Interaction of poly(2-vinyl pyridine 1-oxide) with mercuric ions

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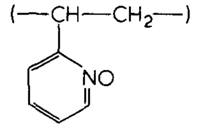
The interaction of poly(2-vinylpyridine 1-oxide) with mercuric chloride forms a stable chelate with mercuric ions in contrast to the monomer analogue 2-methylpyridine 1-oxide. Conductivity and u.v. measurements showed that chloride ions are not involved in the chelate formation and that the molar ratio of Hg^{2+} to the oxide is 1 to 2 in excess mercuric chloride. Viscosity measurements suggest that the chelate is a polyelectrolyte and is formed in both neutral and acid solution. 0.2% $HgCl_2$ causes a remarkable drop in the viscosity of 0.4% polymer solution whereas a similar concentration of $CaCl_2$ has no effect. Temperature change from 27–45°C has little effect on the stability of the chelate. The possible use of this polymer for removing mercuric ions from aqueous solution is discussed.

INTRODUCTION

Highly coordinated mercuric ions are not very stable and although, in general, oxygen donors coordinate only weakly with these ions, pyridine 1-oxide forms hexakis (pyridine 1-oxide) mercury (II) perchlorate[1,2] and 4-methylpyridine 1-oxide forms[3] $[Hg(oxide)_2X_4]^{-2}$ ($X = Cl^-, Br^-, I^-$). Most pyridine 1-oxide complexes are prepared and isolated from organic solvents and pyridine 1-oxide has proved to be a good ligand for many metal ions[4]. Polymeric *N*-oxide complexes have not been reported and in this work an attempt was made to investigate the chelation of poly(2-vinylpyridine 1-oxide)



with mercuric chloride in aqueous solution, using conductivity, u.v. and viscosity measurements.

EXPERIMENTAL

Poly(2-vinylpyridine-1-oxide) (P_2VPO) prepared by oxidizing poly(2-vinylpyridine) (Midland Tar Distillers) with hydrogen peroxide in acetic acid, using the method preivously described[5], was purified twice before use by dissolving in ethanol and precipitating with ether. The white powder polymer was very hygroscopic and soluble in water.

Conductivity measurements were carried out using a CD 6N Taccussel conductometer. The polymer solution was added in portions to the mercuric chloride solution, and stirred continuously until a constant reading was obtained after each addition.

The polymer and the mercuric chloride solutions were mixed and allowed to stand for at least 1 h before the u.v. spectra were recorded.

The viscosity measurements were carried out at 27° ± 0.01°C using a suspended level viscometer with a flow time for water of 102 ± 0.2 sec. The flow time of a solution was taken as the mean of at least two consecutive measurements differing by not more than 0.2 sec, corresponding to an error of 0.002 in η_{sp}.

RESULTS AND DISCUSSION

The addition of $HgCl_2$ solution to P_2VPO increased the conductivity remarkably (*Figure 1*). The conductivity in-

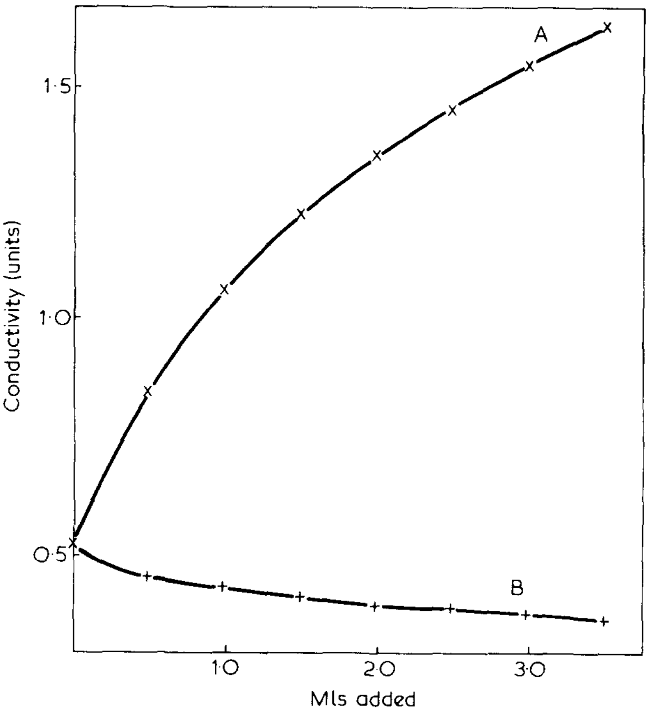


Figure 1 Conductivity of: 40 mls of 0.45% $HgCl_2$ vs. P_2VPO solution added (ml) [Curve A]; 40 ml of 0.45% $HgCl_2$ vs. of H_2O added (ml) [curve B]

