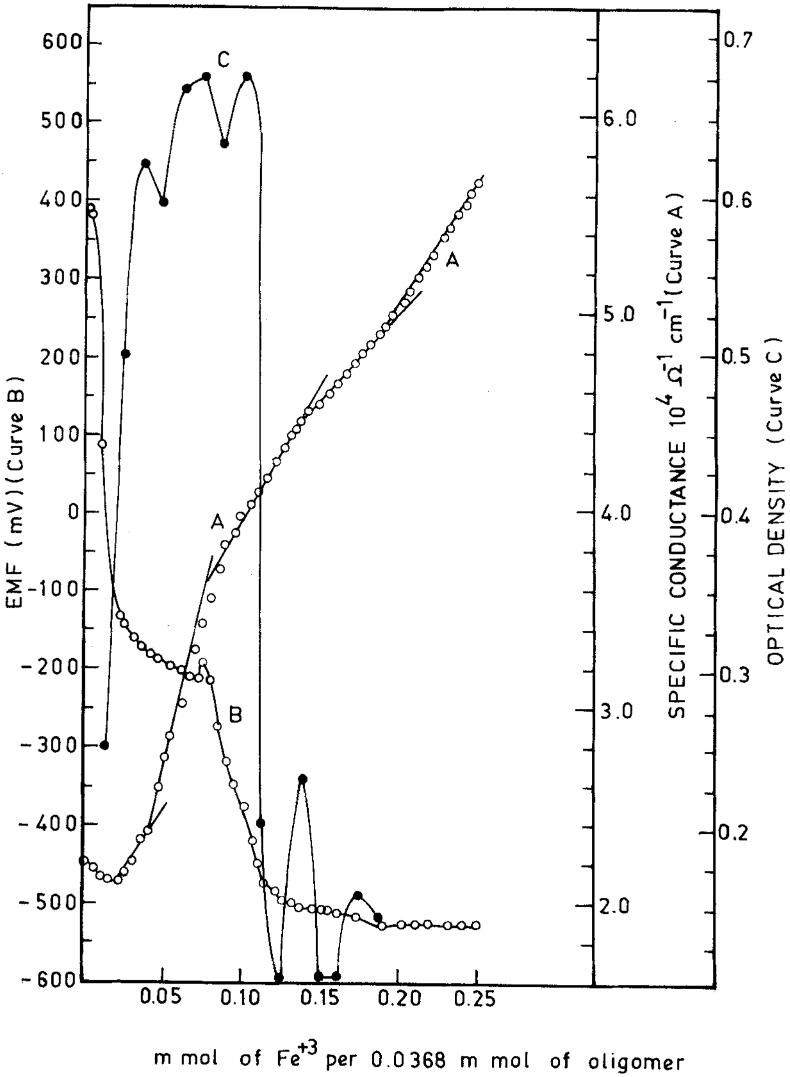


FIG. 7. Variation of conductance (A), EMF (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 2nd stage) with increasing concentration of Fe^{3+} ions.

