

Complexation of poly-2,5-dimethyl-4-vinylethynylpyperidol-4 hydrochloride with transition metal ions in solution

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The interaction of transition metal ions with poly-2,5-dimethyl-4-vinylethynylpyperidol-4 hydrochloride in solution have been investigated potentiometrically, spectroscopically and viscometrically. Influence of ionic strength, composition of solvent and various metal ions nature on the viscosity of polyelectrolyte-metal complexes are discussed.

Keywords Poly-2,5-dimethyl-4-vinylethynylpyperidol-4 hydrochloride; polyelectrolyte-metal complexes; chelate formation; polymer conformation

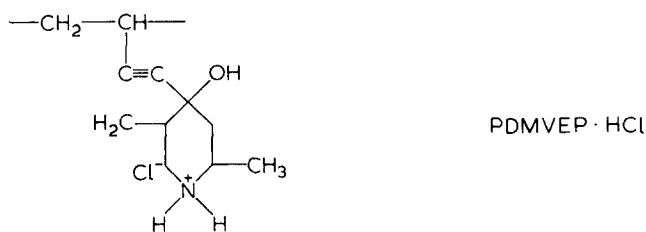
INTRODUCTION

A study of the behaviour of polyelectrolyte-metal complexes in solution is of great interest. The great affinity of functional groups of polymers to transition metal ions suggests their use for sorption, concentration and separation processes¹. Besides, the polymer-metal complexes show a high catalytic activity which simulates the action of metal enzymes^{2,3}.

In the present paper the complex formation of poly-2,5-dimethyl-4-vinylethynylpyperidol-4 hydrochloride with transition metal ions in solution are investigated by methods of potentiometric titration, n.m.r. ¹H spectroscopy and viscometric measurements.

EXPERIMENTAL

Poly-2,5-dimethyl-4-vinylethynylpyperidol-4 hydrochloride (PDMVEP-HCl) was synthesized by radical polymerization as described elsewhere⁴.



The viscosity-average molecular weight of PDMVEP-HCl was calculated according to Mark-Houwink relation in 0.1 M KBr

$$[\eta] = 5.75 \cdot 10^{-6} M^{0.90}$$

and is equal to $250 \cdot 10^3$.⁵ Potentiometric titrations of polyelectrolyte and its metal complexes were carried out on the pH-meter 'pH-121' (USSR) at room temperature. N.m.r. ¹H spectra of polymer and polymer-metal complexes in D₂O registered by nuclear magnetic spectrometer BS 487 'Tels' type (CSSR) in the presence of 0.5 M KCl at a frequency of 80 MHz and room temperature. The chemical shift was measured relative to the internal standard HMDS (hexamethyldisiloxane). Viscosities of polyelectrolyte and its complexes were measured at $25^\circ \pm 0.1^\circ\text{C}$ with an Ubbelohde viscometer. Ionic strength was adjusted to the indicated values by addition of KCl or KBr. The metal salts used here are CuCl₂·2H₂O, Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, FeCl₃·6H₂O and ZnCl₂.

RESULTS AND DISCUSSION

It is known⁶⁻⁸ that the difference of potentiometric curves of polyelectrolytes in the absence and in the presence of transition metal ions is used as evidence of complex formation and consequently for determination of composition and stability constant of polymer-metal complexes.

Figure 1 represents the potentiometric curves of PDMVEP-HCl at ionic strength $\mu = 0.5$ in the presence of various concentrations of cupric ions. It is shown that the addition of Cu(II) ions to the polyelectrolyte solution leads to a reduction of pH values with respect to initial ones. These results can be explained by coordination of ionic groups of polymer with transition metal ions. This feature of polymer-metal complexes which distinguished them from the simple ligands is connected with a high local density of reactionable groups in random coils of macromolecules. This is confirmed by titration of the low molecular analogue of PDMVEP-HCl in the presence of