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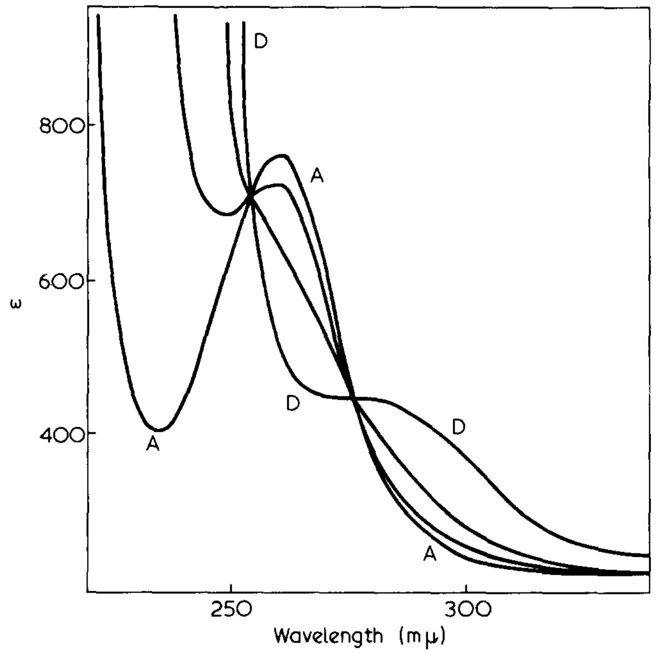


Figure 2 U.v. spectra of 0.4% P_2VPO. A, in H_2O; B, in 0.1% $HgCl_2$; C, in 0.4% $HgCl_2$; D, in 0.8% $HgCl_2$

creased with increase in the concentration of the polymer. This indicates that chloride ions are liberated, and if we assume a coordination between the N–O groups of the polymer and the Hg^{2+} ions, the chloride ions would not be involved. Addition of 2-methylpyridine 1-oxide instead of the polymer to mercuric chloride solution under the same conditions did not increase the conductivity, showing that the polymer interacts with mercuric chloride by chelation.

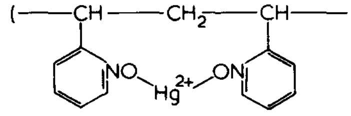
The effect of mercuric chloride on the spectra of the polymer in aqueous medium confirmed this conclusion (*Figure 2*). P_2VPO solution alone showed a band at 261 μm which is due to a π–π^* transition[6] but in the presence of mercuric chloride this band disappeared and a new less intense band appeared at 280 μm. At different concentration of mercuric chloride the spectra showed two clear isosbestic points indicating an equilibrium between the polymer and its complex form:

$$n(\text{Oxide}) + \text{Hg}^{2+} \leftrightarrows \text{Hg}(\text{oxide})_n^{+2}$$

From the spectra it was possible to calculate the amount of free and bonded oxide, and hence the number of oxide groups involved per Hg^{2+}. The association constant (K_{ass}) was calculated by the method of Katchalsky and Miller[7]

$$K_{ass} = \frac{[\text{Hg}(\text{oxide})_n^{+2}]}{[\text{Oxide}]^n\,[\text{Hg}^{+2}]_{\text{added}}}$$

It was assumed that the concentration of the free $HgCl_2$ is the same as the $HgCl_2$ added and in the presence of excess $HgCl_2$ the amount reacted is small. A plot of log[Hg(oxide)$_n^{2+}$] vs. log[oxide] gave a straight line with a slope $n = 2.1$ indicating that two N–O groups are attached to 1 mercuric ion:



The concentrations of the complex and the free species were determined from the intensities of the spectra, and the average value of K_{ass} was found to be 3.8×10^6.

Mercuric chloride solution has no appreciable effect on the spectra of 2-methylpyridine 1-oxide using the same concentration as that of the polymer, in agreement with the conductivity results.