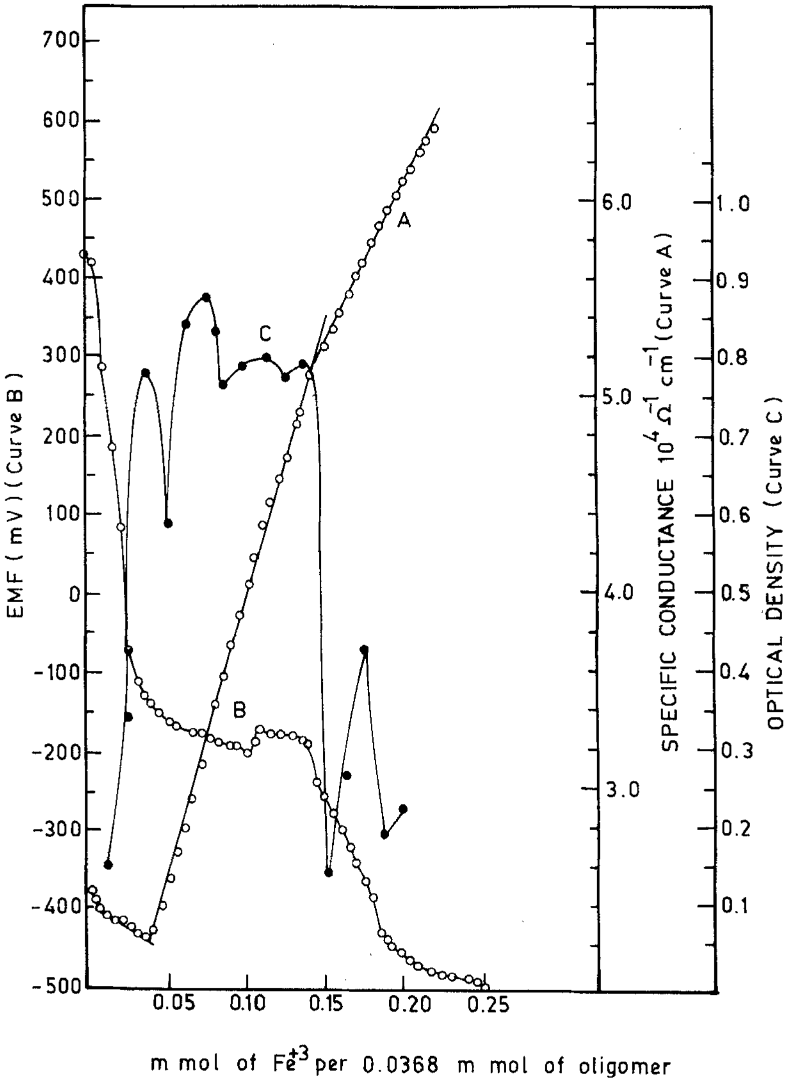


FIG. 8. Variation of conductance (A), EMF (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 3rd stage) with increasing concentration of Fe^{3+} ions.

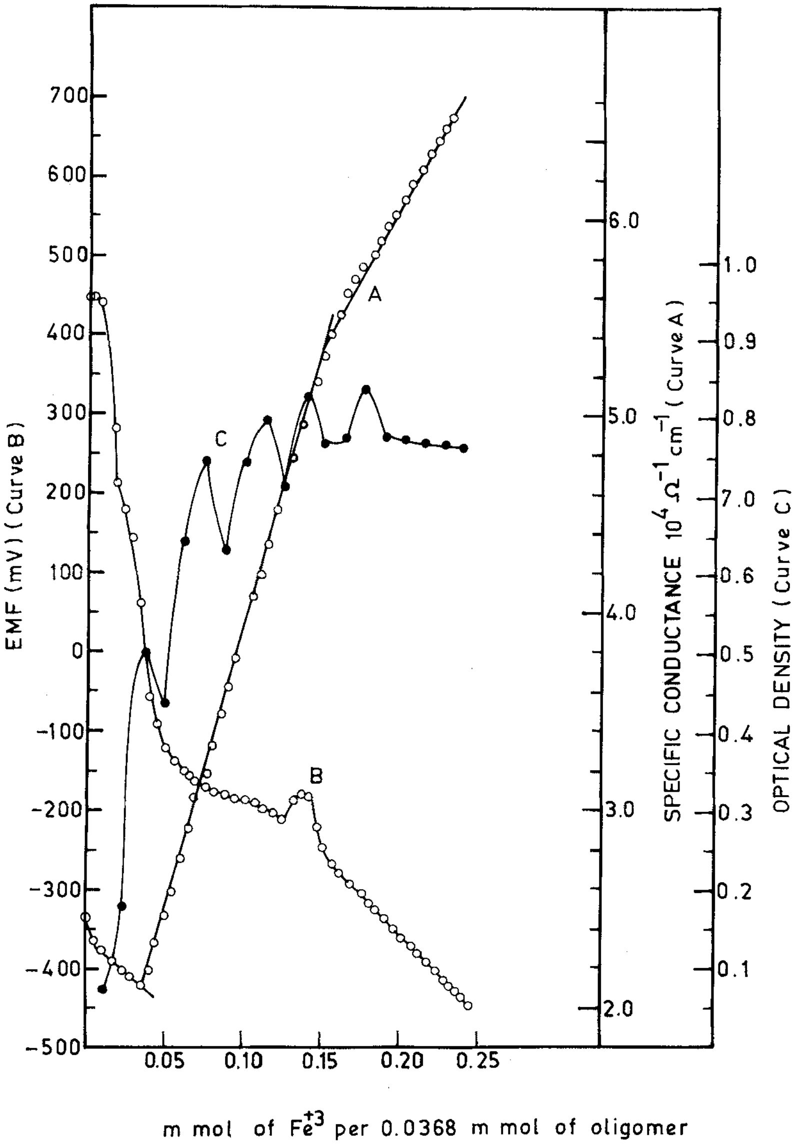


FIG. 9. Variation of conductance (A), EMF (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 4th stage) with increasing concentration of Fe^{3+} ions.