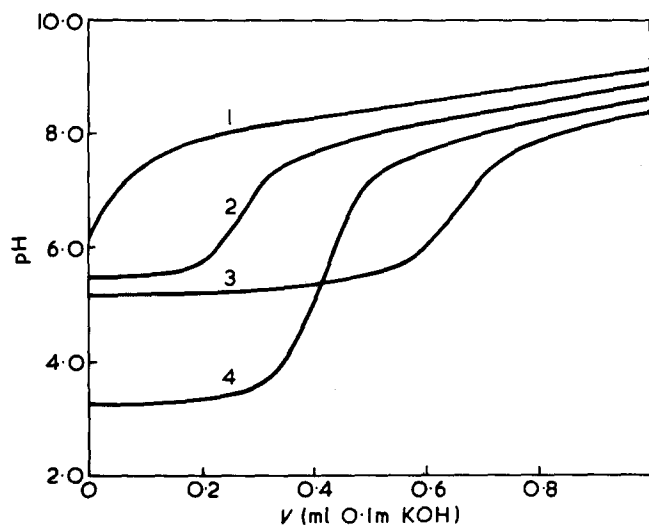


Figure 1 Potentiometric titration curves of PDMVEP·HCl (1) and its complexes (2,3,4) at $\mu=0.5$ M KCl. $[PDMVEP \cdot HCl]=1 \cdot 10^{-2}$ mol l^{-1} ; $[Cu^{2+}]=1 \cdot 10^{-3}$ (2), $2.5 \cdot 10^{-3}$ (3) mol l^{-1} ; $[Fe^{3+}]=1 \cdot 10^{-3}$ (4) mol l^{-1}

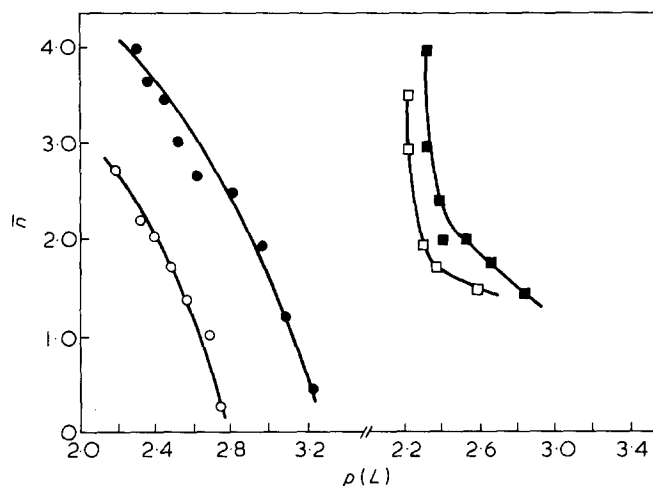


Figure 2 Formation curves for PDMVEP·HCl - Cu^{2+} complexes. (O) water; (●) 0.005 M KCl; (■) 0.5 M KCl; (□) $C_2H_5OH-H_2O$ (9:1 vol%)

cupric ions. An n.m.r. 1H spectrum of monomer-2,5-dimethyl-4-vinylethynylpiperidol-4 hydrochloride is not changed when the metal ions are added.

Various early investigators⁹⁻¹² have shown that the potentiometric data allow determination of the average number of ligands coordinating with central ions. The definition of \bar{n} and stability constant may be carried out by the Bjerrum method⁹, modified by Gregor^{10,11} or Mandel and Leyte¹². For determination of the average number of ligands \bar{n} in coordination sphere we used the Monjol method¹³. It gives the free ligand concentration $[L]$ directly from the calibration data. Figure 2 shows that the calculated value of \bar{n} is equal to 4, i.e. $[PDMVEP \cdot HCl]/[Cu(II)]=4:1$. This suggests that an excess of polyligand concentration the one metal ions are chelated with four nitrogen atoms of the piperidol ring. The steep slope of the curve indicates the close values of consecutive complexation constants. Authors^{14,15} are

agreed that the complexation of metal ions with polyelectrolytes is controlled by conformation of polymer chains. As shown in Figure 2, in water and 0.005 M KCl solutions the values of \bar{n} are approximately 3 and 4 respectively. The slopes of these curves indicate the successive complex formation. Whereas the steep slope of curves begin at $\mu=0.05$ and in $C_2H_5OH-H_2O$ (9:1 vol%) mixtures. The alcohol-water mixtures as well as the ionic strength may be assumed to cause the shielding of polyelectrolyte molecules. In both cases the density of functional groups in macromolecular coils is increased; it influences the stepwise formation constants of complexes. However, the complex formation ability of polyelectrolytes depends on the metal ion type. Under identical conditions the addition of Fe(III) ions to the polyelectrolyte solutions more strongly reduced pH values (Figure 1). It indicates a stronger interaction of Fe(III) ions with PDMVEP·HCl, than Cu(II) ions. The average number of units bound per Fe(III) ions is 6.