In the presence of mercuric chloride the viscosity of 0.4% P_2VPO first decreased rapidly, then gradually reached a minimum when the concentration of the mercuric chloride was increased to 0.2% (*Figure 3a*). At higher concentrations of mercuric chloride the viscosity of the polymer did not decrease appreciably but a white precipitate was formed when the concentration reached 16.4×10^{-3} M mercuric chloride in 33×10^{-3} M P_2VPO, i.e. a ratio of 1 to 2, and this confirms the u.v. spectra results.

The initial viscosity of the polymer solution was high due to the expansion of the protonated polymer chain, in the presence of $Hg(NO_3)_2$ at pH2 was reduced almost to the same value as that observed with $HgCl_2$ (*Figure 3b*). This suggests that the Hg^{2+} replaces the H^+ in the protonated polymer. However, it was interesting to observe that no precipitation occurred until 0.48 $Hg(NO_3)_2$, at pH2. Probably some N–O groups are still protonated at this pH value in spite of the higher affinity for Hg^{2+}, and this keeps the whole chelate in solution.

The viscosity of P_2VPO solution conforms to that of a non-electrolyte polymer, since a plot of η_{sp}/C gave a straight line[8] (*Figure 4*). However, η_{sp}/C against C of P_2VPO in the presence of $HgCl_2$ was non-linear, indicating that the chelate is a polyelectrolyte. This would be expected, if the chloride ions were not involved in the first coordination sphere, thus the chelate would be positively charged.

The effect of $HgCl_2$ on the viscosity of 0.4% P_2VPO was compared with that of $CaCl_2$ (*Figure 5*). In the presence

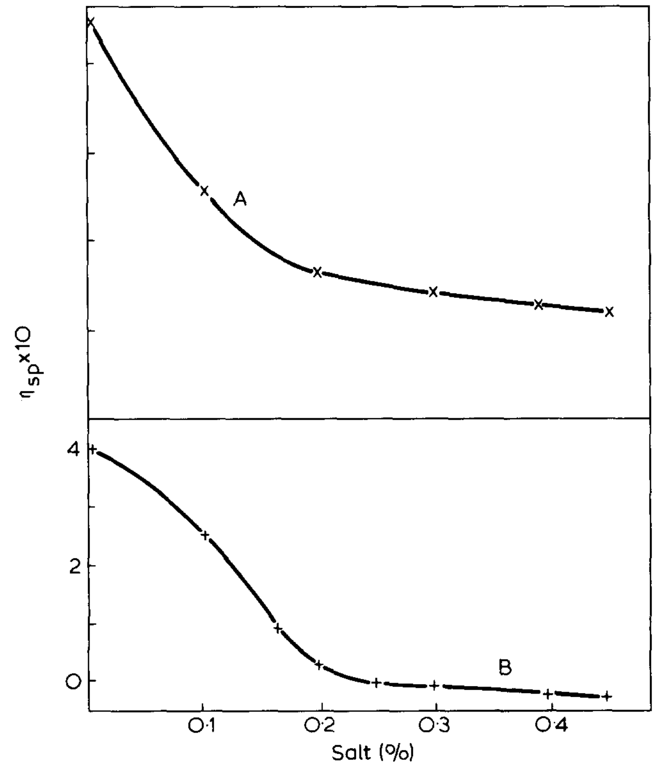


Figure 3 A, η_{sp} of 0.4% P_2VPO vs. %$HgCl_2$; B, η_{sp} of 0.4% P_2VPO (pH = 2) vs. %$Hg(NO_3)_2$ (pH = 2).