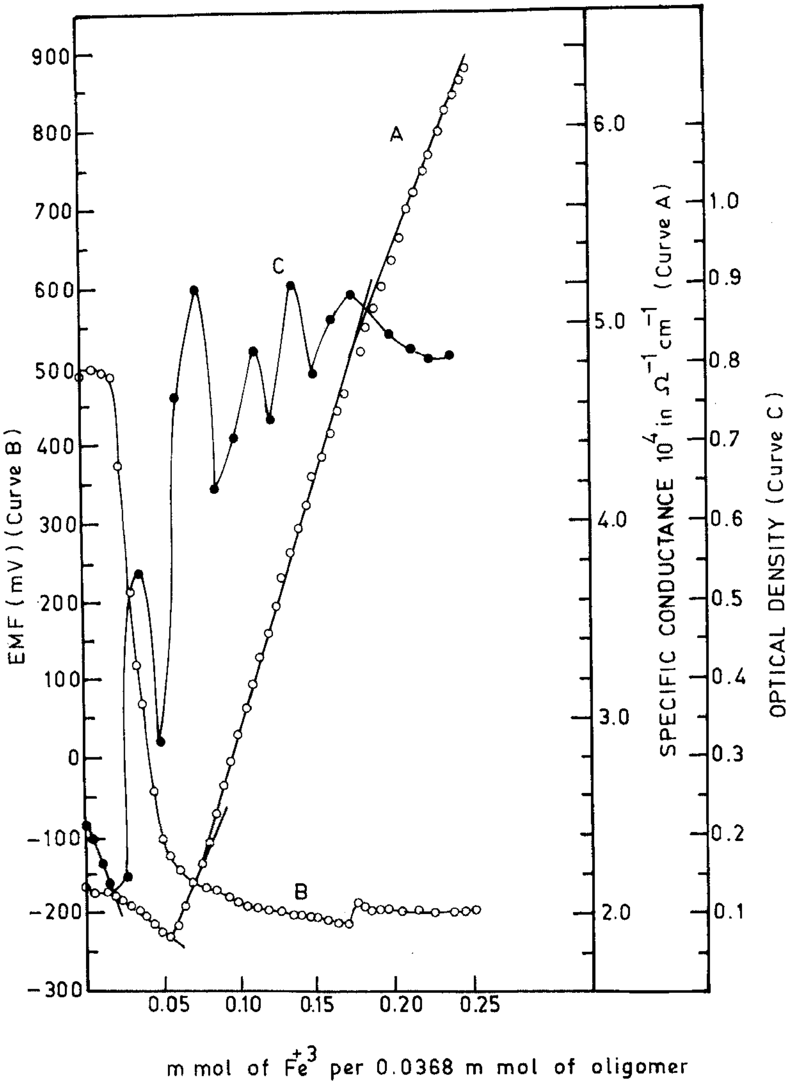


FIG. 10. Variation of conductance (A), EMF (B), and optical density (C) of pentanuclear oligomer solution (neutralized up to the 5th stage) with increasing concentration of Fe^{3+} ions.

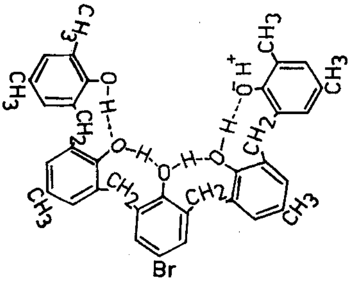
TABLE 1. Observed Fall in Conductance during the First Stage of Interaction with Fe^{3+} Ions

Oligomer molecule neutralized up to	Total fall in conductance (Ω^{-1} cm^{-1})
First stage	0.05×10^{-4}
Second stage	0.10×10^{-4}
Third stage	0.25×10^{-4}
Fourth stage	0.40×10^{-4}
Fifth stage	0.50×10^{-4}

by step interaction with Fe(III) ions is indicated more distinctly in the optical density curves.