It is of interest to study the complex formation between polyelectrolytes and metal ions by spectroscopy^{16,17}. The chemical shifts of CH_3 protons in 2 and 5 positions of piperidole ring (H-2 and H-5 protons respectively) at various Cu(II) ion concentration are shown in Figure 3. The observed chemical shifting of protons to the weak field side is due to deprotonation of quaternary nitrogen atoms owing to substitution of nitrogen-proton bonds to nitrogen-metal ones. The n.m.r. spectroscopy can be used for determination of equilibrium constants and other thermodynamic parameters of complexes. In Figure 4 the dependence of the difference of chemical shift of protons $\Delta\delta = \delta_a - \delta_b$ (where δ_b is the chemical shift of protons in the presence of metal ions; δ_a is the same shift in the absence of metal ions) on f is represented (f represents the molar ratio metal ions to polyelectrolyte). The molar ratio

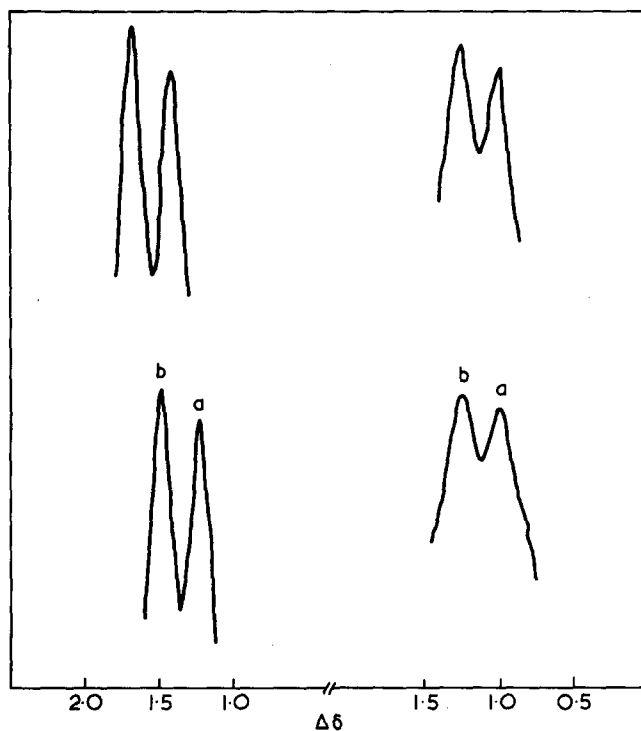


Figure 3 The effect of addition of Cu^{2+} ions on the n.m.r. 1H spectra of H-2 (a) and H-5 (b) protons at 80 MHz

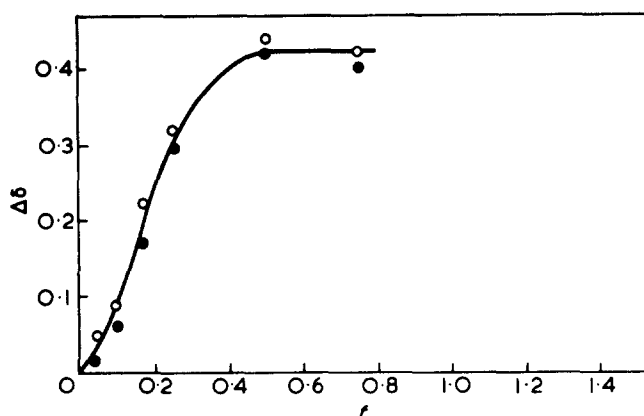


Figure 4 Chemical shifts of H-2 (●) and H-5 (○) protons as a function of f ($f = [\text{Cu}^{2+}]/[\text{PDMVEP} \cdot \text{HCl}]$)