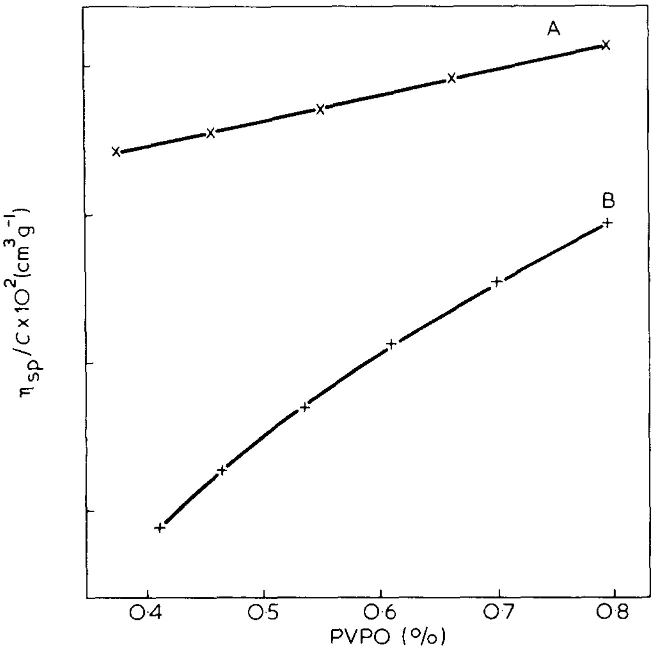


Figure 4 η_{sp}/C vs. [P_2VPO]. Initial concentration 0.8% P_2VPO. A, Polymer diluted with H_2O; B, polymer diluted with 0.45% solution $HgCl_2$

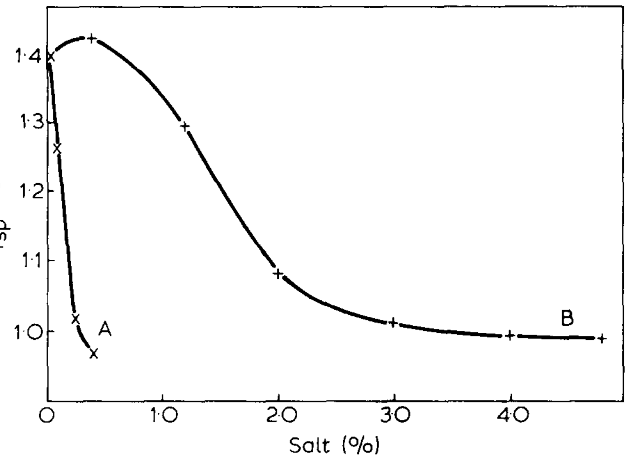


Figure 5 η_{sp} of 0.4% (33 x 10^{-3} M) P_2VPO: A, vs. %$HgCl_2$ added; B, vs. % $CaCl_2$ added.

of 7.3 x 10^{-3} $HgCl_2$ solution the viscosity was reduced sharply reaching a minimum at 0.2% $HgCl_2$, but in the presence of $CaCl_2$ of the same concentration, the minimum was not reached until 4% (0.24 M) $CaCl_2$ or about fifteen times the concentration of $HgCl_2$ was added. It was interesting to observe that in the presence of $CaCl_2$, the viscosity of the polymer first increased slightly then decreased at higher concentrations of $CaCl_2$. This is probably due to tje repulsion of neighbouring positive charges of the N^+–O^-–Ca^{2+} complex leading to an expansion of the polymer chain, but further attraction of Ca^{2+} ions to the N^+–O^- group leads to folding of the polymer chain and hence a reduction in viscosity.

The stability of the P_2VPO–$HgCl_2$ chelate with dilution was followed by measurement of the change in viscosity (η_{sp}/C). For a solution of 0.4% (33 x 10^{-3} M) P_2VPO and 0.45% (16.5 x 10^{-3} M) $HgCl_2$ (molar ratio of 2 to 1) the change in viscosity with dilution is shown in *Figure 6*. Initially, the viscosity increased gradually, but at about 0.03% P_2VPO, rose very sharply. This sharp rise in viscosity suggests that below this concentration the dissociation of the chelate is complete and the polymer retains its normal conformation. The concentrations of the dissociated and the undissociated species at the turning point, conform fairly well with those obtained from the u.v. spectra.

The effect of temperature change on the stability of the P_2VPO–$HgCl_2$ chelate was also investigated by viscosity measurements. In the presence of $HgCl_2$ the viscosity–temperature curve (*Figure 7*) was lower than that of the