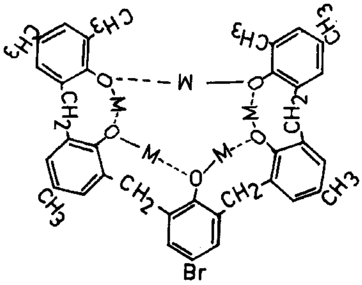
The general features of the conductance, EMF, and optical density curves can be summarized as follows: (a) In the case of a trivalent cation (Fe^{3+}), a fall in conductance was observed in all cases until 1 mmol of metal ions was added per millimole of ligand, whereas for bivalent cations (e.g., Cu^{2+} and Co^{2+}) the fall in conductance at this stage was observed only when the oligomer molecule had a high negative charge. (b) The EMF curves in general showed an abrupt change in potential at certain stoichiometric quantities of the metal ions. (c) The absorption maxima (e.g., Curve C of Figs. 1 to 10) shifted with various stoichiometries of the metal ions.

The amount of fall in conductance at the first stage of interaction with Fe(III) ions (e.g., Curve A of Figs. 6 to 10), gradually increases with an increasing charge in the oligomer molecule (cf. Table 1). Approximately the same amount of fall in conductance was observed during the interaction with bivalent cations (e.g., Cu^{2+} and Co^{2+}) when the oligomer molecule had a higher negative charge. The pentanuclear oligomer molecule (1) probably exists in solution in the following conformation and facilitates intramolecular hydrogen bond formation (3).



(3)

A similar type of conformation has also been suggested by Kämmerer and co-workers for a substituted tetranuclear phenolic oligomer [8]. The coordinating ability of a polymer ligand varies with the conformation of the polymer chain. On this basis, the 1:5 oligomer-metal complex may be represented as



(4)

It is evident from the fall observed in the conductance curves (e.g., Curve A of Figs. 4 to 10) that trivalent cations (e.g., Fe^{3+}) associate more strongly with oligomer molecule compared to bivalent cations (e.g., Cu^{2+} or Co^{2+}). It has also been observed that Fe^{3+} ions associate more strongly if the negative charge on the oligomer molecule is higher. This is evident if one compares the relative fall in conductance in Curve A of Figs. 6 to 10. The stronger association of Fe^{3+} ions may be attributed to its higher charge. The association with bivalent cations becomes appreciable only when the negative charge on the oligomer molecule is high (compare Curve A of Figs. 1 to 5).

The abrupt change in potential in the EMF curves at certain stoichiometric concentrations of metal ions may be attributed to an electron transfer reaction. A phenoxy anion coordinates to the metal ion (M^{x+}) and an electron is transferred from the coordinated phenoxy anion to the M^{x+} ion. This electron transfer step is probably an intracomplex process, and it is likely that electronic and steric factors of the substituents in the ligand directly affect the rate of the electron transfer step. The coordinate bonds between the metal ion and the polymer ligand are probably weakened by the strain produced in the polymer-metal chain by electrostatic repulsion between the cations on the polymer chain or by the steric bulkiness of the polymer ligand. Thus less energy is required to stretch the coordinate bond, and electron transfer occurs more easily than in the monomeric analogue. Such electron-transfer processes are probably reflected by the abrupt potential changes in the EMF curve (e.g., Curve B of Fig. 1 to 10) when definite stoichiometric quantities of metal ions were added to the ligand solution.

The distinct color changes of the solution at various stages of addition of metal ions give additional support to the charge-transfer process. For instance, virtually all complexes and compounds of Cu(II) are blue or green. Exceptions are generally caused by strong ultraviolet bands–charge transfer bands–tailing off into the blue end of the visible spectrum and thus causing the substance to appear red or brown. This is precisely what has been observed during the addition of Cu(II) ions to the ligand solution. At specific stoichiometric quantities of Cu(II) ions, the solution was colored red or sometimes reddish brown. As with most other Co(II) complexes, this ligand also showed a deep blue complex with Co(II) ions. The corresponding Fe(III) complexes were invariably deep red in color. The sharp variation of the absorbance maxima in the optical density curve indicates a distinct step by step interaction of the metal ions with the polymeric ligand.

Thus it may be concluded that some simple physicochemical studies such as optical density, EMF, and conductance measurements provide useful information concerning the step by step interaction of transition metal ions with chelating polymers such as phenolic oligomers and related polymers.

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