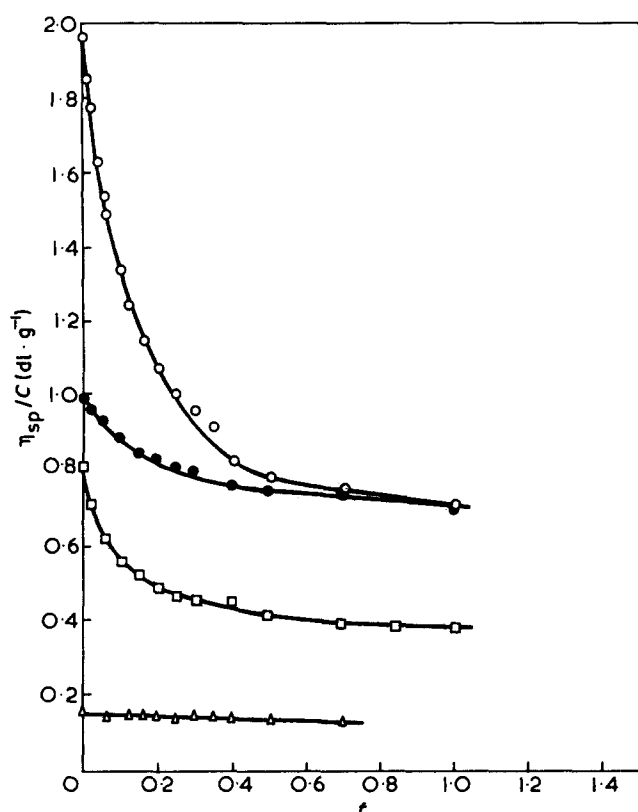


Figure 5 Plots of reduced viscosity ($C = 0.2 \text{ g dl}^{-1}$) of PDMVEPHCl versus f_0 (○) water; (●) 0.01 M KCl; (△) 0.5 M KCl; (□) $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$

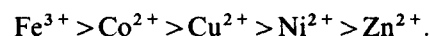
of polyligand-metal complexes obtained from this plot indicates the complex composition $[\text{PDMVEP} \cdot \text{HCl}]/[\text{Cu}(\text{II})] = 2:1$.

We also investigated the influence of ionic strength, solvent composition and metal ion type on the viscosity of the complexes. Figure 5 shows the variation of reduced viscosity, η_{sp}/C with f . The addition of metal ions to polyelectrolyte solution leads to the sharp decrease of η_{sp}/C . The obtained results are analogous to those reported by previous workers^{18,19}. The decrease of reduced viscosity is explained by coiling of macromolecules due to formation of intramolecular

chelate 'bridges'. Earlier⁵ we found that the formation of intrachain 'bridges' in the case of multivalent anions (SO_4^{2-} , PO_4^{3-}) also leads to a strong decrease in the chain dimensions. It may be assumed that both metal ions and multivalent anions act similarly on the hydrodynamic size of macroions.

It is of interest to consider the influence of ionic strength and solvent composition on viscosity of polymer-metal complexes (Figure 5). Curves 2 and 4 in Figure 5 show that the plots of η_{sp}/C versus f in water-salt mixtures are strongly changed in comparison with water solution (curve 1, Figure 5). At high ionic strength $\mu=0.5$ the related viscosity is practically independent of f (Figure 5, curve 4). These data can be explained by change of polyligand conformation and consequently the structure of complexes. At high ionic strength the electrostatic repulsion among pyperidol rings decreased and as a result the local density of free ligands in the macromolecular coils increased. Thus the interaction of metal ions with polyelectrolyte can be controlled by conformation changes in the polymer chain. A similar behaviour of the polyelectrolyte-metal complex is observed in water-alcohol mixture (Figure 5, curve 3). It is possible that the mixture $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ acts as a low molecular weight salt owing to the preferential interaction of hydrophilic parts of the polymer chain with others in organic solvents⁵.

The influence of different metal ions upon viscosity is shown in Figure 6. The coordination ability of these metals takes the following order:



Probably this order reflects the strength of complex formation of DMVEP·HCl with metal ions.

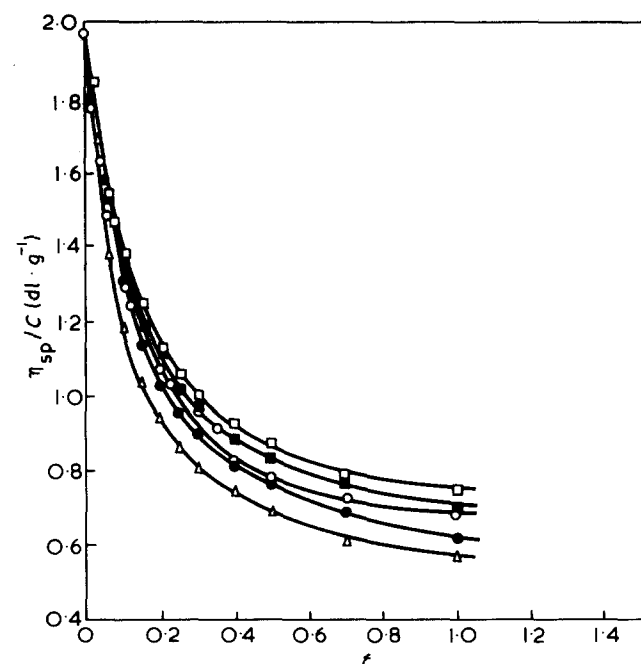


Figure 6 Plots of reduced viscosity ($C = 0.2 \text{ g dl}^{-1}$) of PDMVEP·HCl versus f for various metal ions. (□) Zn^{2+} ; (■) Ni^{2+} ; (○) Cu^{2+} ; (●) Co^{2+} ; (△) Fe^{3+}

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