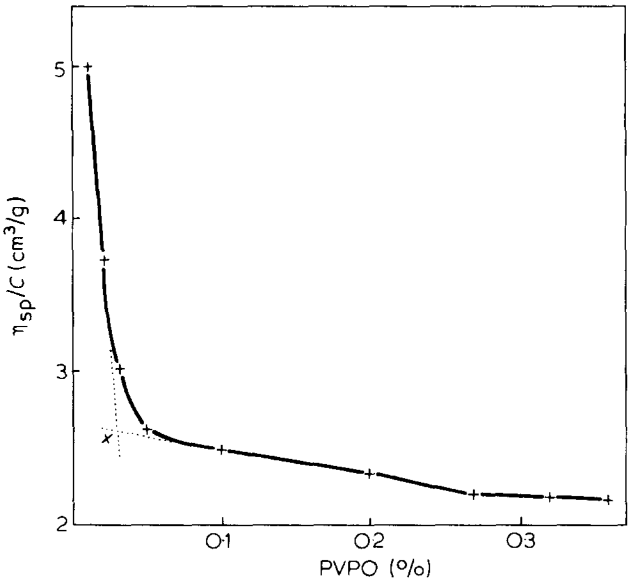


Figure 6 η_{sp}/C vs. [P_2VPO] in the presence of HgCl. Initial concentration 0.4% (33 x 10^3 M) P_2VPO in 0.45% (16.5 x 10^{-3} M) $HgCl^2$. x = 0.03% (2.4 x 10^{-3}) P_2VPO

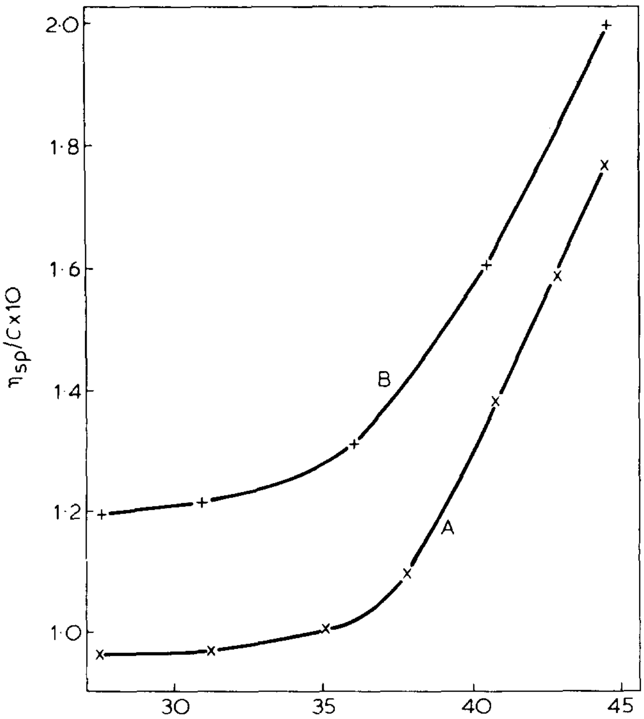
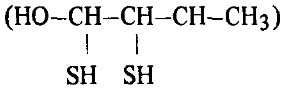


Figure 7 Effect of temperature on the specific viscosity of P_2VPO–$HgCl_2$ chelate solution. A, 0.4% P_2VPO in H_2O; B, 0.4% P_2VPO in 0.45% $HgCl_2$

polymer alone and followed almost the same trend up to about 45°C, showing that the chelate remains fairly stable.

The chelation of mercuric chloride with P_2VPO could have some important implications. Some mercury compounds are employed in pharmaceutical preparations because of their antibacterial action, e.g. ammonia–mercury ointments are used as disinfectants, and mercuric ion complexes with some organic compounds are used as bacteriostatic agents. The poisoning which results from the environmental contamination by the industrial discharge of mercury compounds is attracting considerable attention. Dimercaprol



$$\mathrm{(HO{-}\underset{\substack{|\\ SH}}{CH}{-}\underset{\substack{|\\ SH}}{CH}{-}CH{-}CH_3)}$$

is normally used as a mercury antidote because of its ability to form a chelate with the metal ion. However, in the body fluid, dimercaprol is oxidized fairly rapidly and so it has to be used continuously to maintain the chelation of the mercuric ion; moreover, the use of this antidote has many limitations[9].

Thus a study of the possible use of P_2VPO in a biological system to eliminate a toxic metal ion such as Hg^{2+} is of interest. In this respect three points should be mentioned: (1), P_2VPO is non-toxic[10] and is freely soluble in water; (2) the $P_2VPO{-}HgCl_2$ chelate is more soluble in water than the dimercaprol–$HgCl_2$ chelate which precipitates immediately as we have shown in a preliminary comparison; and (3) P_2VPO has a greater affinity for mercuric ions than for calcium ions under the same conditions.

At present the interaction of P_2VPO with Fe^{3+}, Cr^{3+}, Cd^{2+}, Cu^{2+}, Pb^{2+} are being investigated.

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